

Refined Plasmonic Sensing for Electrified Interfaces

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Wer sich über die Wirklichkeit nicht
hinauswagt, der wird nie die Wahrheit
erobern.

Friedrich von Schiller

Abstract

This thesis introduces and applies a refined in situ, non-invasive plasmonic spectroscopy method using highly homogeneous macroscopic Au nanoarrays to investigate the electrified Au/aqueous electrolyte interface.

This method, called differential Cyclic Plasmo-Voltammetry (dCPV), exploits the specific sensitivity of the localized surface plasmon resonance towards changes in the interfacial properties of Au nanoparticles (NPs). The main contributions to changes of this resonance are the charging of the NPs, chemical interface damping due to adsorbed species, and changes in NP morphology. To validate the applicability of dCPV for the detection of these processes, the change of plasmonic resonances during cyclic voltammetry measurements of well-known reactions is recorded and compared to the corresponding electrochemical current-voltage profiles. Among these reactions are Au oxidation/reduction, competitive coadsorption of oxide species and phosphate/sulfate ions, and Cu underpotential deposition on Au.

As the next step, the method is used to gain insights beyond those achievable by other in situ methods for the characterization of the electrified Au/electrolyte interface. Specifically, the stability of Au in different potential ranges and electrolytes, as well as the interaction between Au and hydrogen, is investigated. Resonance changes due to morphological changes are verified with in situ AFM measurements and corresponding simulations. It is shown that even the onset of hydrogen evolution is accompanied by pronounced morphological changes of the interface, which are far more prominent than those occurring during Au oxidation and reduction. Furthermore, the stability of the interface heavily depends on pH and the presence of cations, the degradation of the electrode being considerably stronger in acidic than in neutral electrolytes. In addition, a clear hydrogen adsorption peak was observed in neutral electrolytes during hydrogen evolution. First experiments are described that explore two further areas of application, namely the characterization of double layer charging under strong non-equilibrium conditions and monitoring of surface changes during the electrochemical CO₂ reduction on pulsed Cu electrodes.

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1. Introduction

The advent of electrochemistry started with the publication of Alessandro Volta’s “voltaic pile” in 1800 [1] and has become a driving force for technological advancement. Among the most critical applications in modern times are batteries, fuel cells, water electrolysis, and corrosion mitigation, to name but a few [2]. However, as technology advances and new challenges arise, the need for advancement in this field has never been greater. “Advancement” nowadays refers to the increase of reaction efficiencies and selectivities, which are vital parameters if solar-to-fuel, artificial photosynthesis, or sustainable battery technologies are to be used on a large scale in the future.

To tune reactions and the design of the electrochemical reactors to the desired efficiencies, more fundamental knowledge about the microscopic processes of electrochemical reactions is needed. In general, in electrochemical reactors, electrical energy is converted into chemical energy due to the forcing of desirable electrochemical redox reactions or vice versa. Hereby, the most critical steps occur at the interface between the electrode and the electrolyte, the so-called electrochemical interface, which is, therefore, the main region of interest. It is there that chemical species undergo changes due to the acceptance or donation of electrons from or to the electrode, which depends on a multitude of parameters. For example, for most chemical species that adsorb on the electrode surface, the crystallographic structure at and close to the place of adsorption impacts the binding energies and, therefore, the reaction kinetics [3]. More complex reactions might have multiple intermediate products and transition steps, which necessitate adequate analysis of the number and the relative size of adsorbed species during the reaction, i.e., in situ, to achieve a deeper understanding of this reaction [4]. The standard electrochemical investigation techniques, i.e., cyclic voltammetry and electrochemical impedance spectroscopy, apply various potential programs to the interface and record the resulting reaction current. While these techniques yield valuable information about reaction kinetics and electric properties of the system, important aspects such as surface morphology, chemical composition, and the details about adsorption/transition states remain elusive [5]. This is why additional in situ/operando characterization techniques have to be employed.

Among the available interface-sensitive techniques are electrochemical scanning tunneling microscopy [6], electrochemical scanning microscopy [7], electrochemical atomic force microscopy [8], and optical spectroscopy, e.g., x-ray scattering and diffraction [9] and UV-Vis reflectance spectroscopy [10]. As chemical reaction steps occur in the order of milliseconds to seconds, optical methods seem especially interesting to use because of their potential to record vast amounts of data on very small timescales. Moreover, optical methods are able to measure the energetic fingerprints of atoms and molecules, which can be used to retrace the progression of a reaction. Some examples of such techniques are Raman scattering [11], Infrared spectroscopy [12], and X-ray absorption spectroscopy [13]. While these methods are powerful and have significantly increased understanding of electrochemical kinetics, they all require expensive state-of-the-art equipment.

A much cheaper and rapidly evolving sensing technique is the use of localized surface plasmon resonances (LSPRs), which is called plasmonic sensing [14]. Plasmons are collective electron oscillations excited on (metallic) nanoparticles when illuminated with light of specific wavelengths. The collective oscillation creates an oscillating electric field around the nanoparticle with a much larger amplitude than the incident light. This field can interact with

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other incoming photons, thus increasing the interaction cross-section of the nanoparticle. The term plasmonic sensing is also used to refer to surface plasmon resonances (SPRs), which are excited at and propagate along the interface between materials of specific dielectric constants and are not the focus of this work [15]. Experimentally, LSPRs occur as a resonance-like increase in optical absorption, reflectivity, and transmission spectra compared to the respective bulk properties of the material [16]. This increase due to plasmonic resonances can be in the order of several magnitudes and is used in Raman and infrared spectroscopy to enhance the optical signals and make these techniques more sensitive such that smaller concentrations of molecules can be probed. These methods are called Surface Enhanced Raman Spectroscopy (SERS) [17] and Surface Enhanced Infrared Absorption Spectroscopy (SEIRAS) [18]. Another way to utilize plasmonic resonances is plasmonic catalysis, where photonic energy is concentrated at nanoparticles and then transferred to adsorbate species in order to influence selectivities and increase reaction rates [19]. This has been explored for multiple reactions and continues to be a center of attention in the photocatalytic community.

Apart from these two important applications of plasmonic effects, a more subtle but equally important aspect of this resonance is that its spectral position can be tuned by changing the morphology, the charge carrier density, and the dielectric surrounding of the nanoparticle. These dependencies can also be used the other way around in order to track changes of the system via shifts in the plasmonic resonance, as detailed in the following. Note that when applying potentials to the nanoparticle, the optical bulk properties also change due to electroreflection. However, this effect is insignificant compared to the plasmonic effect [20].

Some electrochemical reactions lead to changes in the morphology of the electrode, which can affect the reaction rates and the mechanical stability of the system. As the spectral position of the plasmonic resonance depends on the shape of the nanoparticle, any degradation, annealing, or other morphology-altering processes that might occur during an electrochemical reaction will change the resonance [21, 22, 23, 24].

Another important quantity is the charging state of the nanoparticles, which is difficult to measure using standard electrochemical techniques. Charging a particle negatively, i.e., increasing the number of electrons, leads to a decrease of both the plasmon resonance wavelength (i.e., a blue-shift of the resonance) and the full width half maximum of the resonance curve, thus becoming accessible [25, 26, 27]. Positive charging behaves oppositely.

Adsorption of ionic species on the surface of the NPs leads to a change in dielectric surroundings and creates a new damping pathway, the so-called chemical interface damping (CID), which generally red-shifts and broadens the resonance [28, 29]. Additionally, the energetic states of the outermost nanoparticle layer are changed, which could also be viewed as a change in the imminent electric environment impacting the resonance [30], also known as adsorbate damping. This change in resonance has the potential of yielding in situ information on the number of adsorbed molecules, which is a central quantity used to understand reaction pathways and is often elusive, even with state-of-the-art measurement techniques.

This high sensitivity to so many different contributions can be a disadvantage in itself, as the NP/electrolyte interfaces have to be well-defined and free of any unaccounted molecules, e.g., linker and stabilizing agents. Although much research is conducted in this area, it remains difficult to relate these findings to one another. For one, it is still difficult to theoretically predict and explain the impacts of the aforementioned contributions on the plasmonic resonance in electrochemical environments. In addition, the plasmonic systems investigated differ significantly from one another in particle production and complexity. In order to help the development of common ground, a fairly simple, well-determined, and easy-to-use experimental platform is needed.

This work provides a fundamental investigation of plasmonic spectroscopy in electrochem-

ical systems by introducing a multi-particle plasmonic sensing platform that operates on extremely large and homogeneous nanoparticle arrays. The main nanoparticle material will be gold, which is well known for its plasmonic properties and one of the most thoroughly investigated electrode materials. All electrolytes will be water-based; hence, the electrochemical interface will be a metal/aqueous electrolyte interface. As with any electrochemical system, the cleanliness of the electrode surface and the electrolyte and the overall absence of impurities are of utmost importance. To ensure clean and well-defined surfaces, the electrode nanoparticle arrays will be produced via lift-off nanoimprint lithography (LO-NIL). This leads to stable particles without the use of stabilizing or linking agents that could potentially impact the plasmonic resonance.

The goal is to improve in situ LSPR measurements in an electrochemical environment such that changes of interfacial properties can be measured more sensitively than hitherto. This includes being able to distinguish all possible impacts on the plasmonic resonance that occur during electrochemical treatments.

The first step toward this goal will be to establish and design a plasmonic sensing platform that yields stable and interpretable results, which will be called (differential) Cyclic Plasmo-Voltammetry (dCPV). This requires a combination of setup optimization and the development of an ab initio data treatment pipeline. The next step is then to characterize the plasmonic data using the corresponding cyclic voltammetry and electrochemical impedance spectroscopy data. Therefore, standard reactions such as Au oxidation/reduction, sulfate/phosphate adsorption/desorption, double layer charging, Cu underpotential deposition on Au, and hydrogen evolution will be used.

After the plasmonic sensing method is established, it will be used to investigate the stability of the Au/aqueous electrolyte interface. Au, as the noblest metal [31], is also expected to be the least reactive, but it is well known that the polarized electrode surface is not a static entity. Rather, the intrinsic motion of surface atoms might lead to surface reconstruction [32, 33], restructuring and surface roughening [34, 35], place exchange events [36], dissolution and redeposition [37], intercalation of other chemical species [35], or degradation of the electrode, to name but a few. Due to the widespread use of gold as a standard electrode that is often expected to be stable, it is worthwhile investigating it with dCPV, especially considering the sensitivity of plasmonic resonances toward changes in morphology. It will be found that dCPV is sensitive enough to detect hydrogen adsorption on gold and that Au undergoes drastic morphological changes once hydrogen is evolved on it.

With the method developed and the first important discoveries reported, the last step is to expand the method to more complex systems and test out its current limitations. Here, two directions are followed: First, we attempt to resolve changes to the double layer charging during large faradaic currents, which will probe the sensitivity. Secondly, dCPV will be employed to investigate an applied system, i.e., self-organized Cu nanoparticles on Cu during high gas evolution, to test whether plasmonic resonances could be observed and used to analyze the complex processes of this system.

The outline of the thesis is as follows: Chapter 2 will introduce the theoretical background of plasmonics and their dependence on changes to the nanoparticle encountered in electrochemical systems. In Chapter 3, all pre-existing experimental methods, the production process of the nanostructured samples, and the numerical simulation program will be introduced. Chapter 4 shows and discusses the experimental results of the electrochemical, optical, structural, and numerical nanoparticle characterization. Chapter 5 introduces differential Cyclic Plasmo-Voltammetry as an in situ surface sensing technique and discusses some exemplary applications. Chapter 6 expands these to investigate Au-Hydrogen interactions and morpho-

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logical changes of the Au nanoparticles during electrochemical processes. Finally, Chapters 7 and 8 apply dCPV to more complex systems, namely $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox reactions on Au NPs and Cu slabs under gas evolution conditions, the analysis of which will point out current limits and potential evolutions of the method.

2. Theoretical Background

The main topic of this thesis is using plasmonic resonances to sense interfacial properties in electrochemical systems. Hence, an introduction to the fundamentals of plasmonic effects and state-of-the-art on how plasmons react to changes in their environment is helpful to follow the arguments laid out in this thesis.

2.1. Fundamentals of Plasmonics

In general, plasmons are collective electron oscillations in solids created by the interaction between an incoming photon and the conduction electrons of that solid. Depending on whether the oscillations are produced at an interface between a metal and a dielectric or in a nanoparticle, they are called surface plasmon polaritons (SPPs) or localized surface plasmon resonances (LSPRs). The latter are also called particle plasmons and will be the only type of plasmon occurring in this thesis. Hence, all references made to plasmonic effects from here on out will be regarding LSPRs. Both types are extensively discussed in the book “Plasmonics: Fundamentals and Applications” by S.A. Maier [16].

An LSPR is excited if a photon interacts with the sea of conduction electrons in a conductor to the point where the electrons move along the oscillating electromagnetic field, that is the photon, which will be absorbed in the process. The resulting collective electron oscillation can be viewed as a single bosonic quantum particle, called the plasmon, in quantum state n . Its energy is described by $E_n = \hbar\omega_p(n + 1/2)$, where ω_p is the plasma frequency of the metal. For the energies used in this thesis, n is typically very large, which warrants a classical treatment of the plasmon field [38].

Once the electrons collectively shift in a particular direction, a strong electric field is created around the nanoparticle, which is effectively polarized by this shift. The field is particularly strong at sharp edges and acts as a restoring (depolarising) force that enables oscillation of the electric field surrounding the NP, thus increasing its effective photonic scattering cross-section. Plasmonic excitations can, therefore, be viewed as additional contributions to the optical behavior of the metal, which can far outweigh the natural absorption/reflectance properties of the metal in question.

Note that no localized restoring force of this kind can occur for large particles and planar surfaces due to the high number of electrons in the surrounding bulk and the missing confinement [16]. Specifically, the size of the plasmonic NPs needs to be in the order of, or smaller than, the wavelength of the incoming light to avoid strong retardation effects, which will be explained in more detail below.

2.1.1. Analytic Description of Plasmons

Analytical descriptions of classic electromagnetic phenomena, like plasmons, is done by solving Maxwell’s equations on the geometry of interest using suitable boundary conditions. Here, the equations for the simplest analytically possible case, a conductive sphere in a homogeneous and isotropic medium, is presented to illustrate basic plasmonic properties.

Even in this simple case, a quasi-static approximation assumes that the incident wavelength λ is significantly larger than the sphere’s diameter. Hence, the oscillating electromagnetic

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field's phase is assumed to be constant over the sphere's volume. All symbols used in the following equations are summarized in Table 2.1 [16].

Table 2.1.: Summary of the relevant symbols for the analytic description of plasmonic effects.

Parameter	Description
ω	photon frequency
ϵ_m	dielectric constant of the surrounding medium
$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$	metal dielectric function
ϵ_0	dielectric constant
V	volume of the sphere
c	speed of light
e	elemental charge
m_e	electron mass
n	number of electrons
ρ_{el}	charge carrier density
$\sigma_{\text{abs}}(\omega)$	absorption cross-section

The central quantity to describe light-matter interaction, and therefore plasmonic effects, is the absorption cross-section given by

$$\sigma_{\text{abs}}(\omega) = \frac{9\omega\epsilon_m V}{c} \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + 2\epsilon_m]^2 + \epsilon_2(\omega)^2}, \quad (2.1)$$

which is derived from inserting the quasi-static polarizability [16]

$$\alpha = 3V \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \quad (2.2)$$

into the relation [39]

$$\sigma_{\text{abs}} = \frac{\omega}{c} \text{Im}(\alpha). \quad (2.3)$$

$$(2.4)$$

This was derived by Gustav Mie [40] in 1908 by approximating a nanosphere as a point dipole. Note that the result is, apart from the prefactor, also obtained by Kreibig and Vollmer [41].

$\epsilon(\omega)$ is the dielectric function of the sphere and given by [16]

$$\epsilon(\omega) = 1 - \frac{\omega_{\text{plasma}}^2}{\omega^2 + i\Gamma\omega} = \epsilon_1(\omega) + i\epsilon_2(\omega), \quad (2.5)$$

where ω_{plasma} is the metal plasma frequency given by [42]

$$\omega_{\text{plasma}} = \left(\frac{ne^2}{\epsilon_0 m_e} \right)^{\frac{1}{2}} \quad (2.6)$$

and Γ is the relaxation rate of the system given by

$$\Gamma = \left(\frac{m_e}{\rho_{\text{el}} n e^2} \right)^{-1}. \quad (2.7)$$

$\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ of Equation 2.5 can be simplified for the case of high excitation frequencies ($\omega \gg \Gamma$) to

$$\epsilon_1(\omega) = 1 - \frac{\omega_{\text{plasma}}^2}{\omega^2} \quad (2.8)$$

$$\epsilon_2(\omega) = 1 - \frac{\omega_{\text{plasma}}^2}{\omega^3} \Gamma \quad (2.9)$$

which can be put into Equation 2.1 to yield, in the case of frequencies close to the resonance frequency ($\omega \approx \omega_{\text{res}}$), the Lorentz function that is usually used to describe plasmonic resonances [41]:

$$\sigma_{\text{abs}}(\omega) = \frac{\sigma_0}{(\omega - \omega_{\text{res}})^2 + (\Gamma/2)^2} \quad (2.10)$$

These analytic equations describe two basic dependencies of plasmon resonances on the dielectric environment of the nanoparticle and its morphology, as is detailed in the following.

Impact of the Dielectric Environment

In electrochemical systems, the dielectric environment of the working electrode can constantly change due to local shifts in reactant concentration and compositional changes of the working electrode surface. Hence, knowing the general impact of such changes on the plasmonic resonance is important.

The resonance condition of the plasmonic absorption can be found by minimizing the denominator of Equation 2.1.

$$|\epsilon(\omega) + 2\epsilon_m| = [\epsilon_1(\omega) + 2\epsilon_m]^2 + \epsilon_2(\omega)^2 = \text{Minimal} \quad (2.11)$$

In the case of the sphere being surrounded by air or water ($\epsilon_m > 0$), this relation requires $\epsilon_1(\omega)$ to be negative, which is true for most metals. Given that $\epsilon_1(\omega)$ is small around the resonance, the following relation holds:

$$\epsilon_1(\omega) = -2\epsilon_m \quad (2.12)$$

Combining this with Equation 2.8, it follows that for larger ϵ_m , the resonance position is shifted to smaller frequency values, i.e., red-shifted. The physical origin is that in media of higher polarizability, the induced electric field surrounding the nanoparticle gets weakened, decreasing the restoring force and, consequently, the resonance frequency ω_{res} [41].

The most common dielectric environments are air ($\epsilon_{\text{air}} = 1$), water ($\epsilon_{\text{air}} = 1.3$) and SiO_2 ($\epsilon_{\text{SiO}_2} = 1.6$). With nearly constant real parts and insignificant imaginary parts of the dielectric function, their impact on the plasmonic resonance can be modeled with the analytical model. However, the dielectric functions are more complicated for substances like Si, which requires numerical simulations to describe such systems theoretically.

Impact of the Nanoparticle Geometry

Similar to the dielectric environment, the geometry of the working electrode NPs is subject to change throughout experiments and is, therefore, important for later interpretations of plasmonic signals.

Starting from the Mie theory for a sphere in a dielectric medium, the following relation between sphere radius r and resonance frequency can be derived:

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$$\omega_{\text{res}} \approx \frac{0.324\pi c}{n_{\text{m}}r} \quad (2.13)$$

$$\frac{2\pi c}{8n_{\text{m}}r} < \omega_{\text{res}} < \frac{2\pi c}{6n_{\text{m}}r} \quad (2.14)$$

From this, it becomes clear that for rising r , the resonance frequency decreases, thus red-shifting the resonance. One reason for this is the occurrence of depolarising fields for larger geometries, which counteract the restoring force. Equation 2.13 only holds for this analytic case, while more complex geometries have to be simulated numerically, especially if they exhibit sharp edges, which cause additional disturbances to the electric field.

2.1.2. Relaxation Pathways

So far, plasmonic excitation and oscillation have been discussed in an idealized setting and without considering their lifetime. Assuming finite metallic crystals, with differences between surface and bulk lattice, instead of continuous media, for most materials, a single plasmon will most likely scatter in about 10 – 100 ns via either a photon (reemission), a phonon (lattice heating), or by transferring its energy to a single electron. The probability of a plasmon scattering is related to the relaxation rate of the system Γ , which is expressed in the width of the plasmonic resonance:

$$\Gamma = \Gamma_{\text{bulk}} + \Gamma_{\text{surf}} + \Gamma_{\text{ret}} + \Gamma_{\text{inter}} + \Gamma_{\text{hetero}} \quad (2.15)$$

The first contribution is determined by the plasmon-phonon and plasmon-electron interaction, which is summarized in the bulk relaxation rate Γ_{bulk} [41]. Another contribution is plasmons interacting with electronic states at the particle's surface, which is also known as surface or Landau damping Γ_{surf} [41]. Because of this effect, the mean free path length of electrons in the metal and the aspect ratio of the NPs are relevant for the plasmonic behavior. The third contribution is the dephasing of the plasmonic electric fields due to, for example, large NP sizes, as discussed above. The thereby occurring depolarizing fields affect the width of the plasmonic resonance via Γ_{ret} [29]. The last two contributions are only relevant for multi-particle arrays, which interact with one another, giving rise to Γ_{inter} [16]. Additionally, if multiple nanoparticles have slightly different resonance positions, the collective response will be affected by heterogeneous broadening Γ_{hetero} . This is not a plasmonic property by itself but represents an artifact introduced by averaging over multiple plasmonic resonances during a measurement, which is why it is included here.

2.2. Particle Plasmons in Electrochemical Systems

This thesis investigates the impact of electrochemical processes on the plasmon resonance of NPs. While plasmonic catalysis, i.e., the impact of plasmons on the rate of electrochemical processes, is not the main focus, however, as it is the other principal use of plasmons, it is instructive to include a short introduction to this field here.

When exciting plasmons in metal NPs, the photon energy is directly transferred into the metal. After relaxation, the energy is converted into either photons (re-emission), a lattice temperature (phonons) increase, or a few highly energetic electrons. If these hot electrons are not removed from the NP, they will equilibrate by exciting phonons or increasing the average electron temperature.

This makes plasmons very interesting for electrochemical applications, as either of these effects - be it local heating or hot electron creation - could be beneficial for driving electrochemical reactions. In these cases of plasmonic catalysis, the metal NP would be used as a working electrode within an electrochemical reactor, i.e., fixated on a conducting substrate on one side and submerged in electrolytes on the other. During electrochemical procedures, voltages are applied to the NP, changing the charge carrier density and driving faradaic reactions on its surface.

With all of these aspects of photo-electrochemical treatments, it is instructive to summarize the state of the art of those impacts on the plasmonic resonance, which is done in the following.

2.2.1. Impact of Charge Carrier Density

An electrochemical interface is usually the region just around the border between the metal and the electrolyte. On the metal side, electrons are conducting the current, while on the electrolyte side, the movement of ionic species closes the electrical circuit.

If a voltage is applied between the metal and the electrolyte side, a capacitive charging current flows and (dis)charges both sides of the electrochemical interface.

On the metal side, this means an increase/decrease of the charge carrier density within $\approx 0.1 \text{ \AA}$ of the interface; on the electrolyte side, this results in the formation of an electrochemical double layer. In aqueous electrolytes, the latter is conceptually divided into a part with high ion concentration very close to or at the interface, the so-called inner Helmholtz layer, and a more extended region called the outer or diffusive or Guy-Chapman layer. As typically there are multiple species of ions with different charges present in the electrolyte, the composition of both layers varies with potential [5].

Charging and discharging of the metal electrode impact the plasmonic resonance, which depends on charge carrier density as indicated for the metal sphere in Equation 2.7. Note that even in the case of open circuit potential, charges accumulate on both sides of the interface due to the equilibration of the electrochemical potential of the electrons in the metal and of a redox couple in the electrolyte in the system. Consequently, there must be a potential at which the interface is not charged, which is called the potential of zero charge (PZC). Only at the PZC are the plasmonic resonances unchanged due to charging effects.

Several studies have compared experimental results of plasmonic spectra with semi-classical calculations for the charging effect on plasmonic resonances [25, 27, 43, 44]. They all have found that the energy of the plasmon resonance, i.e., the plasmon resonance wavelength, depends on the electron distribution around the surface. In contrast to the classical Mie theory, where a uniform charge distribution is assumed, quantum mechanical effects like electron spill-out cause the distribution to become highly complex, especially around the surface. They found that for an increased number of electrons in the particle, the drop in electron density across the boundary is steeper, and the spill-out is larger, causing the resonance spectrum of the plasmon to be sharper and shift to higher energies. Additionally, it was found that the change in the refractive index due to double layer formation/adaptation is not significant enough to cause these changes [26].

Plasmons themselves could also impact the charge carrier density as they create hot electrons or holes that can be exchanged with adjacent materials to minimize the free energy of the NP [45]. This can be considered as a plasmon-induced photovoltage, which was measured to be up to 100 mV [46] for specific illumination conditions on selected samples.

2. Theoretical Background

2.2.2. Chemical Interface Damping

Bond formation between the NP surface and chemical species changes the energetic structure of the electrochemical interface. These processes happen in any system with aqueous electrolytes and are, hence, of special importance to plasmonic resonances.

Forming (chemical) bonds with the electrode surface at certain potentials is favorable for some chemical species and is called adsorption. Usually, this process is accompanied by at least a partial electron transfer to or from the electrode, which leads to a faradaic current above or below a species-specific onset potential [5]. Over the past decades, especially after the most recent advent of machine learning, mechanistic details of adsorption reactions on the molecular scale have been predicted and measured extensively [47]. Among those are the hydrogen adsorption on Pt [48, 49], the CO₂ ad- and desorption on Cu [50], and the oxidation of Au [51], which vastly improved our understanding of these important reactions.

Apart from the mechanistic details, adsorption reactions can be divided into different cases that are relevant to plasmonics:

- Passivating adsorption, where the adsorbed molecules occupy the reaction centers of the surface, thus hindering any additional reaction after the monolayer is completed. An example for this is CO poisoning of Pt [52].
- Sublayer absorption, where the adsorbed molecules can diffuse into the bulk, effectively reacting multiple layers of the material, as in the case of oxidation of Au [51].
- Deposition processes, where multiple adlayers are stacked on top of one another, as in the case of Cu overpotential deposition [53].
- Underpotential deposition (UPD), where adsorption reactions happen in a potential regime, that should be thermodynamically forbidden due to suitable energetics of the non-ideal surfaces. An example for this is the hydrogen underpotential deposition on Pt [54].

Plasmonically, the adsorption of chemical species onto the surface of the NP leads to new electron energy states with which the plasmon can interact. This leads to a new damping pathway, i.e., chemical interface damping (CID), which generally red-shifts and broadens the resonance [28, 29]. Thereby, a plasmon scatters with an electron of a covalent bond between the adsorbate and surface metal atoms, which excites the electron and either induces desorption or electrochemical reaction of the adsorbate. Naturally, this direct hot electron injection is a key mechanism thought to selectively and controllably enhance reaction rates [55].

The surface has an important impact on the plasmon resonance as it is mostly there that changes in dielectric properties occur, and this is where the induced electric fields are the strongest. Any changes in this region affect the plasmon in some way, which makes them a very potent sensor for changes at electrochemical interfaces [56].

Depending on the exact change of the interface energy states, the bonds between metal atoms and adsorbed species might be so strong that the metal-adsorbate complexes can be treated as an individual layer on top of the metal, which could be modeled via a change in refractive index of the dielectric environment [30, 51].

If a different metal is deposited on the NP, e.g., by reducing metal cations, there is usually no limit to the amount of deposited material, which in turn could exhibit plasmonic properties if the layer grows to a significant thickness [57].

2.2.3. Impact of Nanoparticle Morphology

If the electric potential is increased up to a critical value, some species undergo an electrochemical reaction on or close to the electrode surface. Thereby, electrons are taken from (reduction) or injected into (oxidation) the electrode, which is called a faradaic current. The exact electrical potential at which a specific chemical species can react and how much of the related product is produced depends on their electrochemical potentials, on the energetics of the electrochemical interface, the number of available active sites, the concentration of the educt and the product close to the surface, the binding energy of the adsorbed educt and products and activation energy barriers [5].

All of these aspects depend on the exact surface morphology, which can be tailored to exhibit almost any desirable features, such as the number of under-coordinated sites, surface roughness and chemical heterogeneity, and porosity. Currently, most highly active surfaces include nanopatterning, which introduces a large surface area and many active sites, among other aspects [58].

Regardless of the selected morphology, however, all surfaces experience structural change over time, which is introduced by (1) unwanted reactions changing the chemical composition of the surface, such as oxygen adsorption, (2) corrosion by ionizing electrode atoms, (3) physical change by pitting or thermal reorganization, and (4) electrochemical annealing processes. These changes are sometimes induced by design, but in most catalytic systems, they are unwanted as they reduce the efficiency and longevity of the electrochemical cell.

Specifically for nanoparticles, these unwanted changes in morphology are a challenge, but due to the significant upsides of using nanostructured electrodes, a lot of research has been undertaken to prevent degradation [59, 60].

One of these advantages is plasmonic effects, which also greatly depend on the nanoparticle morphology. As explained above, the size of the NPs determines the resonance position and width, with larger particles leading to higher rates of re-radiation. In comparison, smaller particles exhibit significant increases in their absorption cross-section. Apart from the size, the shape of the NP is also of interest, as it determines the plasmonic mode and the local field distribution and impacts the probability of hot charge transfer. The latter aspect depends on the relation between the mean free path of the electron and the aspect ratio of the particle, with hot carrier generation more likely for high aspect ratios and long mean free path lengths [21, 22, 23, 24].

3. Experimental Details

This chapter will discuss the principles of sample production, the simulations, and the experimental setups used for all experiments of the following chapters. First, the lift-off nanoimprint lithography by which the nanoparticle arrays are produced, will be summarized (section 3.1). Secondly, a detailed introduction to finite-difference time-domain simulations of COMSOL Multiphysics will be given before the relevant simulation setup is discussed in detail (section 3.2). Then, the specifications of the optical and electrochemical experiments will be given individually (sections 3.3 and 3.4) and as a combined experiment (section 3.5). Lastly, the ex-situ structural analysis techniques will be described (sections 3.6 and 3.7).

3.1. Sample Production: Lift-Off Nanoimprint Lithography

All nanostructured samples used in this thesis are produced via lift-off nanoimprint lithography (LO-NIL). The individual preparation steps are shown schematically in Figure 3.1. The fabrication process details are described by Nagel et al. [61]. In short, the sample surface is coated with a lift-off and an imprint resist and then subjected to the following steps: (a) imprinting of the pattern, (b) reactive ion etching, in which the remaining imprint resist is removed from the impressed areas, (c) an isotropic chemical underetching that removes the exposed lift-off resist, (d) a second reactive ion etching, in which SiO_2 in the exposed areas is removed (e) evaporation of Ti/Au, and (f) lifting off the remaining resists, which results in the desired Si/Ti/Au structures embedded in SiO_2 .

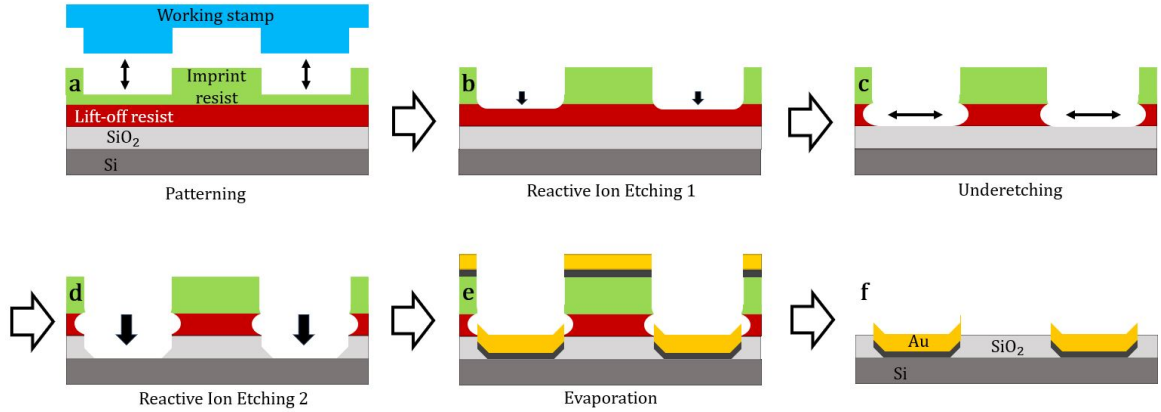


Figure 3.1.: Lift-off nanoimprint lithography (LO-NIL) production schematic

As visualized in Figure 3.1(f), the combination of the isotropic etching step (c) with the second reactive ion etching step (d), leads to wedges at the rims of the SiO_2 -film, which are conserved during the evaporation step resulting in crown-like extrusions at the border of the particles. An example of these wedges can be seen in the first AFM inset of Figure 6.5 and in Figure 4.2.

The nanoparticle array covers an area of $5 \text{ mm} \times 5 \text{ mm}$ of the total $1 \text{ cm} \times 1 \text{ cm}$ surface area of the substrate (n-doped Si wafers (FZ:(111), 1-10 $\Omega \text{ cm}$, Si-Mat Silicon Materials, Germany).

3. Experimental Details

With each unit cell of the array covering an area of $150\text{ nm} \times 150\text{ nm}$ and one NP per unit cell, the arrays consist of about a billion NPs. The back of the substrate is covered by aluminum and subsequently annealed to form a good electrical contact. All samples used in this thesis were produced by either Matthias Golibrzuch, Thomas L. Maier, Andrea C. Sterr, or Simon S. Leisibach.

Overall, the particle size and morphology are relatively homogeneous, as shown in the electron microscopy images in Figure 3.2 for different zoom levels of the same sample. Slight deviations from a perfect circular shape are visible only in the most extensive zoom. It has to be noted, however, that particles will change their shape during measurements and become even more homogeneous, as shown in Figure A.1 of the appendix.

This section has been adapted from M.J. Feil et al. [62].

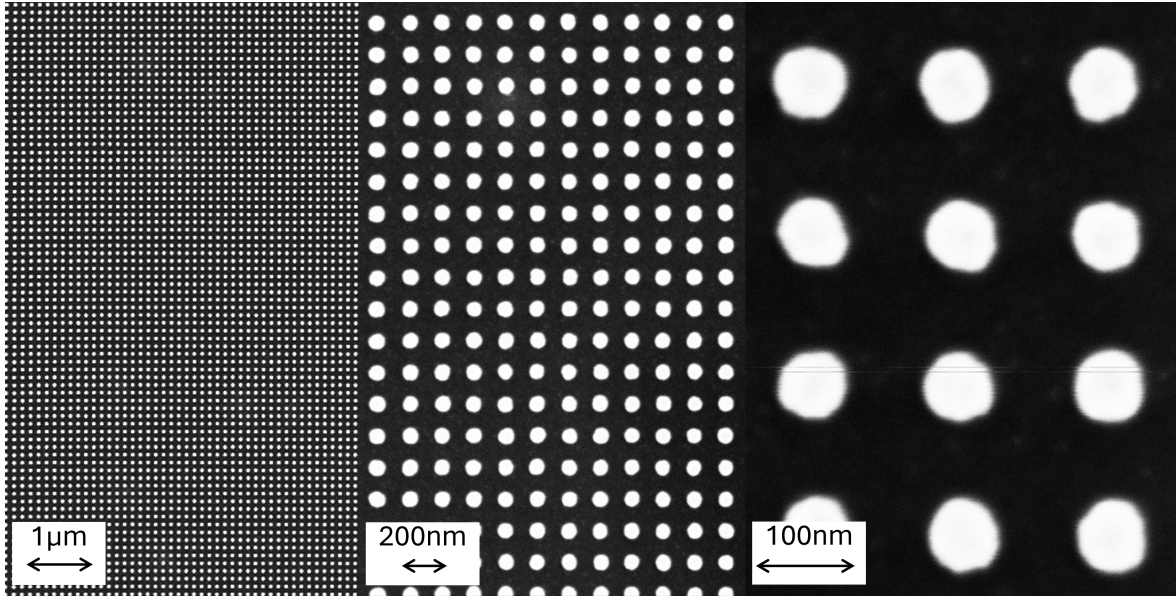


Figure 3.2.: Scanning Electron Microscopy images of an exemplary sample produced as shown in Figure 3.1 for different levels of zoom. The diameter of these NPs is $d_{\text{NP}} = 75\text{ nm}$. White indicates conductive material (gold in this case) and black indicates non-conductive SiO_2 .

3.2. COMSOL Simulation

Most real plasmonic systems are too complex to be calculated analytically, as detailed in Chapter 2, which is why numerical methods, such as finite element method (FEM) simulations, will be used to predict plasmonic behavior. In FEM simulations, the geometry of interest is discretized into a multitude of domains in which the desired equation is solved. In these domains, spatially varying parameters are defined as constant, and the domain boundaries set constraints for the solution of the individual equations. Further details on the mathematics behind FEM simulations can be found in Larson et al. [63].

In general, FEM simulations are only approximations of a theoretical model, which introduces uncertainties to the obtained results. However, these get more precise for finer discretization of the domains, i.e., the mesh, which comes at the cost of increased computation time. Throughout this work, COMSOL Multiphysics 5.6 is used to perform FEM simulations

of Maxwell's equations to find the optical plasmon resonance of selected geometries. This simulation is semi-empiric as the relevant optical parameters, refractive index n , and absorption coefficient k are taken from measured datasets. Specifically, the "electromagnetic wave, frequency domain" module is used in which Maxwell's equations of the form

$$\vec{\nabla} \times \mu_r^{-1}(\vec{\nabla} \times \vec{E}) - k_0^2(\epsilon_r - \frac{i\sigma}{\omega\epsilon_0})\vec{E} = 0 \quad (3.1)$$

are solved for one unit cell of the array with periodic boundary conditions in both x and y direction of the plane. Here, μ_r is the relative permeability, k_0 the damping constant, ϵ_r the relative dielectric constant, σ the conductivity of the medium, $\vec{E}$ the electric field amplitude and ϵ_0 the vacuum permittivity. This formulation of Maxwell's equations is also known as the curl-curl-formulation. It can be derived by inserting the time derivative of Maxwell-Ampere's law

$$\frac{\partial}{\partial t}(\vec{\nabla} \times \vec{H}) = \frac{\partial}{\partial t}\left(\sigma\vec{E} + \epsilon_0\epsilon_r\frac{\partial\vec{E}}{\partial t}\right) \quad (3.2)$$

into the curl formulation of the Maxwell-Faraday equation

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E} = -\vec{\nabla} \times \frac{\partial\vec{B}}{\partial t} = -\frac{\partial}{\partial t}(\vec{\nabla} \times \vec{B}). \quad (3.3)$$

assuming the spatially dependent electric field amplitude $\vec{E}(\mathbf{r})$ to be time harmonic

$$\vec{E}(\mathbf{r}, t) = \vec{E}(\mathbf{r}) \exp(i\omega t). \quad (3.4)$$

3.2.1. Simulated Geometry

The basic metal NP/dielectric geometry used for most of the simulations in this thesis is shown in Figure 3.3(a), and a 2D cross-section is shown in Figure 3.4. The cross-section of the nanoparticle shown in Figure 3.1 is used as a blueprint for the simulation. In both Figures 3.3(a) and 3.4, the light blue area (I) simulates the upper medium, which is water if not stated otherwise, the yellow domain (II) represents the Au NP with its Ti/TiO_x adhesion layer (III), the light grey area (IV) represents SiO₂ and the dark grey block beneath the NP is the Si substrate (V). It has to be noted that for reasons of clarity, two boundaries of the upper medium have been removed, the Ti/TiO_x layers have not been highlighted, and the height of both the upper medium and the substrate has been reduced.

All geometric quantities, except for the TiO_x layer thickness, have been determined by the production parameters, atomic force microscopy, scanning electron microscopy, and ellipsometry measurements. These are shown in Table 3.1 and are valid for all simulations if not stated otherwise. As TiO_x is expected to be formed by partial oxidation due to contact with SiO₂, neither the exact structure nor its thickness is measurable. The thickness of TiO_x given in Table 3.1 has been determined in a previous work [65].

The specific configuration of the excitation ports, i.e., the boundaries where light enters and leaves the geometry, and of the periodic boundary conditions are shown in Figure 3.3(b) as a light blue plane with an arrow pointing towards it and purple planes respectively. For clarity, only one pair of boundary conditions and only the incoming port are shown here.

3.2.2. Mesh Setup

The core part of a FEM simulation is the division of the geometry into domains, which is shown in Figure 3.3(c). In general, simulations get more precise the finer the mesh is. However, a

3. Experimental Details

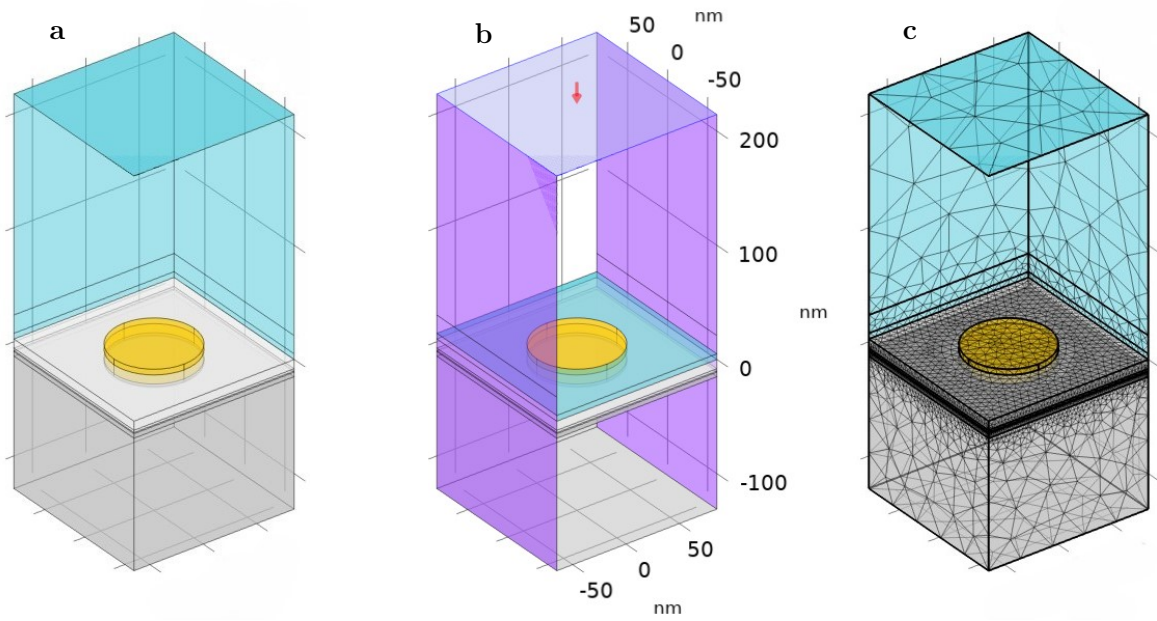


Figure 3.3.: 3D view of the geometry used in the COMSOL Multiphysics simulations. (a) the basic geometry with color-coded materials (yellow: Au, blue: water/air, light gray: SiO_2 , dark gray: Si). (b) highlight of the central boundary conditions (purple: periodic boundary condition, light blue: light incident port, gray: light exit port). (c) meshing of the geometry. Note that two of the boundaries of the upper medium (blue) have been removed for clarity.

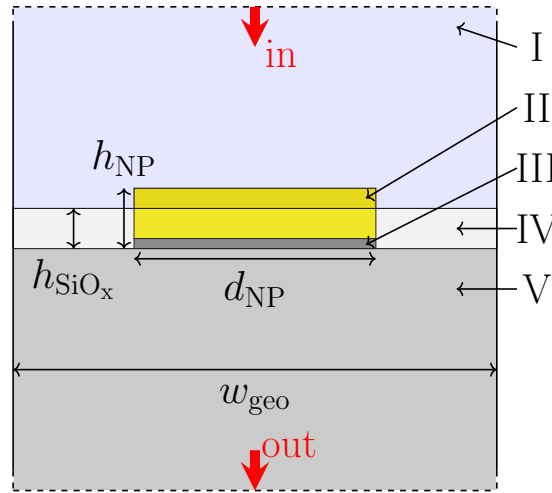


Figure 3.4.: Cross-section of the geometry used in the COMSOL simulations. The numerals indicate different materials. (I) upper medium, (II) Au NP, (III) Ti/ TiO_x adhesion layer, (IV) SiO_2 , and (V) Si substrate. The red arrows indicate the excitation ports of the simulation. Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

Table 3.1.: Geometric simulation parameters and their typical values.

Parameter	Description	Value
h_{NP}	$h_{\text{Au}} + h_{\text{Ti}} + h_{\text{TiO}_2}$	16 nm
h_{Au}	Au nanoparticle height	13 nm
h_{Ti}	Ti adhesion layer thickness	2 nm
h_{TiO_2}	TiO ₂ layer thickness	1 nm
d_{NP}	nanoparticle diameter	75 nm
h_{SiO_2}	SiO ₂ layer thickness	10 nm
w_{geo}	width of the unit cell	150 nm

mesh that is not good enough will not only be inaccurate but will also introduce multiple numerical artifacts that might dominate the actual physical features. If the mesh is chosen too fine, the number of iteration steps might become unfeasibly large, and even such a mesh might not give artifact-free results. This section will detail the specifics of a suitable mesh for our system.

Figure 3.3(c) illustrates the basic principles of a good mesh:

- Geometries of interest and their surroundings must be meshed finely, e.g., the NP and a box surrounding it
- Sharp edges must be meshed finely, e.g., the NP top and bottom circumference
- Boundaries that are connected by a mathematical relation must be meshed accordingly, e.g., the periodic boundaries must be meshed with the exact same mesh
- Mesh domains need to be smaller than any dimension of the macroscopic building block which they are a part of
- Broader regions can subsequently be meshed more coarse moving away from the finer meshed regions, e.g., the upper medium and the substrate

Note that all black parts of the mesh are so finely divided that the small domains cannot be resolved in this image and that all shown domains are only the 2D meshing of the boundary elements. The smallest dimension can be found in the TiO_x and Ti adhesion layers, which are 1 nm and 2 nm thick, respectively.

To ensure a stable simulation, the nanoparticle has to be especially finely partitioned by a lot of small domains. However, as the enhanced electric field surrounding the NP during plasmonic oscillations must also be resolved and reach far into the upper medium, an additional block has been put in to define an area where the partition of the space into mesh elements is fine as well.

For simulations involving electromagnetic waves, the length of the system has to be larger than the wavelength of the incident light. As plasmonic particles are expected to re-radiate light in all directions, the upper medium and the substrate must have a height of at least the simulated wavelength. Note that in Figure 3.3, the height of both these geometries is scaled down for visibility reasons.

3.2.3. Simulated Quantities

Each simulation is conducted for one specific illumination wavelength, for which the equilibrium electric field is calculated on all domains. In the second step, the reflectivity of the

3. Experimental Details

structure is calculated by dividing the power of the incoming electromagnetic wave by the power going out of the system through the input port. Parallel, the transmitted power is divided by the incoming power to yield the transmission of the structure. This is repeated for several different wavelengths at the end of which the full reflectance and transmission spectra of the geometry are retrieved.

3.3. Electrochemical Measurements

In all electrochemical measurements shown in this thesis, either a sample as described in section 3.1 or a pure gold sample of the same size (1 cm $\times$ 1 cm) was used as working electrode (WE). Before every measurement, the WEs were sonicated in acetone and then in isopropanol for 7 minutes each and rinsed under flowing deionized (DI) water before being put into the electrochemical cell, whose details are shown in the following.

3.3.1. Measurement Setup

The main compartments of the electrochemical cell used in this thesis consist purely of polychlorotrifluoroethylene (PCTFE) and are shown in Figure 3.5. Here, the cell is shown from the front. Note that the sample (working electrode) is built in from behind the cell facing forward so that it seals off the main compartment from the back. The reference electrode (RE) compartment and the counter electrode (CE) compartment are movable so that N117 Nafion[®] membranes can be fitted between the compartments to ensure controlled ion transfer. The front of the main compartment is closed off by an optical glass slab that functions as a window for illumination. Leakage is prevented by using o-rings around the sample, the membranes, and the glass window, which are compressed using aluminum profiles. On top of the main compartment are three ports, two of which are used as gas in- and outlet, while the latter is used for electrolyte exchange between experiments. Ar 5.0 gas is flown through these gas ports during experiments if not stated otherwise.

A picture of a fully assembled cell is shown in Figure 3.6(a). The screws on the front aluminum panel are used to compress the compartments and thereby sealing it. The light brown piece at the end of the gas tube connects the cell to the Ar gas bottle, while the rightmost port is left open for the gas to exit the cell. In Figure 3.6(b), the working electrode is shown in the fully assembled cell. The faint golden area in the center of the sample is the nanopatterned array. Note that in this case, a sample employing nanostructures with a side length of 1400 nm is shown as the nanoarrays of interest (75 nm) exhibit even less visible gold structures.

A gold wire sufficiently submerged in the electrolyte of interest is used as the counter electrode and can be seen as the thin golden thread exiting the right compartment of the cell in Figure 3.6(a). In contrast, the mercury/mercurous sulfate reference electrode (MSE 500 mM H₂SO₄, $E_{\text{SHE}} = E_{\text{MSE}} + 650 \text{ mV}$) sits within a glass sleeve that is separated from the electrolyte by a fritte (not visible here) and filled with 500 mM H₂SO₄ to ensure stable long-term measurements. For electrochemical control, a Zahner-Zennium potentiostat is connected to WE, CE, and RE. A schematic of the full setup is shown in Figure 3.7, and a top view picture is shown in Figure 3.8. During measurements, the electrochemical (EC) cell is placed inside an acrylic box, which can be sealed and filled with Ar to ensure the removal of residual oxygen. The electrical contacts and the optical fibers are cast into the walls of the acrylic box to ensure proper gas tightness. The optical setup is explained in section 3.4.

Before every measurement protocol, the cell is cleaned by letting the PCTFE components rest in a 1:1 H₂SO₄:H₂O ($\approx 9 \text{ M H}_2\text{SO}_4$) solution for a night. The reference electrode is

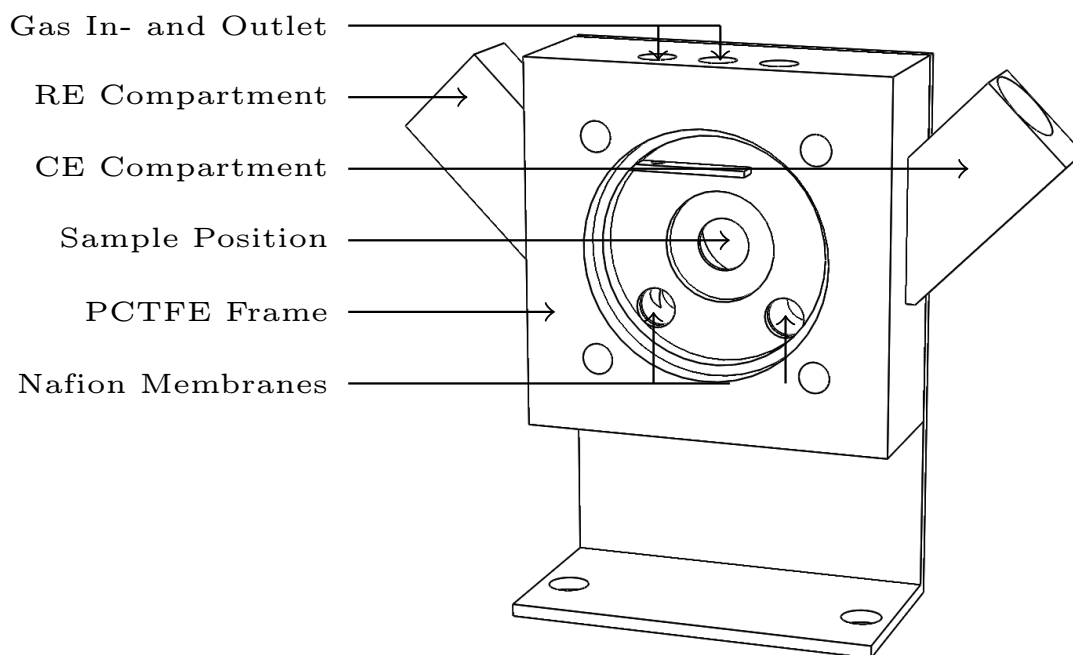


Figure 3.5.: Design of the electrochemical cell, adapted from T.L. Maier.

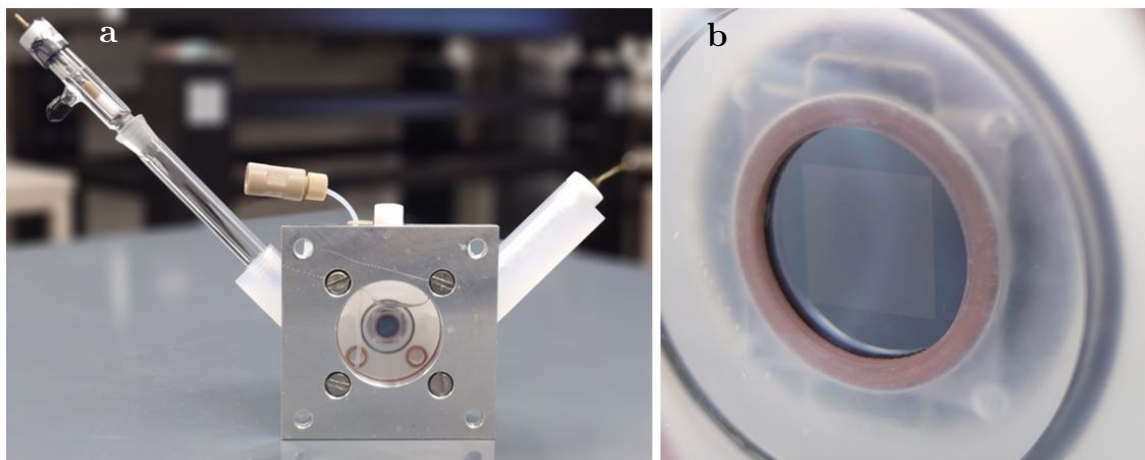


Figure 3.6.: Front view images of a fully assembled cell (a) and a zoomed image showing the sample in the fully assembled cell (b).

stored in a 500 mM H_2SO_4 solution to ensure a defined ion concentration, and the counter electrode is stored in air but protected from dust. After rinsing the cell components, WE, RE, and the CE multiple times with deionized (DI) water ($\rho_{\text{DI water}} = 18.2 \text{ M}\Omega \text{ cm}$), the cell is assembled and properly rinsed once more. Then, the setup is filled with the desired electrolyte and connected to the potentiostat, the gas inlet, and the mechanical holder. If the setup is leak-free, the acrylic box is sealed, and the box and the cell are purged with Ar 5.0 for at least 30 min. The first electrochemical measurement is always a few (≈ 5) cleaning cycles run with 50 mV s^{-1} from just negative of the oxygen evolution onset potential ($E_{\text{RHE}} \approx 1.65 \text{ V}$) to the onset of hydrogen evolution ($E_{\text{RHE}} \approx -0.15 \text{ V}$). The order of the following steps

3. Experimental Details

depends on the specific protocol but always includes measurement of the system impedance and determination of the electrochemical active surface area, which are detailed in the next sections.

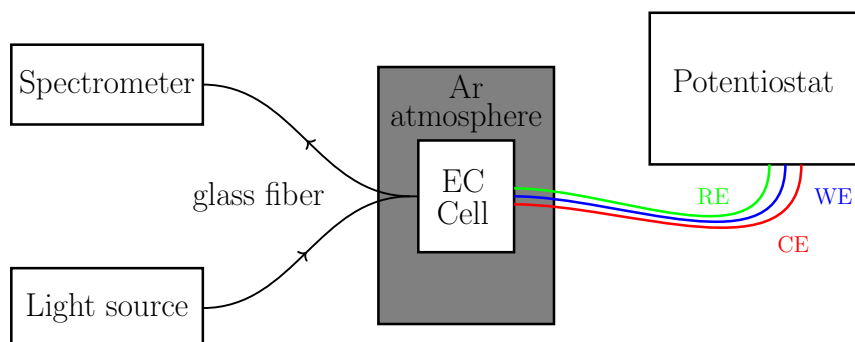


Figure 3.7.: Electrochemical and optical setup used for all electrochemical/optical measurements in this thesis. The electrochemical cell is kept in an acrylic box where an Ar atmosphere is established. During optical measurements, the sample is illuminated from the front by a white light source.

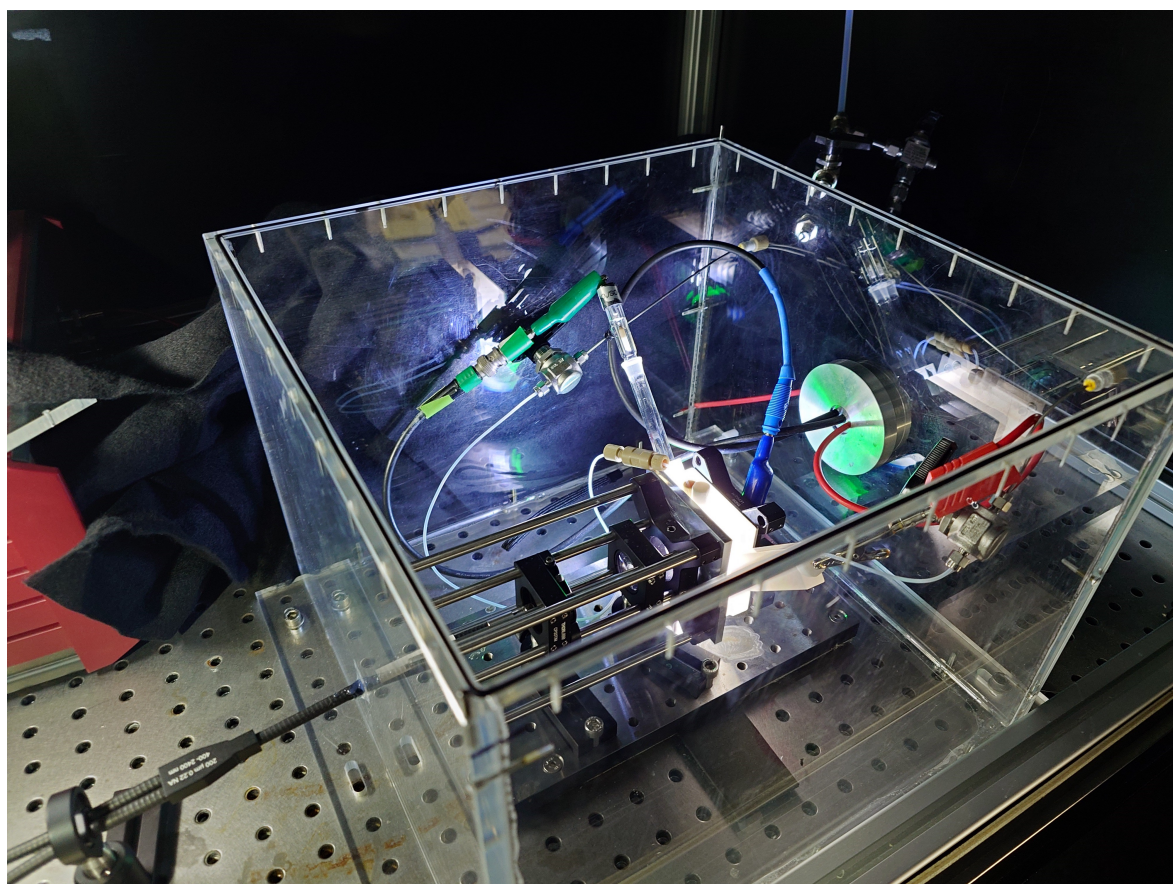


Figure 3.8.: Picture of the main part of the measurement setup. The lid is not placed on the acrylic box in the picture for visibility reasons. Both the optical spectrometer and light source are not shown.

3.3.2. Determination of the Electrochemical Active Surface Area

The Electrochemical Surface Area (ECSA) is the area of the working electrode surface on which electrochemical reactions can occur. It is used to normalize the electrochemical currents so that the activity of different electrodes can be compared. It is calculated via

$$ECSA = A_{\text{Au,geom}} \cdot r_{\text{surf}} \quad (3.5)$$

where $A_{\text{Au,geom}}$ is the geometric surface area and r_{surf} the surface roughness of the working electrode. The former estimates the surface area assuming perfectly flat surfaces, which is why the ECSA is usually larger than $A_{\text{Au,geom}}$. Samples used in this thesis consist of polycrystalline Au and have a moderate roughness ($r_{\text{surf}} \approx 1.4$) and a geometric area of $A_{\text{Au,geom}} \approx 0.063 \text{ cm}^2$. These values differ slightly for each sample due to uncertainties in the production process, which is why the ECSA has to be measured for each sample individually.

It is determined by oxidizing the samples in pH1 100 mM H_2SO_4 at 50 mV s^{-1} up to one monolayer of auric oxide (upper turning potential $E_{\text{upper,SHE}} = 1.680 \text{ V}$) and then integrating the reduction current I_{red} around the auric oxide reduction peak minus the capacitive current I_{cap} to get the total charge $Q_{\text{red,mono}}$ transferred during the reduction

$$Q_{\text{red,mono}} = \int (I_{\text{red}}(t) - I_{\text{cap}}(t)) dt. \quad (3.6)$$

It is assumed that $Q_{\text{red,mono}} = Q_{\text{ox,mono}}$, as long as only minute amounts of gold are lost during the scan. Any measurement of the ECSA is done via a cyclic voltammogram run with 50 mV s^{-1} in pH1 100 mM H_2SO_4 . Figure 3.9 shows this treatment for one exemplary dataset. Using the surface area per specific charge $A_{\text{Au}}/q_{\text{Au}} = 480 \text{ m}^2 \text{ C}^{-1}$ for a monolayer of auric oxide [66], the ECSA can be calculated via

$$ECSA = Q_{\text{ox,mono}} \cdot A_{\text{Au}}/q_{\text{Au}} \quad (3.7)$$

which leads to values of $ECSA \approx 0.07 \text{ cm}^2$. Standard procedure calculates the ECSA via Equation 3.9 for five consecutive cycles and averages them to yield the value used for rescaling the cyclic voltammetry data.

During a measurement day, the area is expected to change, which is why these measurements are often repeated multiple times during a day of measurements.

3.3.3. Electrochemical Impedance Spectroscopy

The previous section showed how cyclic voltammetry is used to investigate the properties of an electrochemical system. Another way to gain information about system-specific properties is the so-called electrochemical impedance spectroscopy (EIS). This technique measures the complex impedance of the electrochemical system by applying a constant potential plus a small alternating perturbation of a defined frequency ω and recording the system's current response (i.e., phase and amplitude) [67]. In this thesis, EIS is done for multiple frequencies between 100 kHz and 100 mHz with 6 sampling points per decade. After recording the data, it is fitted with the expected function for a specific electrical equivalent circuit. The circuit used for all measurements in this thesis is shown as the inset of Figure 3.10(b). The data has been treated via Python with the “impedance.py” package [68].

The equivalent circuit in Figure 3.10(b) models the charging of and the electrochemical reactions at the interface with a constant phase element (CPE) and an ohmic resistance R_p , respectively. The resistances of the solution, the sample and the external circuit are modeled via the resistance R_s , which is in series to the other two. A typical Bode plot of an

3. Experimental Details

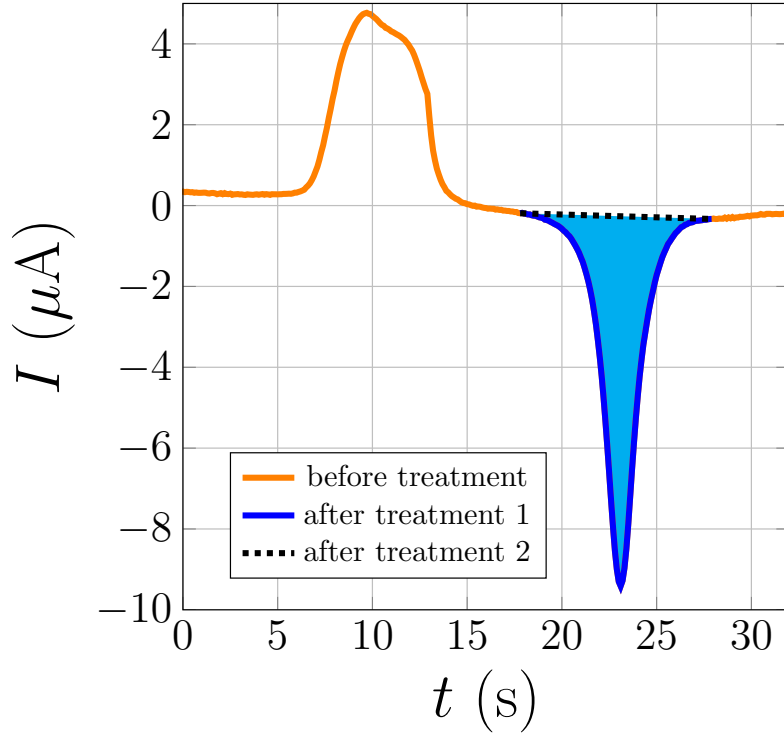


Figure 3.9.: Exemplary dataset for the ECSA determination via integration of the auric oxide reduction peak (cyan area) of a CV recorded with 50 mV s^{-1} in pH1 100 mM H_2SO_4 .

EIS measurement is shown in Figure 3.10 with (a) the absolute impedance $|Z|$ and (b) its negative phase $-\Phi$. The red part of the curves is excluded from the fitting procedure, as their systematic errors are comparatively large. This exemplary dataset is recorded for a potential in the double layer region, which is the standard for retrieving comparable results. For an ideal capacitor, $-\Phi$ is expected to converge to 90° at small frequencies, which is not reached by the samples in this thesis, necessitating the use of a CPE.

The standard procedure is to record and evaluate EIS data for different applied potentials with an equilibration time prior to applying the periodic perturbation of 30 s at each potential to ensure the stability of the current during the measurement. To select the resistance used for IR correction, the resistances are averaged over multiple potentials in the double layer region. If any sample deviates substantially from the progression shown in Figure 3.10, they are excluded from further electrochemical analysis. The extracted parameters R_s , R_p , and the values Q and p of the CPE are discussed in more detail below.

Series Resistance and IR Correction

R_s describes all resistances between the working and the reference electrode, which is mostly the solution resistance, depending on the conductivity of the electrolyte [69]. The value of R_s is approximately 30Ω for 100 mM H_2SO_4 and around 80Ω for 100 mM K_2SO_4 . For once, this value is used to confirm the conducting properties of the sample in question. It is also used to perform an IR correction of the cyclic voltammetry data.

An electrochemical analysis is mainly interested in processes at or close to the surface.

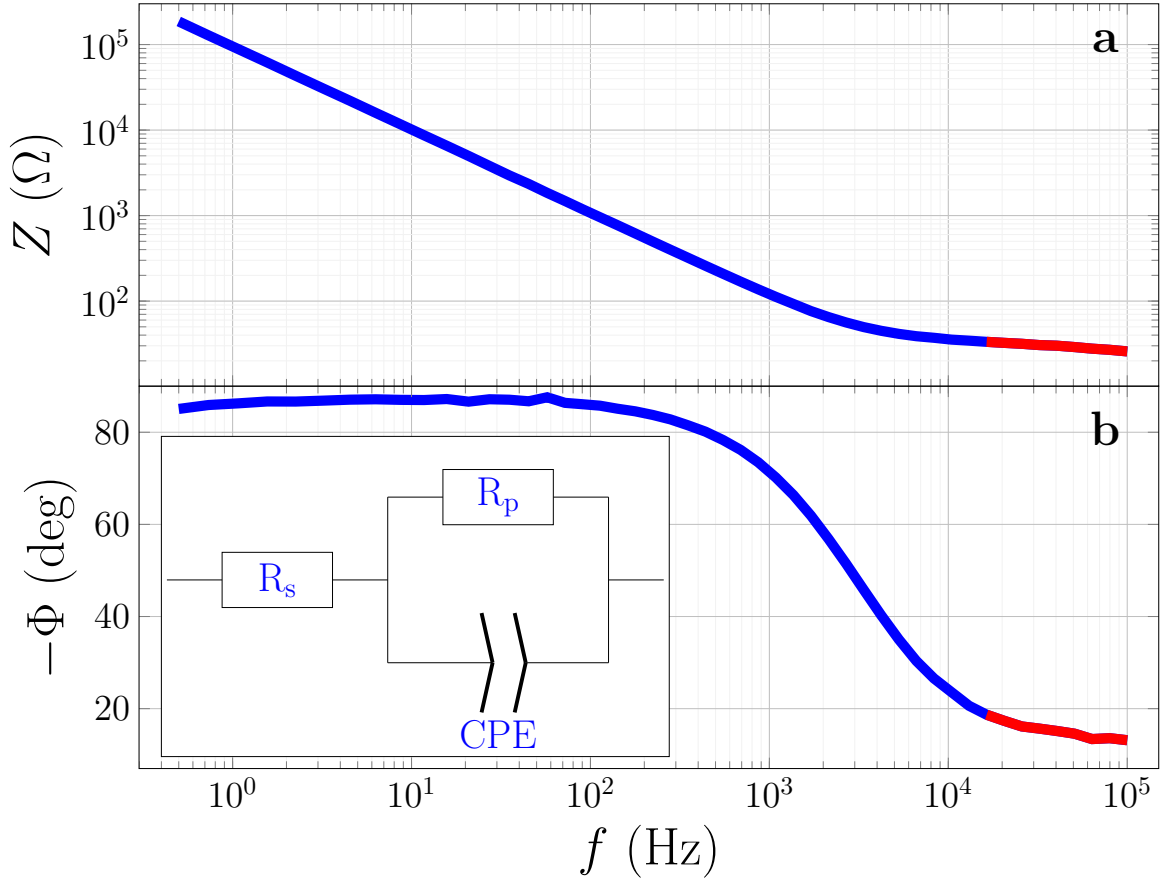


Figure 3.10.: Bode plots of the absolute value of the impedance Z (a) and of the negative phase $-\Phi$ (b) for a nanostructured electrode in the double layer region. Recorded for 6 steps per decade in pH1 100 mM H_2SO_4 . The inset depicts the equivalent circuit used to fit the data.

When a cyclic voltammogram is recorded, it uses the applied voltage between the reference and the working electrode as a variable. However, some of this voltage drops at the solution resistance and not at the interface, which means that the recorded voltage is shifted from the actual potential drop across the interface, depending on the solution resistance. To remove this unwanted contribution, the applied potential U_{applied} is corrected via

$$U_{\text{real}} = U_{\text{applied}} - I_{\text{meas}} \cdot R_s \quad (3.8)$$

where I_{meas} is the current measured at U_{applied} .

Faradaic Resistance

Any electrochemical current consists of a transient capacitive charging current and a faradaic reaction current, which is why both are modeled as parallel elements. The former goes to zero for long measurements at constant potential. The latter is represented via an ohmic resistance R_p , which accounts for the charge transfer resistance across the interface at a specific applied potential. In cases where no faradaic currents are drawn, R_p becomes extremely large.

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Constant Phase Element and Capacitance

The charging of the interface, as described in section 2.2.1, is modeled via a constant phase element (CPE) with an impedance of

$$Z_{\text{CPE}} = \frac{1}{Q \cdot (i\omega)^p} \quad (3.9)$$

where Q and p are the CPE parameters. Although the double layer built-up behaves qualitatively like a capacitor, for most EIS measurements, the imperfect capacitance of the CPE yields consistently better fitting results. The exact reason for this deviation from the perfect capacitor in model systems is still under debate [70]. However, there are indications that the mass transport-dependent electrosorption of anions onto the surface could be the origin of the CPE behavior [71]. In our case, the spatial inhomogeneity of the electrode surface is expected to be one of the origins.

Even if the behavior of the system deviates from a perfect capacitor, its capacitance can be calculated from the CPE parameters Q and p via different ways, depending on the expected geometric properties of the interface. In the case of lateral heterogeneities on the surface, i.e., surfaces that have two or more different regions contributing to the overall capacity C_{DL} , the Brug conversion

$$C_{\text{DL}} = Q^{1/p} \left(\frac{1}{R_s} + \frac{1}{R_p} \right)^{1-1/p} \quad (3.10)$$

can be used [72].

3.4. Optical Measurements

The core part of this thesis is the simultaneous tracking of our working electrode's electrochemical and plasmonic behavior. The reflectivity setup used to excite and record plasmonic effects is covered in this section, alongside the transmission setup that is used to aid plasmonic simulations, as covered in later chapters.

3.4.1. Measurement Setup

A schematic picture of the full measurement setup is shown in Figure 3.7. The right parts, including the potentiostat, the Ar atmosphere, and the EC cell, were covered in section 3.3. Figure 3.11 shows a simplified version of the reflection spectroscopy setup (a) and a modified version used for transmission spectroscopy (b). The latter is only used to record transmission spectra of nanoarrays on SiO_2 substrates. In contrast, the former is used on electrochemical samples, which will be the main focus in the following.

For the optical experiments, a fiber-coupled halogen white-light source (Avantes Avalight HAL-S Mini) is used to illuminate the samples, and an Ocean Optics QE65Pro CCD spectrometer (range: 350 nm-1100 nm) is used to record the reflectance spectra. The optical fibers going from the light source to the sample and the ones going back are partly interwoven (y-bifurcated, Thorlabs), with 19 fiber ends facing the sample, 9 coming from the light source (incoming intensity 50 mW m^{-2}), and 10 going to the spectrometer.

Between the fiber ends and the sample, there is a diaphragm shutter and a biconvex lens ($f = 2.54 \text{ cm}$), which are used to control the light going into the cell and back into the detector. These components, including the EC cell, are placed in optical mounts connected via an optical cage system of 8 steel rods, as shown in the center part of Figure 3.8.

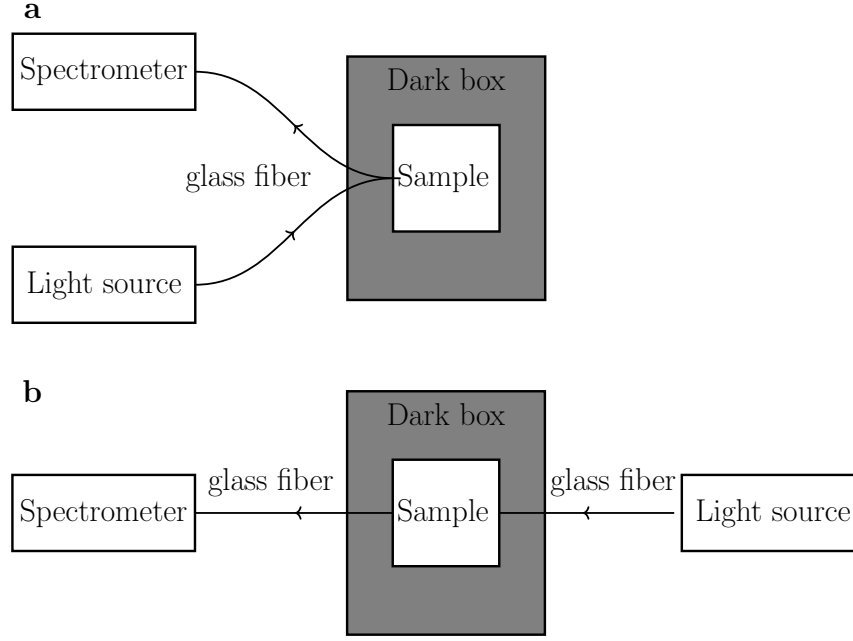


Figure 3.11.: Optical measurements setup for (a) reflectance and (b) transmission spectroscopy. The dark box refers to a space that is not affected by light from outside the box. “Sample” refers to a holder where the sample is placed directly in the beam path.

3.4.2. Spectral Acquisition

The software of the spectrometer, Ocean View, is set to integrate the incoming light intensity over 10 ms and to average over 10 spectra before they are displayed. Accordingly, a spectrum (S) is recorded every 100 ms. From this, the software is set to automatically calculate the resulting reflectance (R) spectra using a background (B) and a reference (Ref) measurement as defined in Equation 3.11.

$$R = \frac{S - B}{Ref - B} \quad (3.11)$$

B is recorded with the light source switched off and Ref is a spectrum of a lift-off nanoimprint lithography produced gold array with a particle side length of 1400 nm, as these arrays have nearly the same surface composition as the working arrays, with $\Theta_{SiO_x} \approx 80\%$ and $\Theta_{Au} \approx 20\%$, but a plasmonic resonance in the near-infrared (NIR) region which is far off the visible spectrum of the investigated plasmonic resonances. Consequently, the overall reflectivity of the reference sample is the same as the samples of interest. It differs only by the plasmonic excitation (resonance), leaving only the spectrum of the samples of interest after applying Equation 3.11. This is shown in Figure 3.12 for one exemplary dataset. It is important to note that the reflectivity caused by the air/glass and the glass/water interface cause most of the reflectivity. At the same time, the plasmonic effect appears only as a modulation. However, the plasmonic peak is clearly visible in the resulting reflectance spectrum, calculated by the Ocean View software. Further details on the features of these graphs are given in Chapter 4.

3. Experimental Details

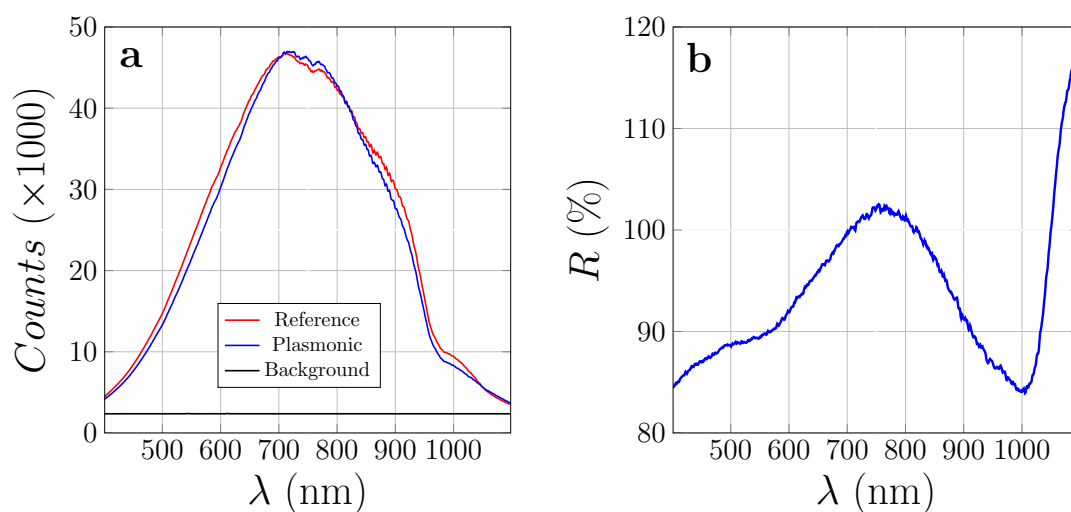


Figure 3.12.: Untreated white light spectra recorded by an Ocean Optics QE65Pro CCD spectrometer. (a) Exemplary reference, background and plasmonic spectra and (b) the resulting reflectance graph.

3.5. Plasmonic-Electrochemical Measurement Procedure

This section details the standard measurement procedure, including electrochemical and optical measurements, as a summary.

1. Light source and spectrometer are switched on
2. Sample cleaning procedure is executed (sonication in acetone and isopropanol)
3. EC cells for the reference sample and the main sample are set up
4. Reference EC cell is put into the optical cage system and reference spectra are recorded
5. Main EC cell is put into the optical cage system (electrolyte: 100 mM H_2SO_4)
6. Ar gas is flushed into the cell, which is connected to the potentiostat
7. The acrylic box is sealed and filled with Ar
8. The continuous recording of the reflectance spectra is started
9. Open circuit potential (OCP) is controlled in the potentiostat software
10. Cleaning CV is conducted (5 cycles, 50 mV s^{-1})
11. ECSA CV is conducted
12. EIS data is recorded
13. Specific measurement protocol of the day is started

Once the optical spectra are recorded, they have to be checked regularly, as bubble creation through reactions and due to the Ar flushing could render the optical data unusable. The

procedure will only be continued after step 9 if the OCP is stable and in the correct range of the specific system. Similarly, the procedure will only commence if steps 10, 11, and 12 yield reasonable results, as discussed above. Steps 5. - 12. are all done with 100 mM H_2SO_4 as the electrolyte. If the main electrolyte of the specific measurement protocol requires another electrolyte, these steps will be repeated for the new electrolyte. This is true even for the ECSA determination of Step 11, which is done to qualitatively relate ECSA measurements in the standard (100 mM H_2SO_4) and the additional electrolyte.

3.6. Atomic Force Microscopy

Atomic Force Microscopy (AFM) measurements were done with a Bruker Dimension Icon in Scan-Assist mode (i.e., using self-optimized peak-force measurements) and data treatment was conducted using the software Gwyddion. All AFM measurements cover at least a $1\text{ }\mu\text{m} \times 0.5\text{ }\mu\text{m}$ area of two different sights on the array. All data sets were treated by removing the 3rd-degree polynomial background and leveled by a three-point plane. The radial profiles were taken by using the ‘Extract angularly averaged profiles’ function, the first step of which is visualized in Figure 3.13. The lines indicate the circle diameter used to create the angular profiles shown in section 6.6. The midpoint, indicated by the number, is selected by hand. AFM data of the pristine samples were recorded right after the production and then compared to AFM data recorded after the measurements.

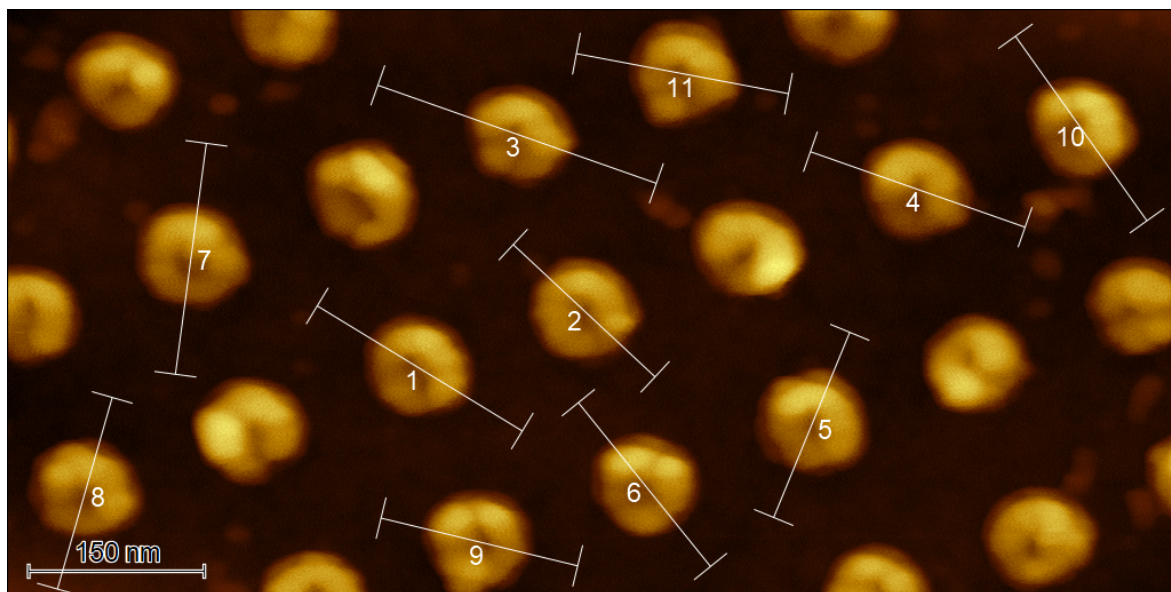


Figure 3.13.: AFM Data treatment via the Gwyddion Software. The lines running through the nanoparticles represent the diameters of the circles along which the angular averaged profiles were calculated. The centers of each line were selected by hand.

3.7. Scanning Electron Microscopy

Compared to AFM, the Scanning Electron Microscope (SEM) has a significantly higher lateral resolution, enabling us to determine the actual diameter of the samples. In a SEM setup, the samples are transferred to an evacuated chamber where they are bombarded with highly

3. Experimental Details

accelerated electrons. Upon impact, these electrons have a chance to generate secondary electrons, which are emitted highly localized. As the secondary electron generation is material-specific, it can also be distinguished whether there is a metal or an insulator at a specific location. In the case of an insulator, the surface is continuously charged when looked at by SEM, which is why the images have to be recorded relatively fast and only once per site. This leads to a lateral resolution of approximately 1nm. An exemplary SEM image of the samples used in this thesis is shown in Figure 3.2. The brighter spots indicate a metal, and the darker spots indicate an insulator.

4. Plasmonic Nanoparticle Arrays

This thesis aims to use the plasmonic resonance of Au nanoparticle arrays as sensors for changes in the metal/aqueous electrolyte interface. As outlined in Chapter 2, multiple aspects of the electrochemical system impact the resonance, which will be quantified and distinguished in Chapter 5. In order to do that, the optical and electrochemical properties of the Au NPs have to be characterized and understood as thoroughly as possible before conducting analytic measurements of the metal/aqueous electrolyte interface. Hence, this chapter will show and discuss the structural, electrochemical, and plasmonic properties of the electrochemical system from experimental and numerical sides.

4.1. Structural Characterization

The nanopatterned Au working electrodes used in this thesis are complex to manufacture, which is prone to introduce heterogeneities and asymmetries to the NP arrays. As the plasmonic resonance depends on the geometry of the particles and the SiO₂-surface within the array, a detailed characterization is warranted, especially when degradation processes are investigated in later chapters.

Ideally, each array consists of a billion flat cylinders with sharp edges, which all exhibit the same height (13 – 16 nm), diameter (75 nm), and interparticle distance (150 nm), such that the Au coverage is about 20% in the patterned area. The most important properties of the NP arrays are their homogeneity and low defect density. The former is necessary to avoid heterogeneous broadening of the plasmonic resonance, as explained in section 2.1.2 and investigated in more detail in section 4.4.5. The latter refers to the number of nanoparticles removed, misplaced, or destroyed during production. As explained in section 3.1, the production process is a highly complex sequence of steps, where the composition of the resulting samples is comparable between different batches but at the expense of introducing defect sites in the array. A selection of such defect sites is shown in Figure 4.1. These images were specifically selected to represent typical nanoparticle array defects and do not represent the entire array. Figure 4.1(a) shows a bridging between two nanoparticles, which can also be seen in the other images. These are introduced through an aged master stamp used in the patterning process (Figure 3.1(a)). If their density gets too large, the master stamp is renewed. In images (b) and (d), the imprint resist was damaged by accidental scratching of the surface and bubble formation during the resist application. This caused the deposition and lift-off process to malfunction, resulting in empty spaces instead of nanopatterns. Finally, Figure 4.1(c) shows the rims of the patterned area, which often have defects, as the border of the patterned area is most susceptible to defects in resist displacement and slightly tilted samples when applying the master stamp. More information on and types of array defects can be found in the PhD thesis of M. Golibrzuch [73].

Altered structures, such as the bridging or the elongated nanoparticles at the edge, exhibit different plasmonic behavior than the regularly patterned regions, which is why a sample will only be used if at least 90% of the array consists of regular nanoparticles. The assessment of this aspect is eyeballed via optical and scanning electron microscopy. A “regular nanoparticle” is defined as an NP that is surrounded by 8 undamaged NPs. That means macroscopic areas

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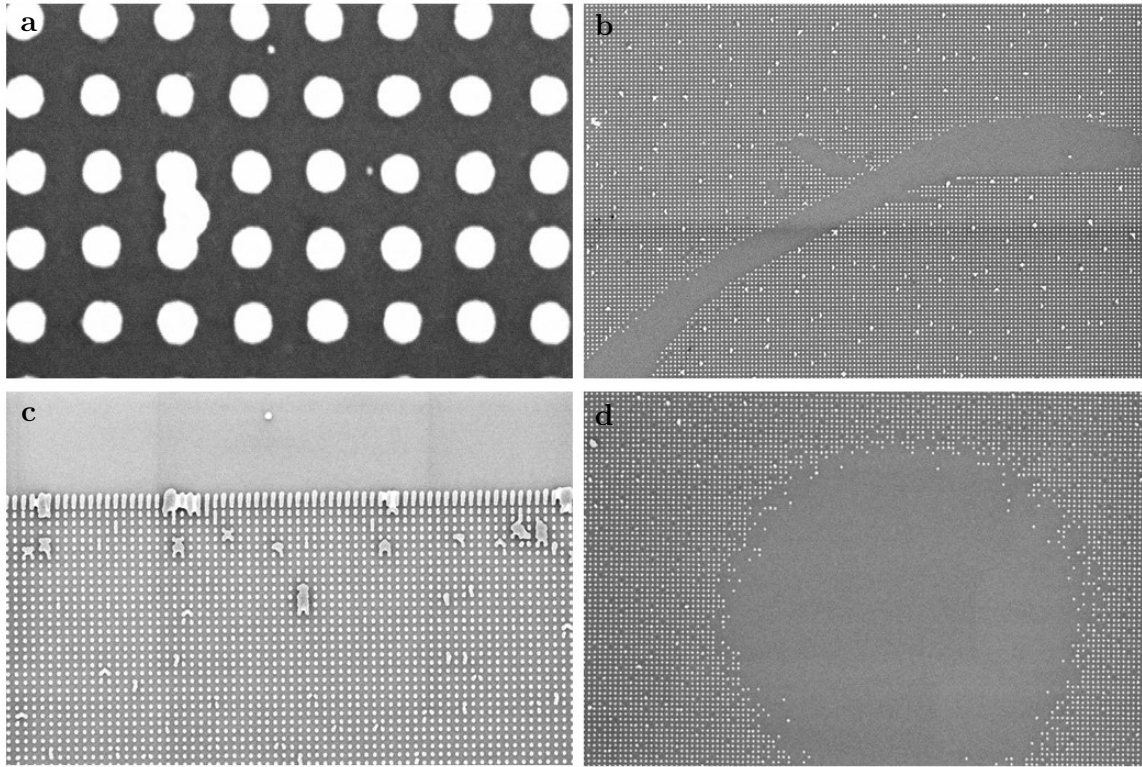


Figure 4.1.: SEM images of typical nanoparticle array defects. (a) Bridging between two nanoparticles, (b) scratches in the resist, (c) edge defects, and (d) bubble formation in the resist. The SEM images were recorded with the help of S. Stork.

of missing NPs are not considered irregular, but the NPs at the edge of such an area are.

Electrochemically, missing nanoparticles do not disturb the signal, as the ECSA normalizes all current values, as long as the absolute current is not too low or that other reactive surfaces (e.g., the Ti layer) are exposed. The latter is not the case, as the SEM would depict conductive surfaces as bright. Optically, the missing or additional reflectivity compared to the reference sample will slightly affect the spectrum, which is discussed in more detail in section 4.3.

The other important property of the NP arrays is their morphological homogeneity, which is illustrated in Figure 4.2. The histogram (a) shows the distribution of the nanoparticle radii displayed in (b). The average diameter is approximately 75 nm with only very few particles in the range of $> \pm 1$ nm. This excellent horizontal homogeneity in radial distribution enables the use of multi-particle spectrometry in later chapters. Nevertheless, the finite width of the distribution will need to be evaluated regarding their contribution to the plasmonic resonance, which is done in section 4.4.5 via simulations. The AFM image shown in Figure 4.2(c) illustrates the vertical component of the morphology. Note that x - and y -axis scale identically while the vertical axis was rescaled ($\approx \times 10$) for better visibility of the surface configuration. As introduced in section 3.1, the production technique creates crown-like structures on the rim of the particles, which, if upscaled as they are here, give the impression of a rather heterogeneous caldera-type structure. Apart from the upper part, however, the NPs exhibit very similar morphologies, especially considering the huge vertical scale. On top of that the crowns are lost during electrochemical treatments, which will be discussed in detail in section 6.2.

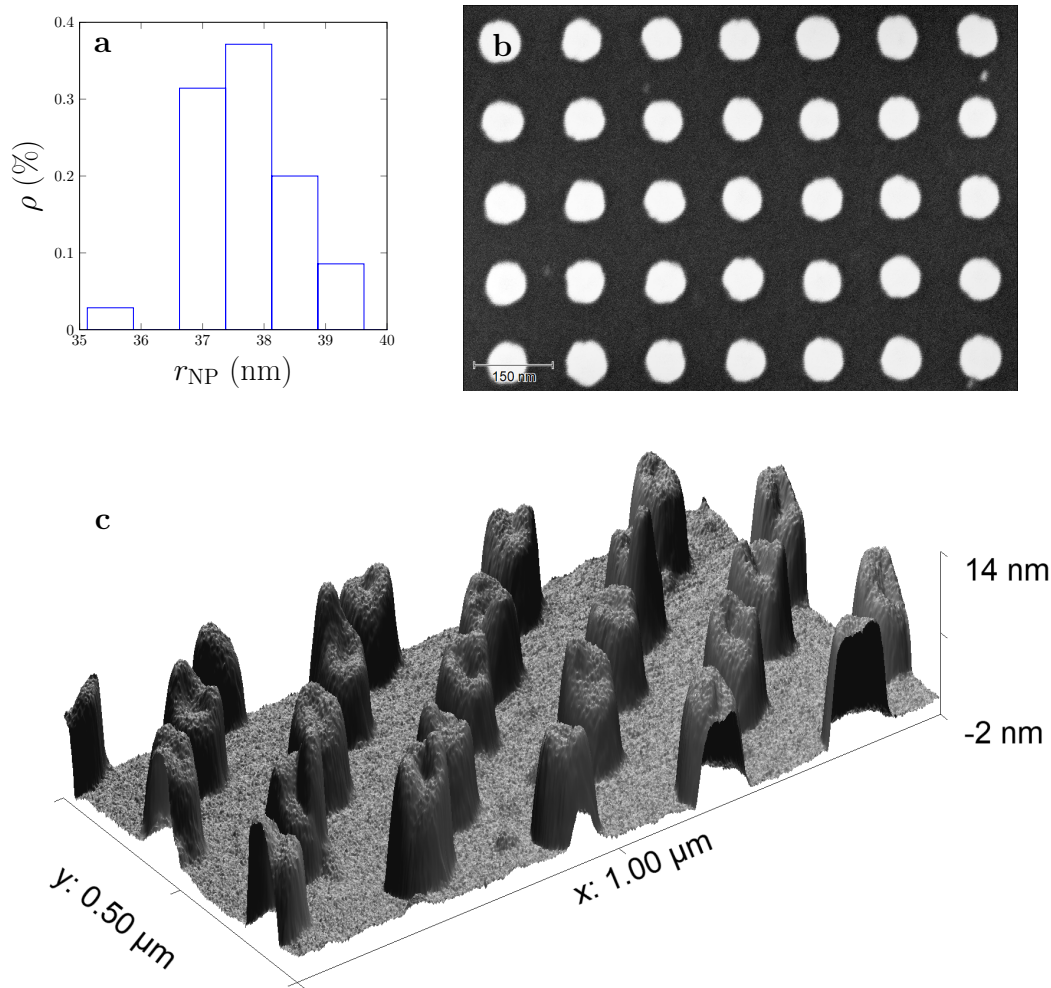


Figure 4.2.: Structural analysis of the nanoparticle arrays. (a) histogram of the nanoparticle radii of the SEM image shown in (b). (c) 3D AFM picture of one nanoparticle array. In the latter, the z-axis is scaled up by a factor $\approx \times 10$. Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

4.2. Electrochemical Characterization of Au/Ti NP Arrays

Electrochemical systems are very sensitive to chemical impurities, especially if charging and adsorption processes are to be analyzed, which are so small that even minute amounts of impurities would invalidate any conclusions. Moreover, we are aiming to disentangle charging, adsorption and morphological changes. This is only possible without reactions/processes that we cannot account for. Hence, this is why every single setup of the electrochemical cell has to be characterized to ensure that

- (1) the nanoparticle arrays are not contaminated with another metal or organic residues from the production procedure
- (2) the electrolyte contains only the desired species in a predetermined concentration
- (3) the cell is not contaminated

4. Plasmonic Nanoparticle Arrays

- (4) the nanoparticles are stable and in ohmic contact with the electrolyte and the potentiostat
- (5) the electrodes are properly connected to the potentiostat

These aspects are confirmed by analyzing standard cyclic voltammograms and electrochemical impedance spectroscopy data (cf. section 3.3) multiple times during each day of measurements. In the following, representative datasets for standard CV and EIS data illustrate typical properties of the systems used in this thesis. All samples are selected using the criteria outlined below.

4.2.1. Cyclic Voltammogram of a Au NP Array in 100 mM H₂SO₄

Figure 4.3 shows the CV of a Au NP-array in 100 mM H₂SO₄ scanned from $E_{\text{RHE,upper}} = 1.62 \text{ V}$ to $E_{\text{RHE,lower}} = -0.27 \text{ V}$ with a scan speed of $\nu = 50 \text{ mV s}^{-1}$. Any applied potential in this thesis is limited by the H₂O oxidation/reduction reactions, which dominate the faradaic current for potentials $E_{\text{RHE}} > 1.8 \text{ V}$ and $E_{\text{RHE}} < -0.3 \text{ V}$. These limits are only exceeded if the hydrogen evolution reactions are of interest. The current density j is normalized to the ECSA.

Starting at $E_{\text{RHE,start}} = 0.67 \text{ V}$ in anodic direction, the first feature is the (bi)sulfate adsorption peak ranging from 0.67 V to 1 V. In this process, the $\text{SO}_4^{2-}/\text{HSO}_4^-$ species attach to the Au surface atoms, which is accompanied by a partial charging of the surface ($j > 0 \text{ A}$). At some point, the NP surface has attained full coverage; thus, the probability of adsorbing more ions decreases until it is not possible anymore [74, 75]. Further details will be discussed in section 5.3.2.

At $E_{\text{RHE}} = 1.35 \text{ V}$, the Au surface atoms are oxidized by forming Au oxide, which occurs at different potentials for different crystal orientations. For amorphous gold, no distinct peaks are expected. Similar to the (bi)sulfate adsorption, the current for the Au oxidation drops once the Au oxide monolayer is near completion. Upon turning the scan direction, the current drops to zero and starts to get negative at $E_{\text{RHE}} = 1.4 \text{ V}$, which is the onset of the Au oxide reduction. In sulfuric acid, the reduction of Au oxide does not exhibit facet-dependent features but only one single sharp peak at $E_{\text{RHE}} = 1.21 \text{ V}$ [76, 77]. Directly after the Au oxide reduction subsided ($E_{\text{RHE}} = 1 \text{ V}$), (bi)sulfate starts to be desorbed, and the Au surface is adsorbate free at $E_{\text{RHE}} = 0.6 \text{ V}$, scanning in cathodic direction. From there until $E_{\text{RHE}} = 0 \text{ V}$, no faradaic reaction occurs, which is why the current drawn in this region is fully capacitive. This and the sulfate ad-/desorption potential region are called the double layer region. Negative current corresponds to negative charge accumulating at the interface, and vice versa [5]. For potentials $E_{\text{RHE}} < 0 \text{ V}$, hydrogen evolution from protons dominates the CV. Even though protons are consumed, the pH is stable at 1, as the initial concentration is not changed significantly by the measurements conducted in this thesis unless explicitly stated otherwise. The potential range is limited to small currents for standard CVs, so that the sample can be cleaned without corroding it.

Any sample will be excluded from further analysis if its standard CV does not exhibit these exact features in a comparable current range ($\pm 5\%$). Given that it passes this stage, most types of contamination, such as organic or metallic species, can be excluded. However, the most critical impurity, Pt, can be fully ruled out with a $\nu = 100 \text{ mV s}^{-1}$ CV that reaches further into the hydrogen evolution region. Upon the backscan, a positive current flows around $E_{\text{RHE}} = 0 \text{ V}$, indicating that hydrogen oxidation is occurring, which cannot happen on Au, as shown in Figure 4.3(b) where no deviation of the current around $E_{\text{RHE}} = 0 \text{ V}$ of

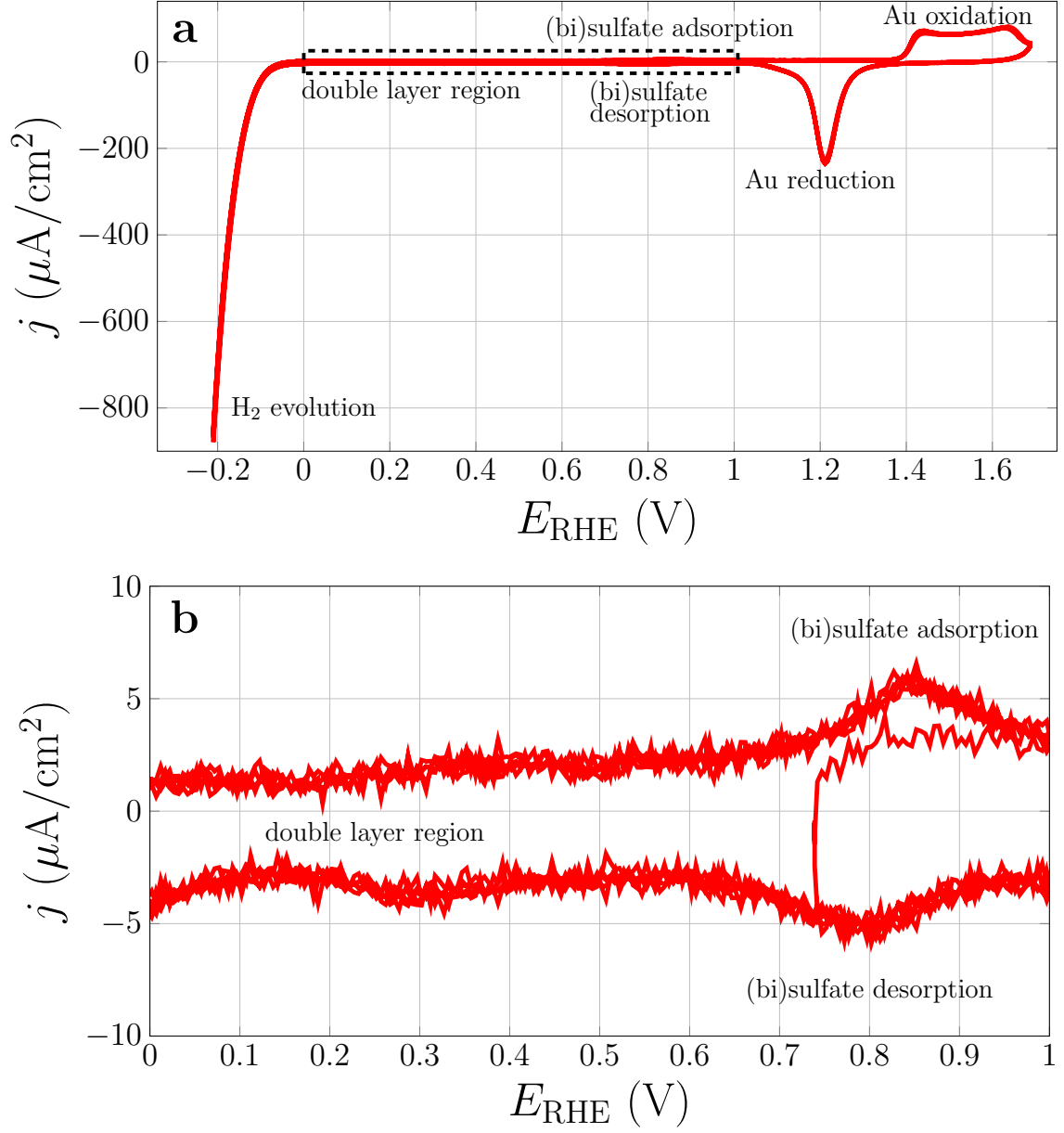


Figure 4.3.: (a) Cyclic voltammogram for a nanostructured working electrode in 100 mM H₂SO₄ with descriptions of the electrochemical reactions. (b) shows the zoom into the region marked by the dashed box in (a). $\nu = 50 \text{ mV s}^{-1}$.

the backscan is visible. This additional step is not shown here and is usually performed once at the beginning and once at the end of each measurement day.

4.2.2. Electrochemical Active Surface Area

The ECSA is calculated according to the procedure outlined in section 3.3.2 and is used to calculate the current density j and the specific capacitance c . With the occurrence of array defects from production, as shown in Figure 4.1 and differences in the roughness of pristine samples, the ECSA is comparatively variable, which is why samples within a range

4. Plasmonic Nanoparticle Arrays

of $5 \text{ mm}^2 < ECSCA < 10 \text{ mm}^2$ will be used. Any ECSCA smaller than the lower boundary does not have a sufficient number of NPs on the surface or possesses an unusual smoothness of the NP surfaces, which indicates a deviation in the production process. If the ECSCA is too large, this indicates a non-negligible amount of Au has been deposited beside the array.

Over a day of measurement, the ECSCA is expected to change due to roughening and corrosion of the NP array, which is shown in Figure 4.4(a). Usually, the standard CVs are run with multiple cycles (3-5), each of which can be used to calculate the ECSCA, shown by the vertical spread of the blue dots. The orange marks represent the average of these individual measurements. The x-axis describes the number of electrochemical measurements, such as CVs and EIS, done on that specific date. Note that a cleaning CV of 5 min and an analytic CV of 120 min (each consisting of multiple cycles) are counted as one treatment each. The decrease between the ECSCA at treatments 1 and 10 is most likely due to the removal of bridge defects (cf. Figure 4.1) and excess Au on the fringes of the patterned area in between these two treatments. The subsequent rise for later treatments is assumed to be related to morphological changes, which will be discussed in detail in Chapter 6. In general, the latest ECSCA value will be used for each treatment to calculate j and c , respectively.

4.2.3. Electrochemical Impedance Data

The remaining two parameters that are determined to characterize the Au nanostructure array are specific capacitance and series resistance. They are measured via EIS and are shown for a potential sweep in Figure 4.4(b) and (d), respectively. Note that the potentials are applied consecutively starting from the largest without returning to the OCP in between and held for approximately 3 min each, which corresponds to an effective sweep rate of $\nu < 0.5 \text{ mV s}^{-1}$. Note that some of the measurements have different step sizes. Most of the potential steps are either in the double layer region or in the (bi)sulfate ad-/desorption (or phosphate for pH7 electrolytes) region where no faradaic current is expected to occur. Hence, the system is assumed to be in a steady state at every potential for $\nu < 0.5 \text{ mV s}^{-1}$. In Figure 4.4(b), the potential dependence of the specific capacitance is shown for three different buffered electrolytes, which had different ions and pHs. For the two pH7 electrolytes (red, green lines), the progressions of the capacitances start with a maximum at $E_{\text{RHE}} = 1.1 \text{ V}$, decrease for more negative potentials until $E_{\text{RHE}} < 0.6 \text{ V}$ and start to rise for even more negative potentials. The EIS data for the pH1 electrolyte (blue line) covers a smaller potential window and seems to be shifted compared to the other curves. The reason for this is the difference in the anion, which is $\text{HSO}_4^-/\text{SO}_4^{2-}$ for the pH1 and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ for the pH7 solution. The former has a more negative adsorption potential than the latter, shown in Figure 5.7 and discussed in more detail in section 5.3.2. The behavior for $E_{\text{RHE}} < 0.6 \text{ V}$ is difficult to interpret. For once, the point of zero charge (pzc) is expected to be in this region [78, 79, 80]. However, the heterogeneity and polycrystallinity of the sample surfaces are expected to alter the capacity around pzc beyond what has been measured for plain surfaces, making it impossible to extract a value for the pzc from the capacitance data alone. A more detailed analysis and discussion on this topic has been done by T.L. Maier [81].

Regarding the selection of suitable samples, the important aspect of the capacitance curves is their overall progression, which is sufficient as long as the main features are within the value range depicted in Figure 4.4(b). Much more indicative of errors in the manufacturing of the solid-solid interfaces of the sample is the shape of the Bode plots, shown in Figure 3.10. This is an example of very well-defined and impurity-free solid-solid interfaces, which in the case of production problems, bend upwards for larger frequencies or exhibit a bump around $f = 10 \text{ kHz}$.

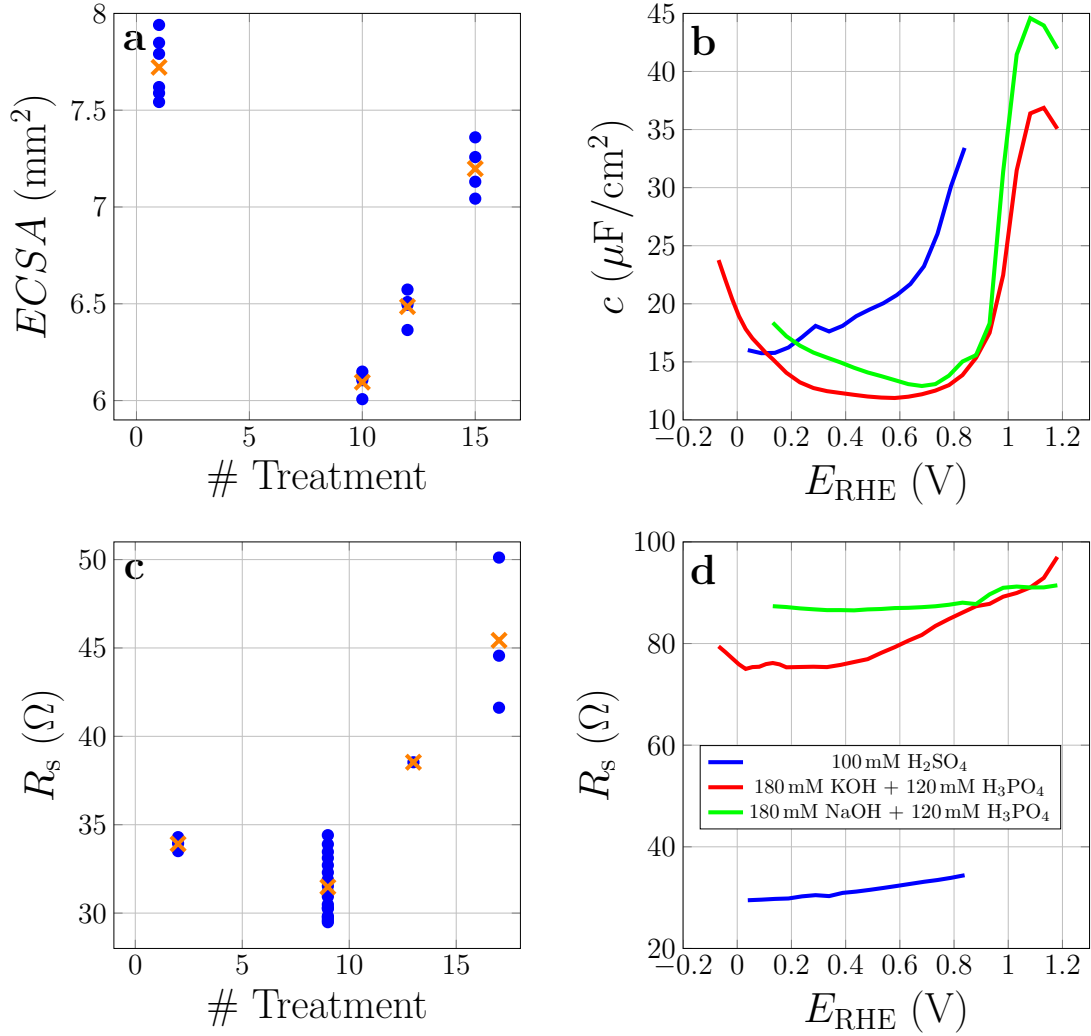


Figure 4.4.: Analysis of electrochemical system parameters. Evolution of the ECSA (a) and series (c) resistance R_s during a measurement day. Each CV and EIS measurement performed during that day is noted as a treatment. Multiple data points were acquired for every ECSA and R_s measurement. Potential dependence of the specific capacitance c (b) and the series resistance R_s (d) versus the applied potential for Au NP arrays in different electrolytes. $\text{pH}(180 \text{ mM KOH} + 120 \text{ mM H}_3\text{PO}_4) = 7$, $\text{pH}(180 \text{ mM NaOH} + 120 \text{ mM H}_3\text{PO}_4) = 7$, $\text{pH}(100 \text{ mM H}_2\text{SO}_4) = 1$. Each potential was applied for 30 s before the impedance data was recorded for approximately 3 min. The general potential step size was 50 mV, with a smaller step size (25 mV) sometimes used for higher resolution.

The progression of the series resistance obtained from the same datasets as the capacitance is given in Figure 4.4(d). Most importantly, the resistance of the acidic system is much smaller than both neutral systems, which is expected due to the high conductivity of H^+ -ions present in acidic media [82]. A sample will only be used for further analysis if the series resistance is within the range $20 \Omega < R_s < 40 \Omega$ for 100 mM H_2SO_4 and $60 \Omega < R_s < 100 \Omega$ for 180 mM KOH + 120 mM H_3PO_4 or 180 mM NaOH + 120 mM H_3PO_4 . Any larger deviation from

4. Plasmonic Nanoparticle Arrays

these values indicates either a malfunction in the manufacturing process or a connectivity problem of the EC setup.

Just as for the determination of the ECSA, the series resistance is tracked throughout the measurement day, as shown in Figure 4.4(c). This is important, as the IR correction (cf. section 3.3.3) has to use the actual value of the series resistance, which is mainly impacted by changes in the electrolyte composition. The solution resistance is expected to increase over time as there is a net consumption of protons during the measurements presented here. Again, it has to be noted that the individual treatments range from CVs in the double layer region without any hydrogen evolution to CVs, which evolve enough hydrogen to form bubbles on the sample surface. Regarding the large increase between measurements #13 and #17 in Figure 4.4(c), there has been a high hydrogen evolution reaction (HER) current drawn in between, which changed the pH slightly to more alkaline values (pH 1.1), alongside with a high coverage of bubbles which usually do not detach until the sample is taken out of the solution.

4.2.4. Photochemical Potentials

For most of this thesis, the working electrode will be illuminated via a white light source (cf. section 3.4) throughout the measurement procedures to excite plasmons. As detailed in Chapter 2, plasmons can contribute to either heating or hot charge carrier transfer. Moreover, n-doped Si is used as a substrate which has photoelectronic properties. Therefore, assessing the photochemical effect induced by the light is vital. Figure 4.5 shows a control experiment in the form of two cyclic potential treatments with the exact same operation parameters, which were taken consecutively on the same sample. One was recorded under “dark” conditions, and the other under illumination, typical for plasmonic measurements. There is no shift in onset potentials or an increase/decrease of the current visible for the full potential range. Additionally, the impact of light on the OCP is $\Delta E < 4\text{ mV}$ compared to the dark OCP (not shown here). This leads to the conclusion that the light does not impact the electrochemical performance in any significant way.

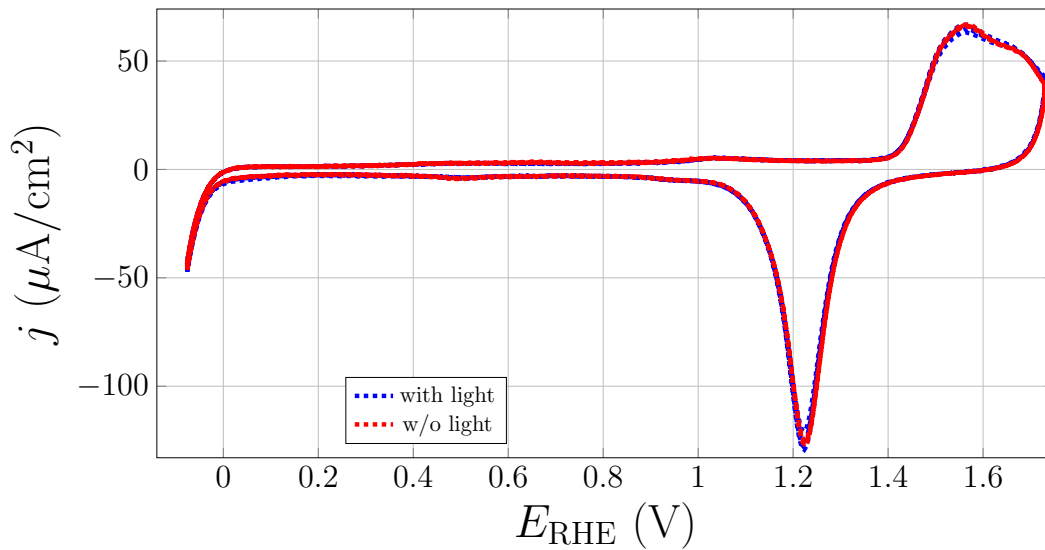


Figure 4.5.: Cyclic voltammograms of Au NP arrays in buffered pH6.8 180 mM KOH+120 mM H_3PO_4 with illumination (blue line) and without illumination (red line).

4.2.5. Bifunctional Mechanism

Finally, for the electrochemical characterization, the bifunctional mechanism occurring on the nanostructured samples in all electrolytes presented in this thesis has to be mentioned.

The insulating oxide surrounding the nanoparticles leads to a bifunctional mechanism that shifts the HER onset toward lower overpotentials compared to a plain Au working electrode [83]. This can be seen in Figure 4.6 for (a) 100 mM H_2SO_4 and (b) 180 mM $\text{KOH} + 120 \text{ mM } \text{H}_3\text{PO}_4$. Figure 4.6 compares CVs for a nanostructured and a plain Au electrode in different electrolytes. While the current density progression and absolute value are comparable for the Au oxidation/reduction reaction, a clear shift in HER onset potential is visible for the nanostructured samples in both cases. The mechanism behind this effect in alkaline electrolytes is described by a hydrogen spillover from the adjacent Si oxide surface onto the Au particle, which bypasses the slow water dissociation step and hence improves the kinetics of the HER. For acidic electrolytes, the increase is thought to originate from the Si oxide surface providing additional adsorbed H^+ ions from its termination at low pHs, thus increasing the H_2 evolution rate [83]. This effect will be present in all measurements involving hydrogen evolution; however, as the detailed kinetics of the HER are not of interest in this thesis, this effect is assumed to be of no significance to the conclusions found in this thesis.

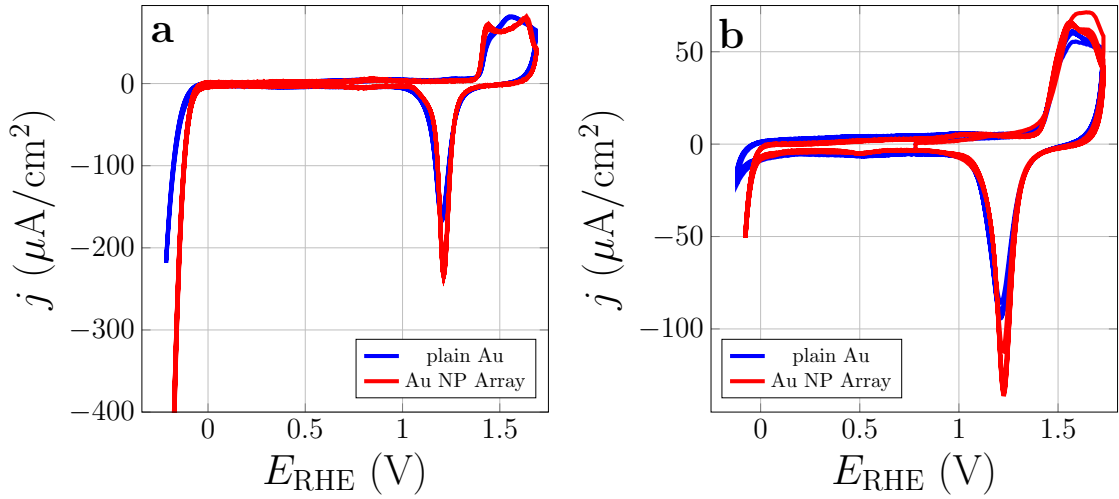


Figure 4.6.: Cyclic voltammograms for a nanostructured (red) and a plain Au working electrode (blue) in (a) pH1 100 mM H_2SO_4 and (b) pH6.8 180 mM $\text{KOH} + 120 \text{ mM } \text{H}_3\text{PO}_4$.

4.3. Plasmonic Characterization

Plasmonic properties of Au NP are strongly influenced by (1) the geometry of the NPs, (2) the heterogeneity of the arrays, (3) the number of missing/deformed particles, and (4) the dielectric environment of the NPs. None of these aspects can be analyzed by purely electrochemical methods, and even structural analysis, such as AFM, yields only insights into the surface topology of a few nanoparticles. Consequently, the plasmonic properties of a specific sample can only be determined spectroscopically, which has been introduced in section 3.4. In this section, the physical details of these spectra will be discussed, while more general trends of plasmonic properties, such as the impact of material combinations and heteroge-

4. Plasmonic Nanoparticle Arrays

neous broadening, as simulated via finite-difference time-domain (FDTD) simulations, will be introduced in the following section.

4.3.1. Basic Spectral Properties of Au NP Arrays

Plasmons contribute to the optical properties of the nanoparticle material. As such, it increases reflectance and absorbance (i.e., extinction) and decreases transmission of the base material in a system-specific spectral range. Figure 4.7(a) shows reflectance spectra of pristine nanostructured samples in water from different production batches. The plasmonic resonance takes the form of the bell-shaped reflectivity peak in region II, which can be seen for all samples. However, the progressions of all spectra differ in various features, such as the resonance position, width, and absolute height. On top of that, the behavior of the curves also differs in regions I and III. In the former, for some curves (blue, cyan, and green), the reflectivity increases for smaller wavelengths, while it decreases for the others (orange and red). The only similarity seems to be that this deviation occurs directly below $\lambda < 600$ nm. In region III, there is a similar trend in that for some curves (green, orange, and red), the reflectivity increases significantly. In contrast, it exhibits less drastic changes for the others (blue and cyan). Again, the changes seem to occur for wavelengths larger than $\lambda > 950$ nm. The choice of the regions is designed to isolate the plasmonic effect from other effects, which will be explained in the following.

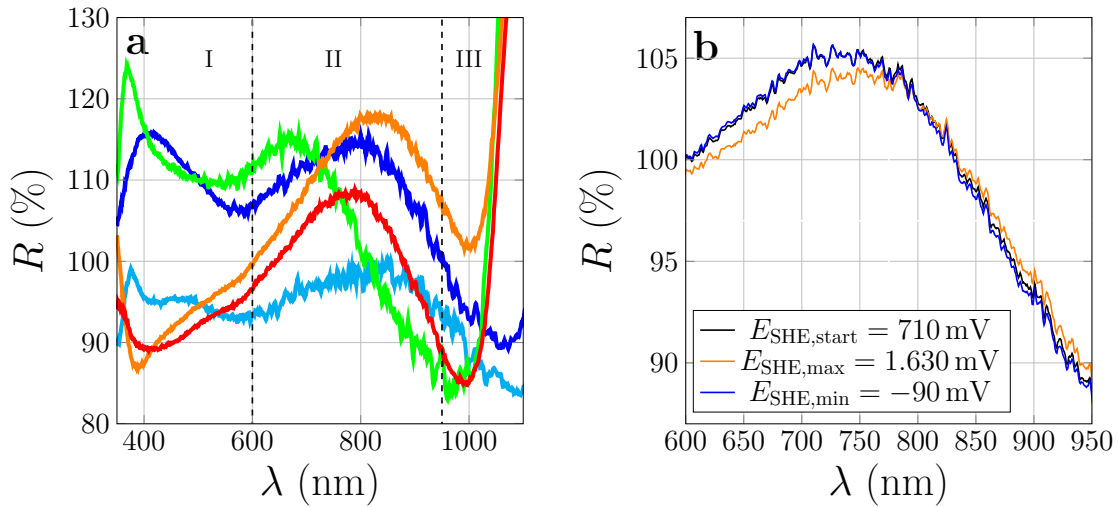


Figure 4.7.: (a) Exemplary reflection spectra of pristine samples from different production batches. The numerals label the three different spectral ranges. (b) Exemplary data set of one resonance dependent on the applied potential.

The behavior of the spectra in region I is a combination of the plasmonic resonance and gold intraband absorption. While the increase of the reflectivity due to the plasmonic resonance gets weaker for wavelengths further away from the resonance position, the Au intraband absorption gets stronger for smaller wavelengths, which leads to a decrease in reflectivity. These effects are wavelength-dependent and lead to different spectral progressions in region I depending on their relative strength. The strong increase seen in region III originates from the aluminum back contact. For photons of wavelengths $\lambda < 950$ nm, the silicon substrate absorbs most of the photons entering into the substrate, which can then not be reflected back to the detector. For photons of $\lambda > 950$ nm, silicon becomes transparent, leading to the

photons being reflected at the aluminum back contact and being able to reach the detector.

This explains the mechanisms behind the deviations in regions I and III. However, both these effects occur in all samples but in completely different quantities. This qualitative difference in the progressions can be explained by how these spectra are calculated. As introduced in section 3.4.2, all reflection data shown in this thesis are calculated with respect to a reference sample, which ideally has the same reflection spectrum as the samples of interest without the plasmonic effect present. However, this would require the exact same coverage of gold and the exact same SiO_x roughness of both the reference and the samples of interest. Due to the complex production procedure, slight deviations will occur between all sample batches, which is why each spectrum in Figure 4.7(a) has unique features, especially in regions I and III. Most of the deviations are due to the usage of different n-Si substrate batches and the unavoidable introduction of array defects (cf. section 4.1). If the Au coverage is exactly identical, there is no deviation expected for region I. However, if the sample of interest has a lower (higher) Au content than the reference sample, the intraband absorption will increase (decrease) the reflectivity. The same argument can be made for the roughness and the reflection at the back contact: If the roughness is larger for the reference than for the sample of interest, there will be more light diffusion at the SiO_x interface and, hence, fewer photons getting reflected at the aluminum back contact. Divided by one another, this leads to an increase in reflectivity in region III. Most of these differences are introduced due to the difficulty of creating the sample-geometry of interest (i.e., circular nanoparticles with a diameter of $d_{\text{nano}} = 75 \text{ nm}$) in comparison with the reference samples-geometries (i.e., square-shaped nanoparticles with a diameter of $d_{\text{nano}} = 1400 \text{ nm}$) and due to the differences in machinery available for the production at different points in time during this thesis.

The latter is also the reason for the differences in plasmonic resonances occurring in region II, which is primarily due to systematic variations in the evaporator/etching processes. These also lead to the spread in geometric parameters of the nanoparticles used throughout this thesis (cf. Table 3.1). As explained in Chapter 2, a change in any one of these will result in a shifted, scaled, and/or broadened resonance spectrum. It has proven difficult to reproduce the height of the nanoparticles up to sub-nanometer accuracy, which would be necessary due to the high sensitivity of the plasmonic resonance on the height of the nanoparticles.

All of the samples whose spectra are shown in Figure 4.7(a) were ruled as suitable for further experiments, as only the qualitative shape in region II will be relevant for further processing and they all exhibit a clear resonance. Considering the deviations in the production process and the sensitivity of the resulting reflectance spectrum to the differences between reference samples and samples of interest, these spectra are surprisingly similar in overall progression.

A more advanced aspect of these curves is their noise level, which can range from sub-nanometer level (red) to several nanometers (cyan). These differences stem from the optical setup itself and the measurement conditions. As light is guided via an optical fiber, the system is sensitive to mechanical vibrations, leading to a specific noise pattern, with noisier data for larger vibrations. Additionally, before every measurement, the reference spectrum is recorded anew. Consequently, the electrochemical cell of the reference sample has to be removed from the optical system, and the cell containing the sample of interest has to be added to it. In the current setup, this cannot be done without introducing slight vibrations directly into the optical cage system, which is why there is always a certain amount of noise present in the optical measurements. It must be noted that the noise visible here is static, i.e., a constant modulation on the actual progression. Moreover, there is also the occurrence of random flickering of the data due to the resolution limit of the detector. Still, this statistical noise is far below the static modulation seen here. In the following, the static noise will be called static modulation. An example of static modulation is shown in Figure 4.7(b), which

4. Plasmonic Nanoparticle Arrays

shows three slightly different spectra of the same sample with the same modulation pattern on the progression. The black curve is without applied potential, while the orange and blue curves represent the most shifted states during one measurement. The difference is introduced by applying a potential to the samples, which is discussed in further detail in the following chapters. Here, this should only illustrate that the change between two spectra of the same sample with a potential applied is barely visible to the naked eye (the difference between the black and the blue curve) and that the static modulation is far larger than the peak-to-peak distance of the blue and the black curve. This necessitates an in-depth data treatment which is presented in the next section.

4.3.2. Fitting of the Spectra

In order to categorize the plasmonics, the progressions of the reflectance spectra have to be fitted with a suitable function in order to extract their resonance position λ_{res} and their full width at half maximum W with good enough accuracy.

First, as explained above, both regions I and III will be disregarded, as these parts of the spectra are dominated by other effects. Secondly, the spectrum of region II is fitted with an asymmetric Breit-Wigner function given by

$$R = A + \frac{a}{(f(\lambda, q)^2 - \lambda_{\text{res}}^2)^2 - \lambda_{\text{res}}^2 \gamma^2} \quad (4.1)$$

here A , a , q , λ_{res} , and γ are the fit parameters and $f(\lambda, q)$ is an asymmetric function [84] which is given by

$$f(\lambda, q) = \lambda \left(1 - q \frac{\lambda - \lambda_0}{y} \cdot \exp\left(\frac{-(\lambda - \lambda_0)^2}{2(2\gamma)^2}\right) \right). \quad (4.2)$$

The fit parameters A , a , q are used to adapt the fit function to the different features introduced by the choice of reference and the production procedure, as detailed above. λ_{res} and γ , on the other hand, are parameters used to describe the plasmonics of the system. The latter one is called the damping parameter, but most commonly, the full width half maximum *FWHM* of the Breit-Wigner function is used to describe the damping of an oscillating system instead. *FWHM* is derived by λ_{res} and γ as follows:

$$FWHM = \sqrt{\lambda_{\text{res}}^2 + \lambda_{\text{res}} \gamma} - \sqrt{\lambda_{\text{res}}^2 - \lambda_{\text{res}} \gamma} \quad (4.3)$$

The asymmetric function $f(\lambda, q)$ is used to modify the Breit-Wigner function to track any underlying asymmetries arising from the Au intraband transition, which is expected to slightly impact the reflectance spectrum in region II as well.

Figure 4.8(a) shows an exemplary fit alongside its corresponding optical data. Here it can be seen that Equation 4.1 fits the data in region II very well, and deviations from the fit are only starting to occur on the borders to the neighboring regions I and III.

The use of Equation 4.1 is founded in the derivation outlined in Chapter 2, which ended with a Lorentz function for describing the resonance of the plasmonic peak. It must be noted that Equation 2.10 is derived for a metal nanosphere in an isotropic medium and is only valid for high frequencies around the plasma frequency of the metal. In the case of spectra, as shown in Figure 4.7(a), a broader range of frequencies has to be taken into account to generate reliable and accurate fit results. Hence, Equations 4.1 and 2.10 differ in the variable that they employ to describe the resonance, apart from the power of this variable (squared in the former, linear in the latter). This difference is substantial, as it changes the progression of the possible curves. To illustrate the difference, one dataset is plotted versus the photon frequency alongside several fit functions in Figure 4.8(b). The asymmetric Breit-Wigner fit

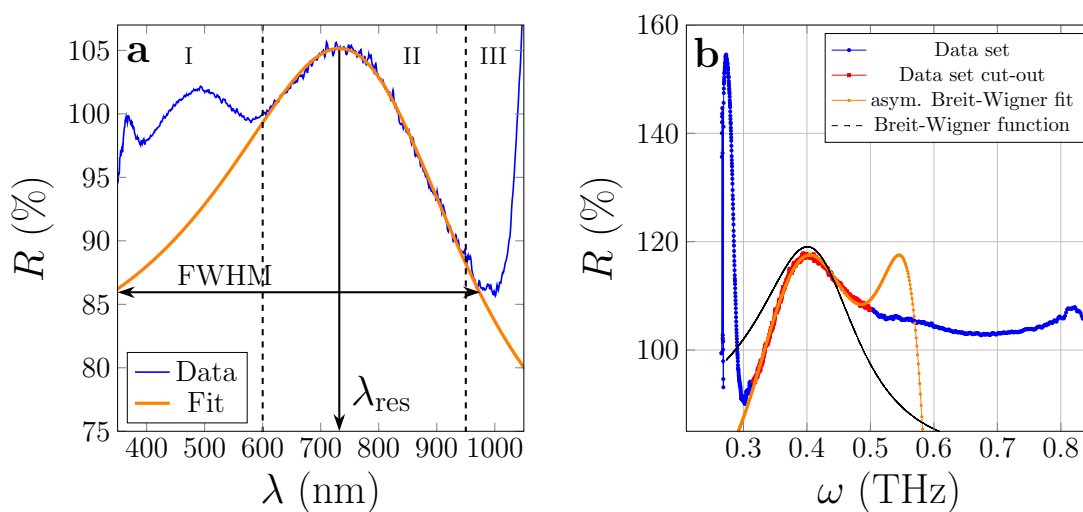


Figure 4.8.: Fitting of the optical data. (a) Exemplary Breit-Wigner fit function alongside the plasmonic fit parameters $FWHM$ and λ_{res} . (b) Different fit functions with respect to frequency ω . Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

was done using Equation 4.1 with ω instead of λ and the Breit-Wigner function (dashed black line) represents a hand-selected function that illustrates how the progression of Equation 4.1 with $f(\lambda, q = 0) = 0$ (no asymmetry) looks like with ω as the variable.

The asymmetric Breit-Wigner fit (orange line) tracks the data (red points) rather well but at the expense of an additional peak occurring at larger frequencies. The reason for this peak is the overall difference in the progression of the data (blue line) and the Breit-Wigner function (dashed black line). While the former is higher on the right side of the peak compared to its left, it is the exact opposite for the Breit-Wigner function. This causes the asymmetric function in the fit (orange line) to introduce unphysical features that are highly volatile to small changes in the original data. Note, however, that the shape around the plasmonic peak in Figure 4.8(b) can be expected to be tracked rather well even by the Breit-Wigner and the Lorentz function, as expected from the derivation in Chapter 2.

Overall, it is concluded that Equation 4.1 is suited for accurately fitting the optical data generated in this thesis, although it deviates from the theoretical equations.

4.4. Simulation of the Optical Properties

The analytical description of plasmonic effects is limited to simple geometries (e.g., spheres) in isotropic media and cannot describe more complex systems like ours. However, it is vital to have a theoretical description of the elusive plasmonic effect to better understand the details of plasmonic spectra and the change thereof during electrochemical treatments. The aim of this section will be to adopt a numerical approach utilizing semi-empiric FDTD simulations (cf. section 3.2) to replicate experimentally measured spectra of nanostructured arrays. To configure such a simulation, the main challenge to overcome is the selection of suitable optical datasets for Au and Ti. For this, several plasmonic spectra have been recorded using less complex systems, which will serve as a standard to match when evaluating the simulations. The details of these standard samples are given below. After configuring the simulation,

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the complexity is then increased step by step to finally match the desired system. The measurements on and simulations of the NP arrays on SiO_2 were acquired together with J. H.P. Fischbach in the course of his Bachelor's thesis.

4.4.1. Transmission Spectroscopy

The nanostructured working electrode samples with Si substrates are too complex to simulate without prior investigation and calibration of the simulation. Hence, at first, a simpler type of sample will be used for the adaptation of the simulation, before switching back to the working electrodes.

The reduction in complexity is done by using the same nanoparticle arrays as introduced in Chapter 4.1 and placing them on a SiO_2 substrate (V in Figure 3.4). This enables the use of transmission spectroscopy, which is more accurate and easier to realize than reflection spectroscopy. Hereby, the main simplification is using a glass substrate without nanoparticles as the reference, which circumvents any mismatches between reference and samples of interest (cf. section 4.3.1). Additionally, transmission measurements are easier to perform, as transmission can be measured on a line with the pin size detector and the pin size light source on opposite sides. For the full reflection spectrum, however, an integrating sphere would have to be used (in our case, only 0° -reflection is recorded). The optical setup for the transmission spectroscopy is shown in Figure 3.11(b). Further, the complex refractive index of SiO_2 is nearly constant in n and vanishing in k , which is the same for water and air (the two upper media). Thus, the resulting wavelength dependence of the surrounding material is strongly suppressed, leaving a clear plasmonic resonance curve.

Reference Measurements

Some examples of the standard plasmonic transmission spectra are shown in Figure 4.9 with air as upper medium (I in Figure 3.4) for different nanoparticle heights.

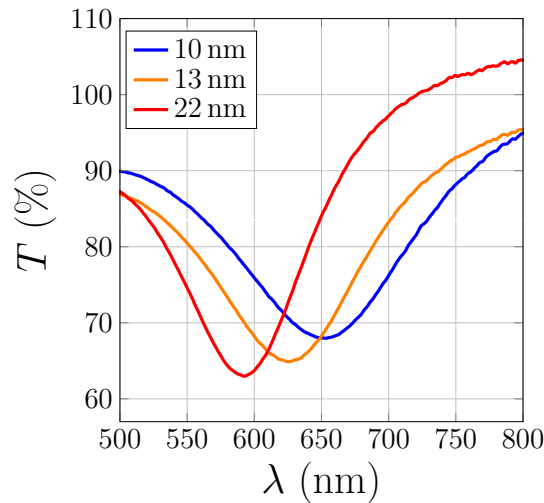


Figure 4.9.: Optical transmission spectra of Au nanoparticle arrays in SiO_2 in air for samples of different nanoparticle heights.

The height given in the legend and functions as a label for the samples refers to the intended production height from which the actual height deviates slightly, as shown in Table 4.1. It has to be noted that the nanoparticles of these specific samples are not surrounded by an additional

SiO₂ layer but sit on a flat surface (i.e., IV in Figure 3.4 is air). The plasmonic peak occurs as a minimum in the transmission measurements, because the increase in extinction lowers the number of photons passing through the sample. The resonance positions are shifted to smaller wavelengths for higher nanostructures. These will serve as the standard that the simulation has to replicate before being considered for more complex systems, such as samples with a Si substrate, among other systems.

Table 4.1.: Comparison of the intended production height of the samples, alongside the real height as measured by AFM. The Ti height is always intended to be 3 nm, and the samples are labeled by their intended Au height.

Production Height of Au (nm)	Total Production Height (nm)	AFM Height (nm)	Difference (nm)
7	10	12.7 ± 0.3	2.7
10	13	16.9 ± 1.2	3.9
13	16	17.0 ± 0.5	1.0
13	16	17.6 ± 0.4	1.6
16	19	21.8 ± 0.5	2.8
22	25	25.0 ± 0.6	0.0
24	27	29.0 ± 0.6	2.0

4.4.2. Selection of the Correct Optical Data Sets

The simulation geometry, the mesh, and the entry and exit ports of the simulation setup are shown in Figure 3.3. Before any simulation can be done, the optical properties of all materials (Au, Ti, TiOx, Air, H₂O, and SiO₂) in the geometry must be defined. For this, pre-existing datasets must be used, and all those with the correct spectral range are listed in Table 4.2.

Table 4.2.: Summary of the optical datasets used to simulate the physical system, alongside with their abbreviation used in this thesis.

Author	Abbreviation	Material	Source
Johnson & Christy	JC	Au	[85]
Werner	Wer	Au	[86]
Lemarchand	Lem	Au	[87]
Barber & Weaver	BW	Au	[88]
Olmon	Olm	Au	[89]
Mash & Motulevich	MM	Ti	[90]
Johnson & Christy	JC	Ti	[91]
Werner	Wer	Ti	[86]
Green	—	Si	[92]
Daimon	—	H ₂ O	[93]
Gao	—	SiO ₂	[94]
Siefke	—	TiO ₂	[95]

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For air, n is set to 1, and k is set to 0. Regarding the optical properties of H_2O and SiO_2 , the literature is in agreement, and regarding TiO_2 , there is only one viable dataset available. However, the most important datasets are those of Au and Ti, which are plotted in Figure 4.10(a) and (b). As is evident from this figure, there is a disagreement in the data for the refractive index n and the damping constant k . While this disagreement is more clear in the Ti data, the plasmonic resonance is particularly sensitive to the progression of the Au data, which is why even these seemingly minute differences have to be considered. One of the reasons for the deviations is the different gold samples, which can range from thin film to bulk and from amorphous to single crystalline. Concerning our Au NPs, it is not evident which type of Au- and Ti-morphology is present after production and by which dataset it is best represented. It has to be noted that the Ti is expected to oxidize to some extent during the production procedure, which cannot be measured but was determined by simulation in the Master Thesis of M.J. Feil [65] to be $h_{\text{TiO}_2} = 1 \text{ nm}$ which will be used unless stated otherwise. Further, the actual height of Ti and Au individually can not be determined via AFM measurements.

Raster Simulations of Au NP Arrays on SiO_2

Without being able to measure optical constants ourselves and with the spread in the literature, several Au/Ti combinations must first be simulated and compared to the experimental model spectroscopic data to single out the most suitable datasets for our systems. This is done in two steps: First, a raster simulation of all possible combinations of datasets for Au and Ti and all reasonable Au/Ti height combinations is conducted. As a benchmark for these simulations to be considered as suitable, their simulated resonance position must be within $\pm 2 \text{ nm}$ of the measured result. All combinations that passed the first step are then evaluated regarding their *FWHM*, which is again compared to the corresponding measured spectrum. Of those combinations of datasets and Au/Ti heights, the one that fits best is selected. That results in a final dataset combination for Au and Ti alongside a better understanding of the actual Au and Ti heights.

The set of necessary simulations is unfeasibly large, so one reduced simulation is done in advance to exclude some possible combinations and make the following raster analysis more efficient. First, only nanoparticles of height $h_{\text{Au}} = 22 \text{ nm}$ are simulated for different optical dataset combinations with the predefined Ti bilayer thickness ratio. The results of these simulations are shown in Figure 4.10(c) and (d). All of these spectra follow the same progression with a clear minimum around the expected resonance position $\lambda_{\text{res}} = 591 \text{ nm}$ (dashed black line). The only exceptions are the “Wer” dataset for Au and the “Wer” dataset for Ti, which deviate significantly from the expected position and are, therefore, excluded from further considerations.

The evaluated resonance positions obtained after step 1 are summarized in tables such as Table 4.3. From this example, two trends become apparent: First, the resonance position gets blue-shifted, i.e., decreasing resonance wavelength for increasing Au height, and second, for increasing Ti height. Therefore, it is not surprising that the resonance positions are similar along a diagonal in this table, with the effects of increasing Au and decreasing Ti canceling out.

In the second step, all suitable simulated transmission curves are shifted in y-direction to match the minimum of the measured curve. This is done for better comparability between simulations and measurements and is shown in Figure 4.11(a) for one exemplary curve. All suitable curves from Table 4.3 are shown in their shifted form in Figure 4.11(b). For clarity, only the simulated progressions around the resonance are shown here. This reduces the number of suitable simulations to only two (light blue and green), but as the raster simulation

was done in step sizes of 0.5 nm for both the Ti and Au height, it can be assumed that the most fitting value lies in between.

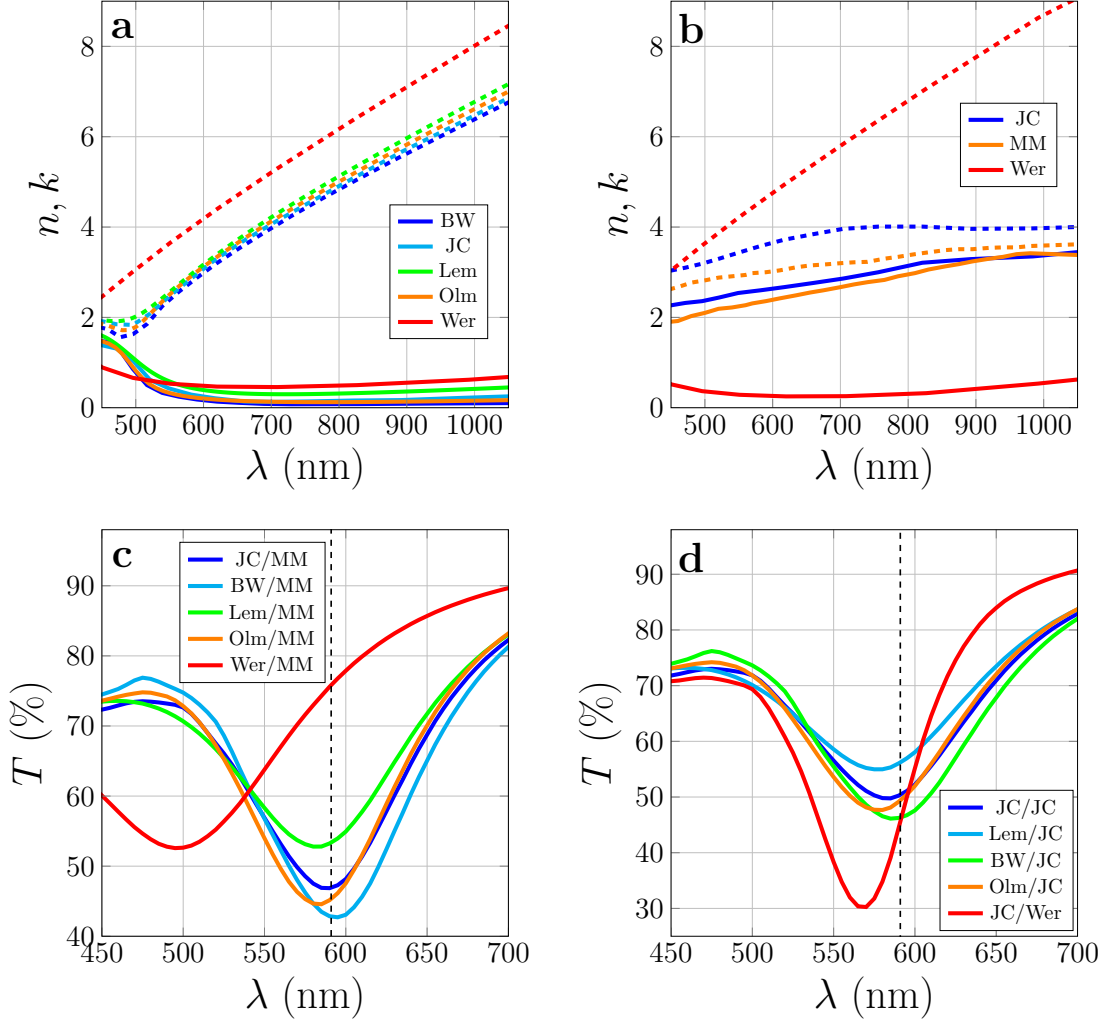


Figure 4.10.: Semi-empiric FDTD simulations of Au NP arrays. Comparison of refractive index n (solid lines) and damping constant k (dashed lines) datasets from the literature for (a) Au and (b) Ti. (c) and (d) show simulations of the transmission of Au NP arrays ($h_{\text{Au}} = 22$ nm, $h_{\text{Ti}} = 2$ nm, $h_{\text{TiO}_2} = 1$ nm,) on SiO₂ substrate in air for different combinations of optical datasets X/Y. X refers to the dataset used for Au, and Y refers to the dataset for Ti. For more details on the abbreviations and on the other datasets used, see Table 4.2. (c) contains simulation results for different Au datasets with (a) the same MM Ti dataset and (b) the same JC dataset for Ti. Additionally, (b) contains a simulation using the JC/Wer material combination. The dashed black line in (c) and (d) represents the expected resonance position of the simulated sample $\lambda_{\text{res}} = 591$ nm, as measured by optical spectroscopy.

The result of the raster simulation regarding the optical datasets is JC for Au and MM for Ti, which will be used for all simulations conducted in this thesis. All best-fitting Au and Ti heights are shown in Table 4.4. While the resulting simulated Au and Ti heights are

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Table 4.3.: Resonance positions of the simulated spectra of the 10 nm-sample using the JC/MM datasets for Au/Ti. The expected resonance position for the 10 nm-sample is $\lambda_{\text{res}} = 651$ nm and all simulations within a 2 nm range are marked green. The simulation of the expected production height is marked blue. Below the Ti a TiO_2 layer of thickness 1 nm was simulated.

Ti (nm)	Au (nm)							
	10.0	10.5	11.0	11.5	12.0	12.5	13.0	13.5
1.0	681	673	661	660	654	648	643	639
1.5	678	670	663	657	651	646	641	637
2.0	674	667	660	654	649	644	638	634
2.5	670	663	656	651	646	641	636	632
3.0	665	659	653	647	642	637	633	628
3.5	660	654	648	643	638	633	629	625
4.0	654	649	643	638	633	629	625	620

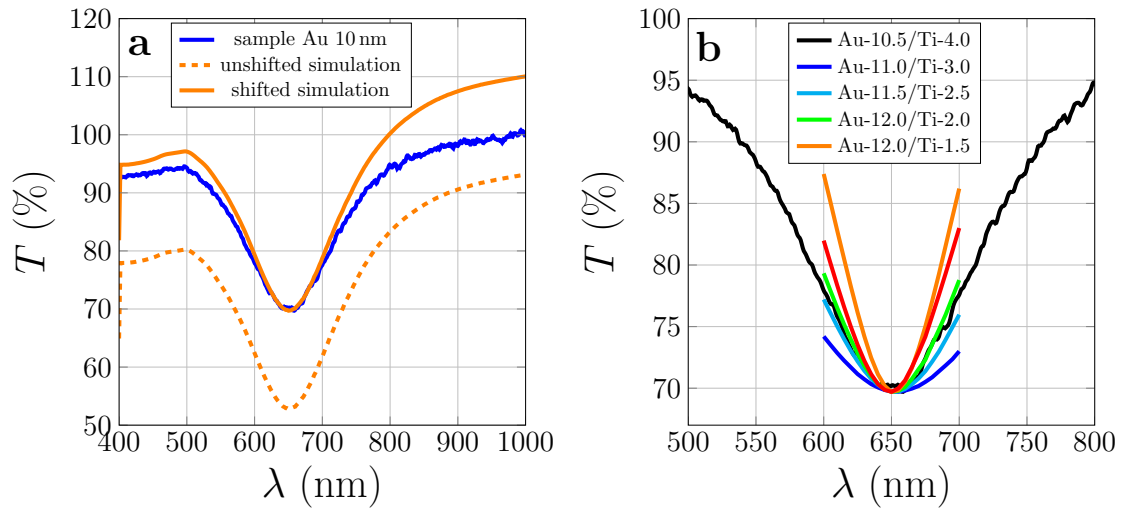


Figure 4.11.: Comparison of the simulated FWHM to the measured spectrum. (a) Adaptation of the simulated curve to the measured curve by shifting in y-direction to match the minima. (b) Plotting all suitable curves of Table 4.3 after being shifted alongside their corresponding measurement.

closer to the AFM-measured NP height than the originally intended height, they are still quite distant to the measured value. Nonetheless, two conclusions can be drawn from this: First, the production seems to consistently underestimate the amount of evaporated Au and Ti and secondly, there seem to be two groups of samples: (1) with a very thick Ti layer (≥ 3.5 nm) and (2) with a thinner Ti layer (≤ 2.5 nm). The evaporation process is expected to over- or underestimate the amount of evaporated metal for both Au and Ti, which, therefore, cannot be the origin of this difference in apparent Ti layer thickness. Consequently, another process is interfering with the Ti layer, which might be the reason for the remaining mismatch in Table 4.4 and will be investigated in the next section.

Table 4.4.: Final results of the simulations using the JC/MM datasets.

Sample (nm)	Au Sim (nm)	Ti Sim (nm)	Total Sim (nm)	Production (nm)	AFM (nm)
7	9.0	4.0	14.0	10	12.7 ± 0.3
10	11.5	2.5	15.0	13	16.9 ± 1.2
13	17.0	1.0	19.0	16	17.0 ± 0.5
13	14.5	2.5	18.0	16	17.6 ± 0.4
16	17.0	4.0	22.0	19	16.9 ± 1.2
22	21.5	1.5	24.0	25	25.0 ± 0.6
24	25	3.5	29.5	27	29.0 ± 0.6

4.4.3. Impact of Ti Oxidation on the Au Plasmon Resonance

All samples that showed a smaller Ti height in Table 4.4 were from a production batch about 6 months old at the time of the plasmonic measurements. In contrast, all of the other samples were measured shortly after production. Hence, the most likely reaction the Ti layer is subjected to is oxidation with oxygen from air, in which the sample is stored. This can happen as no surrounding SiO₂ layer protects the Ti adhesion layer. Here, the samples were produced with as few additional layers as possible for the sake of simplicity, thus leaving the SiO₂ layer out. In addition to that, the production procedure becomes less complex, as the etching step into the SiO₂ layer is not necessary, thus introducing fewer array defects. In the following, the basic partial oxidation of Ti is modeled via increasing the TiO₂ layer thickness while reducing the Ti layer thickness to keep the overall height constant.

Figure 4.12 shows two measurements, T13-1 (dashed black line) and T13-2 (dashed blue line), which were both intended to have a Au height of 13 nm, but the former has been stored in air for 6 months, while the latter is only a few weeks old. It can be seen that the transmission curve of the fresher sample is blue-shifted compared to the older sample and exhibits a smaller plasmonic resonance, i.e., the minimum is not as pronounced. On top of that, three simulated transmission curves have been added, adapted from the best-case simulation discussed in the previous section, but with different ratios of Ti/TiO₂. As is evident from the figure, not only the change in resonance position but also the change in width can be explained by increasing the TiO₂-content of the adhesion layer. The reason for both changes with smaller and smaller Ti content is the weakening of the plasmonic resonance of the Ti layer. All metal nanoparticles exhibit some form of plasmonics, and in close contact, these effects interfere with one another. Consequently, if Ti has a blue-shifted plasmon resonance, it would be expected to (1) shift the resonance of the dominating Au plasmonics to smaller wavelengths and (2) potentially decrease its strength due to a destructive superposition of induced electric fields. With this, it can be assumed that most of the remaining differences between simulations and AFM measurements shown in Table 4.4, are related to the unaccounted oxidation of the Ti layer.

It is, therefore, concluded that all electrochemical samples must have a protective SiO₂ layer covering the sides of the NPs to such a height that Ti is neither in contact with air nor with electrolyte. This geometry has already been introduced in Chapter 3 and used for all electrochemical measurements shown so far.

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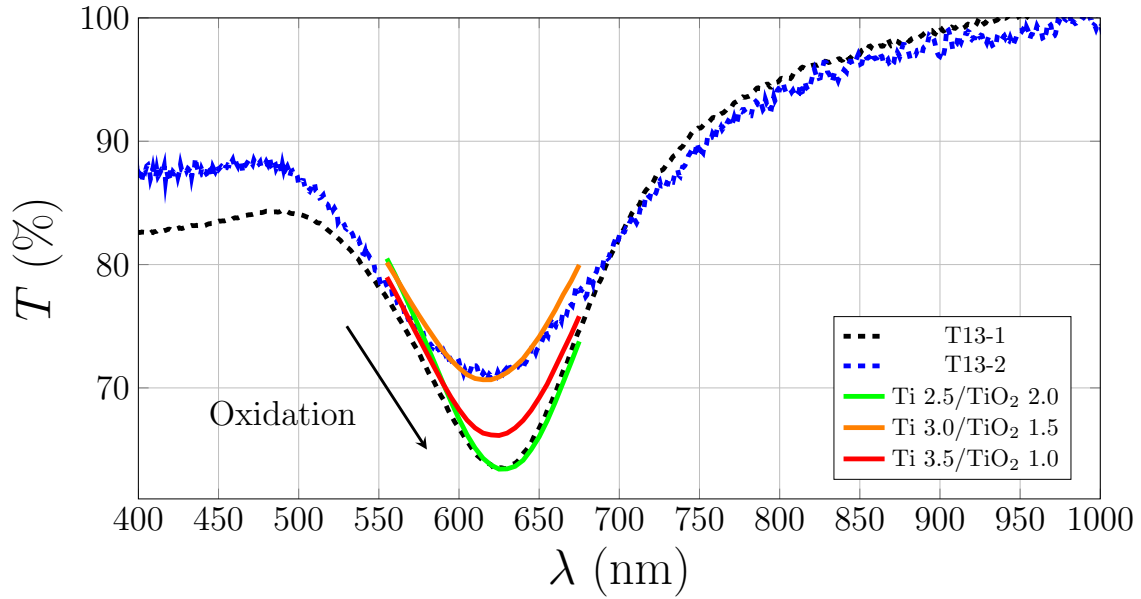


Figure 4.12.: Comparison between measured transmission spectra of an aged (dashed black line) and a fresh (dashed blue line) sample and simulations (green, orange, and red solid lines) with varying Ti/TiO₂ contents in the adhesion layer.

4.4.4. Optical Impact of the Electrolyte

In the course of this thesis, plasmons will most often be investigated in aqueous electrolytes. However, there are no studies on the change in optical properties of deionized (DI) water with and without the addition of ions. Even if the spectra of both cases are similar, the change in electrostatics could impact the plasmonic resonance. Hence, a comparative measurement has been conducted, the results of which are shown in Figure 4.13.

Figure 4.13(a) shows three transmission curves of one sample (22 nm) in air, DI water, and 100 mM H₂SO₄ (here denoted as “acid”). Both of the latter ones are red-shifted by approximately 40 nm with respect to the air measurement. Between DI water and acid, no shift is visible. Figures 4.13(b) and (c) show the resonance positions λ_{res} and the *FWHM* of comparative measurements for samples of different heights. Similar to the spectra in (a), there is a red-shift between air and the other two dielectrics, but basically no difference between acid and DI water. This can be explained by the increased polarizability of water compared to air, which reduces the restoring force of the oscillation by shifts in ions and water dipoles (cf. section 2.1.1). Further, it can be concluded that the ions in solution do not impact the plasmonics in a meaningful way and can, therefore, be simulated as DI water, which will be done in the following.

4.4.5. Simulation of the Electrochemical System

To close this chapter, the electrochemical samples, i.e., Si substrate, water as upper medium, Ti/TiO₂ adhesion layer, and a protective SiO₂ layer covering the lower half of the Au NPs, are simulated and discussed.

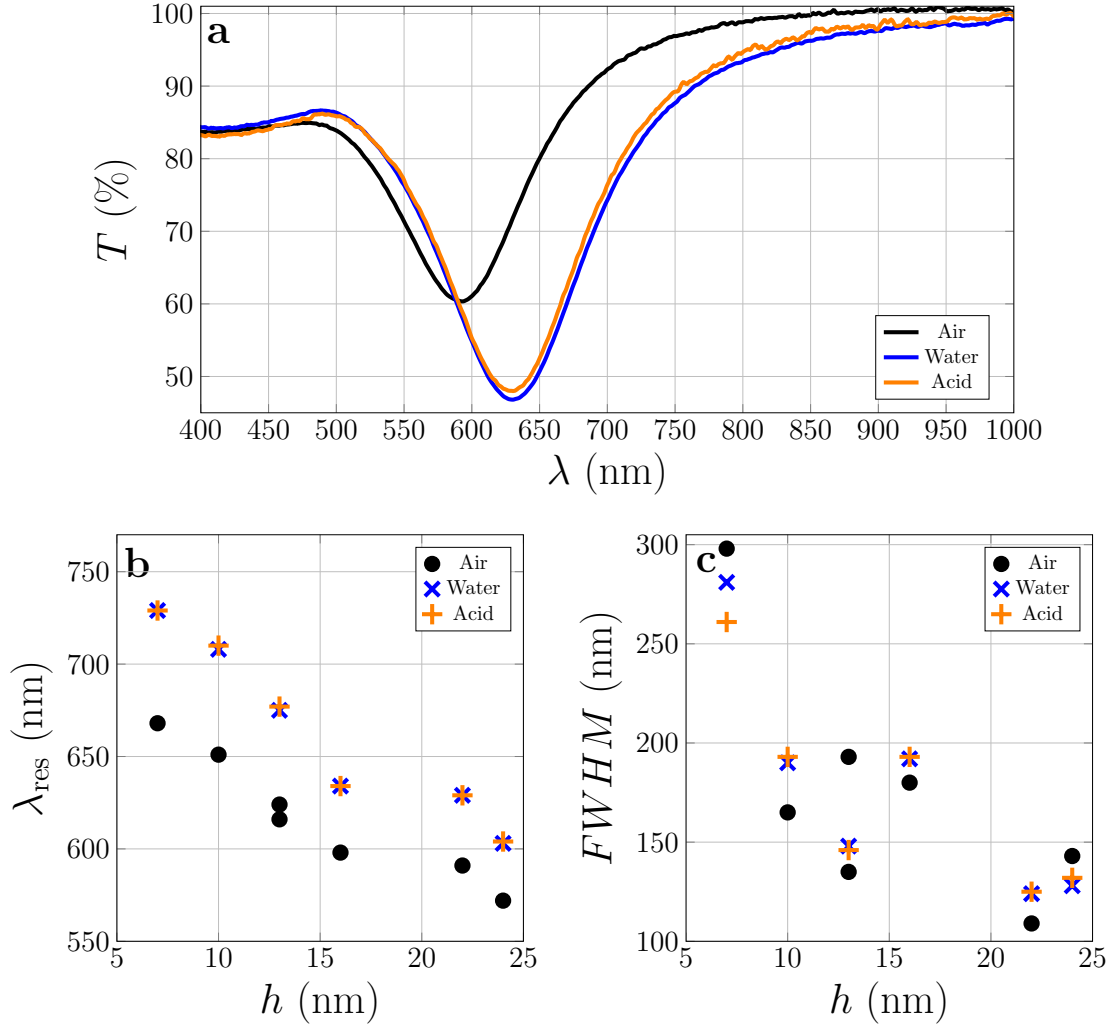


Figure 4.13.: Optical transmission spectra of one Au nanoparticle array on a SiO₂ substrate in air, water, and 100 mM H₂SO₄ (a). Comparison of the resonance position (b) and width (c) for samples of different heights in different dielectric media (SiO₂ substrate).

Heterogeneous Broadening

Figure 4.2(a) introduced the approximate distribution of the NP diameter, which can be expected to contribute to the heterogeneous broadening of the plasmonic resonances. Using the simulation framework established before, the reflectance spectra of various NP radii can be simulated and superposed on each other. Figure 4.14 shows such spectra for the diameters indicated in the legend, which match the x-values of the histogram in Figure 4.2(a). The black dotted curve (“avg”) indicates the weighted average of all the colored spectra. The weight corresponds to their value in the histogram of Figure 4.2(a). As evident from the graph, the average lies perfectly on top of the green curve for $r_{\text{NP}} = 37.5$ nm, which is exactly the intended geometry (diameter of 75 nm). The reason for this is that the curves to the left and to the right of the green one cancel each other out nearly perfectly. It has to be assumed that this level of perfection is due to the idealized geometry of the simulation and that there is some form of heterogeneous broadening in real systems due to differences in

4. Plasmonic Nanoparticle Arrays

geometry. However, this simulation shows that heterogeneous broadening is severely limited and will, therefore, be disregarded in the rest of this thesis.

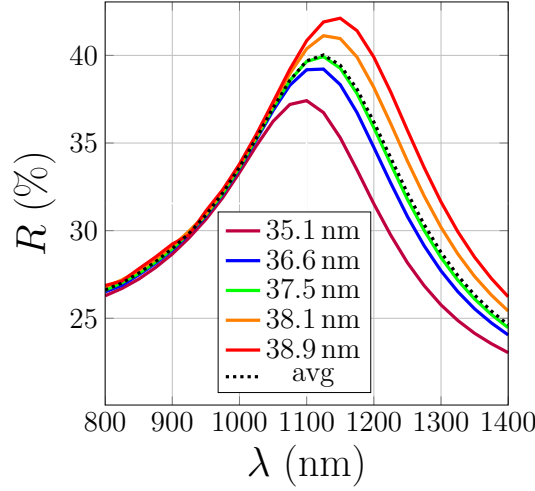


Figure 4.14.: Simulation of the heterogeneous broadening of the samples introduced in Figure 4.2 in DI water. The legend indicates the radii of the NP that were simulated to obtain the corresponding spectra. The black dotted curve represents the weighted average of all curves with the weights taken from Figure 4.2(a) for the respective radii.

Impact of the Different Surrounding Media

The general shape of the plasmonic spectra (cf. Figure 4.7) is similar to those reported in the literature [96, 97]. However, the width of the spectra obtained in this thesis is larger than in other experiments. It is necessary to single out the origin of the width to allow for a comparison of all the following findings with the literature. Hence, a simulation has been conducted where the simplest system, i.e., Au NP arrays surrounded by water, is simulated first. Then, more and more materials are added, and their spectra are compared. The results of this can be seen in Figure 4.15. For better comparability, all resonance positions have been shifted to 0. The first simulation of just Au NPs in water (blue line) shows a sharp resonance curve ($FWHM = 86$ nm), as usually seen in the literature for colloidal particles. Then, the Ti layer ($h = 3$ nm) is added below the Au NPs, which increases the width substantially to $FWHM = 250$ nm (orange line). Finally, the Si substrate is added, which again increases the $FWHM$ to 303 nm (red line). For the last simulation, the Si substrate without NP is simulated first and subtracted from the data, which results in the red curve.

These results show that most of the large resonance width originates from the adhesion layer and the Si substrate. Compared to colloidal particles, which are often used in the literature, it is to be expected that our nanostructured working electrodes exhibit broader resonances. The simulations substantiate this expectation.

Limitations of the Simulation

In this section, several quantitative dependences of simulated plasmonic resonances on their dielectric environment and geometric properties of the NP are shown and discussed. The simulations worked particularly well for nanostructured SiO_2 , whose plasmonic spectra could

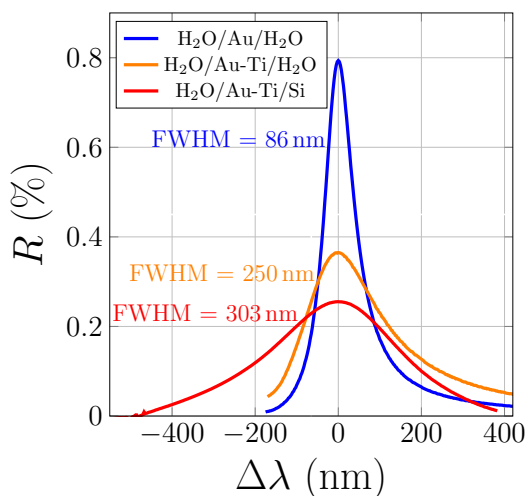


Figure 4.15.: Simulated reflectance spectra for a Au NP array submerged in H₂O (I: H₂O, II: Au, III: H₂O, IV: H₂O, V: H₂O), bimetallic 13 nm Au/3 nm Ti NP array submerged in H₂O (I: H₂O, II: Au, III: Ti, IV: H₂O, V: H₂O) and for a bimetallic (Au/Ti) NP array on a Si substrate in H₂O (I: H₂O, II: Au, III: Ti, IV: H₂O, V: Si). The numerals refer to the partition introduced in Figure 3.4. Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

be replicated with high accuracy. However, once we switch to plasmonic samples designed for electrochemical use, there is a limit to the simulations' ability to pinpoint the exact resonance position. This can be seen in a comparison of the resonance positions of the simulations of Figure 4.14 ($1050 \text{ nm} < \lambda_{\text{res,sim}} < 1200 \text{ nm}$) and the measurements of Figure 4.7 ($700 \text{ nm} < \lambda_{\text{res,exp}} < 900 \text{ nm}$). The former is the best replication via simulation, including all the available geometric and compositional information, and there is still a significant difference in absolute resonance positions. This could be due to several unknown factors, which are listed below.

- (1) The exact optical constants of the n-doped Silicon.
- (2) The exact chemical composition and spatial distribution of the TiO_x layer.
- (3) Deviations in the form (i.e., roughness) cannot be incorporated into the geometry.
- (4) Variations in charge distribution due to build-up of the EC interface.

Especially (1) and (2) play an important role in determining the resonance position of the resulting simulated spectra. However, these two aspects are expected to be constant with time, as both are covered by a thick ($h_{\text{SiO}_2} \approx 8 \text{ nm}$) layer of SiO₂ which prevents reaction with air and electrolytes. Assuming contributions (1) and (2) to be constant would lead to a constant shift of the simulated and measured spectra, meaning that any change in the resonance positions should be replicated well, even on a quantitative level.

This concludes the electrochemical and plasmonic description of the samples used in this thesis. In the following chapter, the plasmonic properties will be used to analyze electrochemical interface properties which relies strongly on a basic understanding of the nanostructure arrays and their plasmonics.

5. differential Cyclic Plasmo-Voltammetry

This chapter closely follows the line of argument of the paper “Characterization of Different Au/Electrolyte Interfaces via In Situ Differential Cyclic Plasmo-Voltammetry” by M.J. Feil et al. [64].

5.1. Introduction

This chapter introduces the samples described in Chapter 4 as a multi-particle plasmonic sensing platform for changes to the electrochemical interface. As introduced in Chapter 2, the plasmonic resonance depends on the electron density, the morphology, and the energetic state of the metal NP surface, which are all affected when applying an external potential to the interface. With the necessity to disentangle all of these various contributions, using LO-NIL to produce the underlying nanoparticle arrays is vital. This ensures not only reproducible and scalable but also clean surfaces (cf. section 3.1). Yet another advantage is the homogeneity of the NPs in the array, which exhibits negligible heterogeneous broadening (cf. section 4.4.5) and enables us to employ multi-particle spectroscopy and relate the result of processes happening on the whole array to those on the individual NPs. Moreover, all metal-semiconductor contacts are electronically and mechanically stable because of the SiO₂ layer covering the Ti/TiO₂-adhesion layer, as found necessary in the previous chapter.

It is shown that with these samples and adequate data treatment, the double layer charging, adsorption of anionic species, and gold oxidation/reduction can be clearly distinguished. Finally, in a first proof of concept, this method will visualize and quantify different stages of the Cu under- and overpotential deposition on polycrystalline Au NPs.

5.2. Plasmo-Voltammetry

5.2.1. Plasmonic Time Series

The center of this method is recording plasmonic spectra of NP arrays while subjected to electrochemical measurements, such as CV and EIS. This is done with 10 spectra per second (cf. section 3.4.2), which are then treated as stated in section 4.3.2, resulting in a distinct λ_{res} and $FWHM$ every 100 ms. Consequently, these two fit observables can be plotted versus time, as shown exemplary for λ_{res} in Figure 5.1(a) for a cyclic voltage scan from $E_{\text{RHE}} = -156 \text{ mV}$ to 1.715 V , driven with 50 mV s^{-1} for 5 cycles. There is a clear periodicity in the behavior of λ_{res} and the overall progression seems to follow the voltage profile (E_{RHE}) rather well, except for more round transitions at the turning points of the voltage. The details of this exact behavior are discussed below.

5.2.2. Cyclic Plasmo-Voltammetry

Another more intuitive representation of the plasmonic data is the cyclic representation, which we denote as a Cyclic Plasmo-Voltammogram (CPV). Here, the resonance wavelength is plotted versus the corresponding applied potential, as depicted in Figure 5.1(b). The coloring is the same as in (a), i.e., the CPV starts at dark blue and goes to dark red. For better visibility,

5. differential Cyclic Plasm-Voltammetry

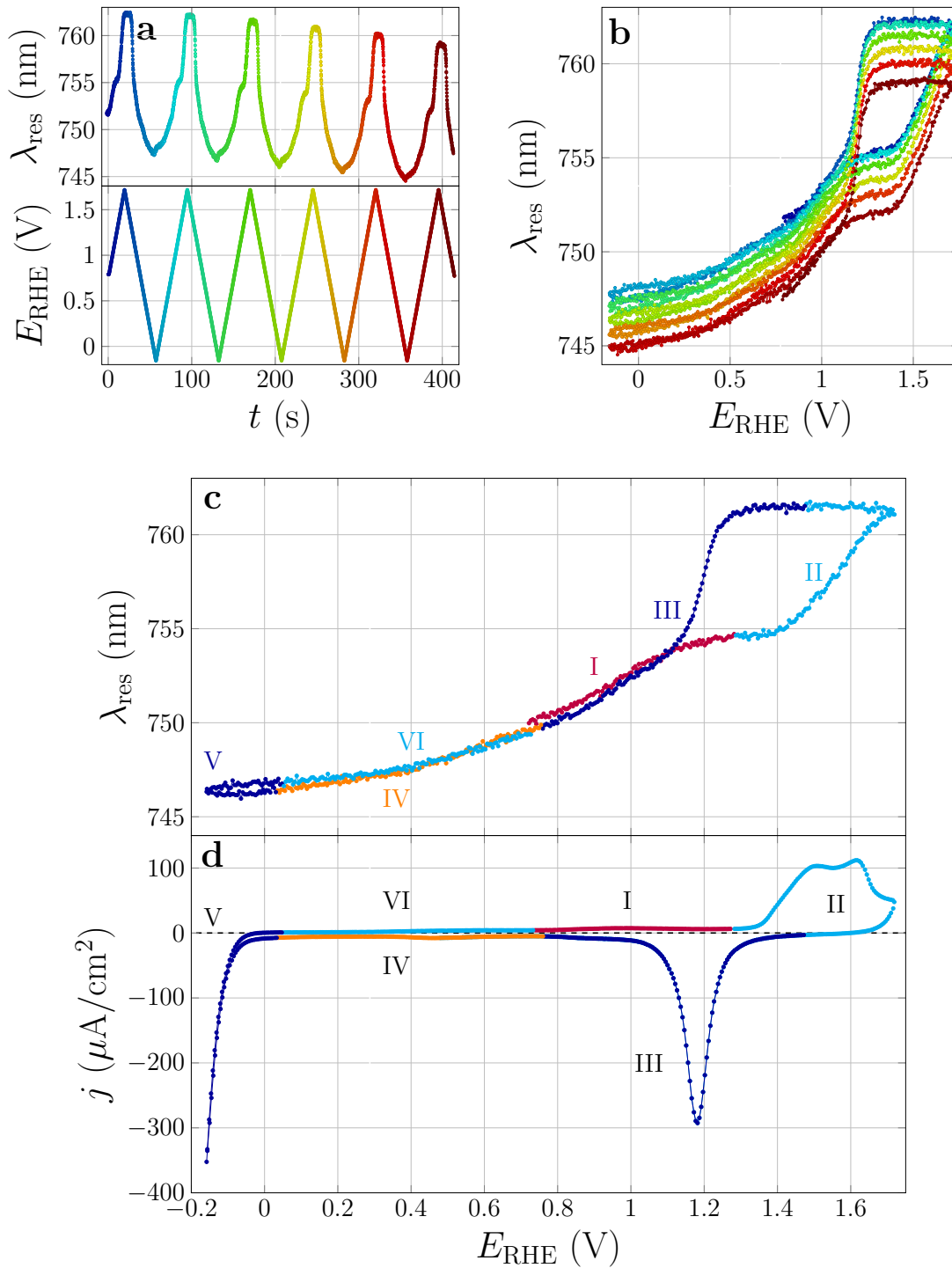


Figure 5.1.: Exemplary curves of Plasm-Voltammetry. (a) Plasmonic resonance positions λ_{res} with respect to time and the concurrently recorded voltage profile ($E_{\text{RHE}} = -156\text{ mV}$ to 1.715 V , driven with 50 mVs^{-1} for 5 cycles). (b) Cyclic Plasm-Voltammogram of the λ_{res} -data shown in (a). (c) One cycle of the CPV shown in (b) alongside the corresponding CV (d) with markers indicating different potential areas. (a) and (b) are adapted with permission from [64]. Copyright 2025 American Chemical Society.

only one of the cycles of the CPV is shown in Figure 5.1(c) alongside its corresponding CV (d). Starting at $E_{\text{RHE,start}} = 0.74 \text{ V}$ cycling upwards (region I), the resonance wavelength increases linearly up to 1.15 V , where it flattens out (lower branch of the hysteresis between region I and II), before it increases again sharply up to the turning point (region II). Then it flattens out and sharply decreases (upper branch of the hysteresis, region III) at around 1.15 V . The slope decreases gradually for the rest of the cycle (region III latter half, region IV and region V first half) until the lower turning point, which is replicated on the way back (region V second half and region VI) to the starting point. Comparing it with the CV in Figure 5.1(d), it can be seen that the increase in region II corresponds to the oxidation of Au while the decrease in region III corresponds to the reduction of Au oxide. The double layer region (regions IV and VI) shows a linear behavior in CPV and CV, but the decrease in the slope of the CPV is not reflected in the CV. Region V shows hydrogen evolution occurring, which is not replicated in the CPV. All in all, some of the features obtained are replicated in the CPV. However, while this representation has its applications (cf. Chapter 6), it is unintuitive for comparing optical and electrochemical measurements, which is why, in the following section, another representation will be introduced.

5.2.3. differential Cyclic Plasco-Voltammetry

A qualitative difference between CPVs, as shown in Figure 5.1(b), and CVs (cf. Figure 5.1(d)) is that the former tracks a parameter that is directly related to the state of the system, while the latter tracks the change thereof. In other words, the plasmonic resonance position depends on the total amount of transferred charge $Q(t)$ of, for example, oxidized Au while the CV tracks the current density $I(t)$ of Au oxidation, i.e., $I(t) = dQ(t)/dt$. Hence, to compare the optical data to cyclic voltammograms, a differentiated representation of the optical signal is generated, which we refer to as differential Cyclic Plasco-Voltammogram (dCPV) for the resonance wavelength versus potential and differential plasmonic width voltammogram for the full-width half maximum versus potential representation. The abbreviation dCPV is used in the same way as the term CV, as name for the method (i.e., voltammetry) and for the resulting graph (i.e., voltammogram) depending on the context.

Data Pre-Treatment

Before the derivative with respect to voltage $d\lambda_{\text{res}}/dE$ can be taken, the data has to be pretreated to obtain clear progressions. The code used to do this is written in Python, and all relevant functions are given in section A.5 of the appendix. It has to be noted beforehand that the number of outliers must be in the order of $\leq 1\%$ of all data points. Any data set with more deviations is excluded from further treatment. Given that, all outliers have to be adjusted as described in the following. Here, the term outliers refers to all data points that are either singularities or a result of recording errors. Singularities are data points that significantly deviate in λ_{res} -value from all those in their immediate surroundings (cf. appendix section A.5.2), which originates mostly from bubbles interfering with the light path. In short, the mean value of ten data points $[i - 10, i - 1]$ is taken and compared to the value of the following data point i . If this value exceeds the pre-calculated mean by a certain threshold, it is set to the pre-calculated mean value, and the algorithm moves to the next data point. The threshold is scan rate dependent to prevent this adjustment from removing actual features, such as the Au oxide reduction, which exhibits the largest change in λ_{res} of all reactions resolved with dCPV in this thesis (region III in Figure 5.1(c)). For slower scan rates, the distances in λ_{res} of data points during the Au oxidation are smaller. Hence, the threshold has to be set to a lower value.

5. differential Cyclic Plasm-Voltammetry

Recording errors occur when the hardware fails to save spectra, thus leaving the data points unequally spaced. At times, the system lags behind, thus saving multiple consecutive spectra with the same timestamp. Although both system failures are rare, they can still lead to unphysical features in the differentiated data set. For missing data points, the algorithm checks for unequal spacings between all data points and inserts an artificial point, which is the mean of both neighboring points in the x- and y-direction (cf. appendix section A.5.3). For the latter issue, new time values are created to fill the hole in the timescale with equidistant values, which are then distributed to the corresponding λ_{res} -values (cf. appendix section A.5.4).

Smoothing and Differentiating via a Savitzky-Golay-Filter

With all the outliers removed, the curve must still be smoothed before being differentiated. In general, the most efficient way of doing both steps would be to use a Savitzky-Golay-Filter [98], which replaces the λ_{res} -value of data point i by calculating a weighted average of the surrounding data points $[i - (n - 1)/2, i + (n - 1)/2]$. The most important part is the selection of the weights, which is called kernel. With the right choice of kernel, the data can be smoothed and differentiated by just using this simple kernel-weighted averaging for all data points. Unfortunately, the mathematical prerequisite for this to work is that the data points are equally spaced in voltage E_{RHE} . While most of the voltages are equally spaced due to the equidistant recording steps and the constant scan rate, any significant IR correction (cf. section 3.3.3) shifts the voltages, invalidating kernel smoothing and differentiation.

To avoid introducing artifacts for regions of high current (and therefore significant IR correction), the smoothing and differentiation will be done by fitting the data points surrounding a specific point $i \in [i - (n - 1)/2, i + (n - 1)/2]$ with a second-degree polynomial and differentiating the resulting function once with respect to E_{RHE} . The value of this differentiated function at position i is the smoothed and differentiated value of the dCPV at position $E_{\text{RHE}}(i)$ (cf. appendix section A.5.5). This treatment leads to the same result as using the respective kernel for equally spaced data points, which is why this process is still called Savitzky-Golay-Smoothing in this thesis. An example of this treatment is shown in Figure 5.2. In Figure 5.2(a), a test function $f(E) = E^2 + g(E)$ is plotted (black dots), where $g(E)$ is a Gaussian random noise function. The ideal squared function is shown as a solid black line. For each fit, which is a squared function, $n = 5$ data points were used. For visibility, the plotted fit functions cover only the data points used for the respective fit. In Figure 5.2(b), the values of the slopes of the fit functions at that particular E -values are plotted, which represent the smoothed and differentiated curve shown in Figure 5.2(a). The fit functions for the black dots in (b) are not shown in (a).

Even though the original function is subjected to noise, the resulting differentiated function comes close to the ideal, which would be $df(E)/dE = 2E$, proving the method's effectiveness. However, there are still visible deviations, which could be removed by increasing the window sizes. Hence, $n = 31$ is chosen for CVs recorded with a scan rate of $\nu = 50 \text{ mV s}^{-1}$ and $n = 301$ for $\nu = 2.5 \text{ mV s}^{-1}$ to ensure appropriate smoothing. It must be noted that increasing window size n reduces noise, but physical features get smeared out. This will be discussed later in this section. Additionally, the borders of the smoothed curves are changed by another numerical artifact. If a data point does not have a sufficient number of neighbors in either of both directions, i.e., it is too close to either end of the curve, the method fills in those missing data points by extending the curve artificially. The closer the point is to the edge, the more data points have to be added, which might introduce unphysical features. The choice of how these data points are added is determined by a squared fit of the last $(n - 1)/2$ real data points, which then gets extended to create an additional $(n - 1)/2$ data points. Using the common

window lengths, as stated above, it follows that the first and last 50 mV of each CV branch are potentially compromised.

After discussing in detail how the data is processed to obtain a dCPV, the relation between a cyclic voltammogram (CV) and a dCPV is shown and discussed step by step in the following.

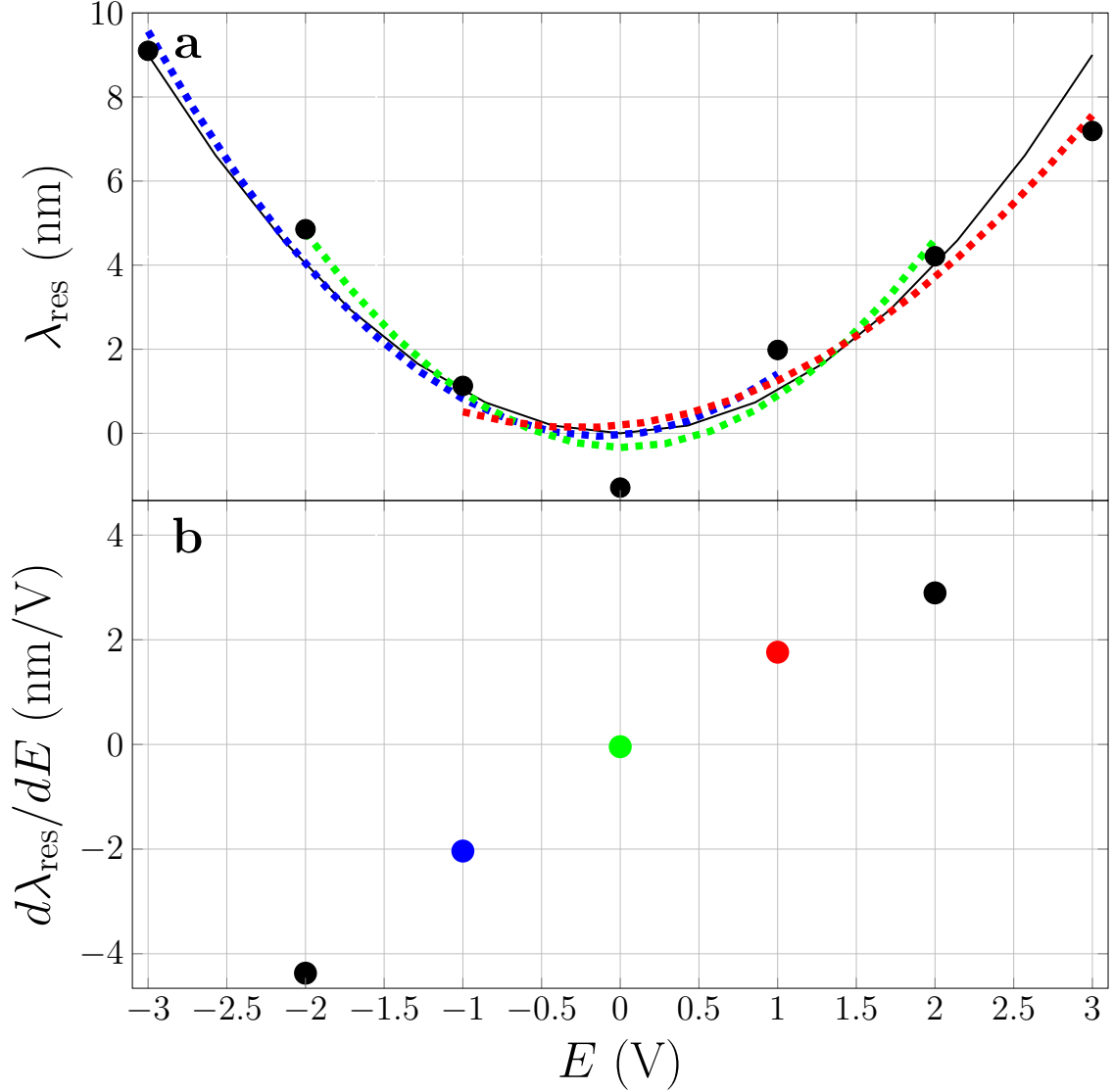


Figure 5.2.: Data smoothing and differentiation by the Savitzky-Golay-Method. (a) Exemplary data set (black dots) of a squared function with noise, the ideal squared function (solid black line), and fit functions (dashed blue, green, and red lines). (b) resulting values for the smoothed and differentiated data set in (a). The fit functions for the black dots in (b) are not shown in (a).

Comparison between dCPV and CV

Figure 5.3 shows the resonance wavelength (a), the current (b) and the applied voltage (c) versus time during one voltage cycle, starting at $E_{\text{RHE,start}} = 740 \text{ mV}$, as indicated by the black circle in Figure 5.3(d), versus time for a Au NP array in a phosphate-containing elec-

5. differential Cyclic Plasco-Voltammetry

trolyte. The data and the regions are the same as in Figure 5.1. In region I, the dominating mechanism is the adsorption of HPO_4^{2-} (H_2PO_4^-) on the Au surface of the NPs. In the λ_{res} -t-plot (Figure 5.3(a)), an increase from 752 nm to about 755 nm is visible, which is of the same order of magnitude as the changes in λ_{res} for the gold oxidation (region II) and the consecutive gold reduction/ HPO_4^{2-} (H_2PO_4^-) desorption (region III). The former ranges from 755 nm to 762 nm while the latter two reactions show a combined change of $\Delta\lambda_{\text{res}} \approx 10$ nm back to 752 nm. In region IV(VI), the current is mostly due to capacitive charging (discharging) of the double layer, which manifests itself in a change of $\Delta\lambda_{\text{res}} \approx \pm 4$ nm in Figure 5.3(a). In contrast to gold oxidation/reduction reactions, HPO_4^{2-} (H_2PO_4^-) adsorption and double layer charging/discharging occurs without significant charge transfer (c.f. Figure 5.3(b)). Region V encompasses the hydrogen evolution reaction, which exhibits a large minimal current compared to the rest of the CV but only a slight bump in the λ_{res} -t-plot.

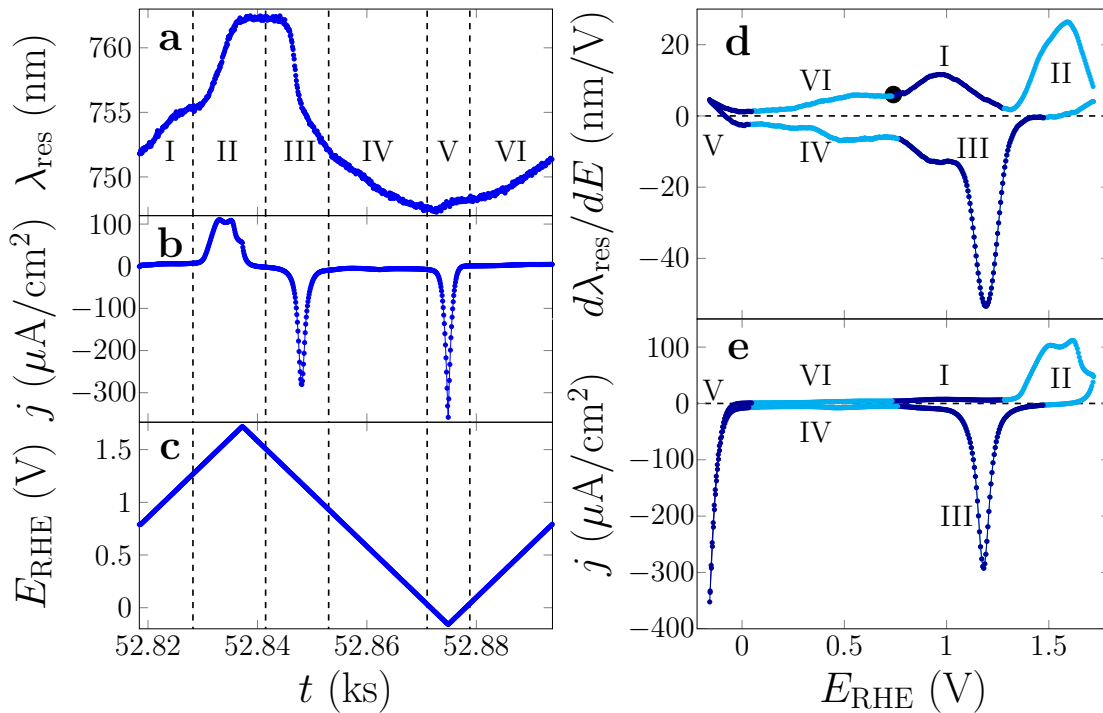


Figure 5.3.: (a) λ_{res} versus time, (b) current versus time and (c) applied voltage versus time for one cycle of a cyclic voltage scan, (d) differential Cyclic Plasco-Voltammogram (dCPV) and (e) the CV of a Au nanoparticle array in 120 mM H_3PO_4 + 180 mM KOH. The numerals indicate different regions of interest in the dCPV and the CV and the black circle in (d) indicates the start of the scan. Scan rate: 50 mV s^{-1} . Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

The relations between the plasmonic signal and the current can also be seen in Figures 5.3(d) and (e). The numerals and corresponding ranges are the same as in Figure 5.3(a)-(c), and any positive (negative) data point in the dCPV refers to an increase (decrease) of λ_{res} at that specific potential. Region I shows a positive Gaussian-shaped adsorption curve, which can be related to the HPO_4^{2-} (H_2PO_4^-) adsorption. At the beginning of region II, the signal drops notably at $E \approx 1.3$ V, before rising again concomitant with the gold oxidation. Region III comprises the reduction ($E > 1.1$ V) of gold-oxide formed in region II and the

desorption of HPO_4^{2-} (H_2PO_4^-) ($E < 1.1 \text{ V}$). Anodic and cathodic branches of the double layer region in regions IV and VI start out parallel (higher to lower potentials) and, beginning at $E \approx 0.4 \text{ V}$, undergo a considerable narrowing. Comparing these two branches, the overall downward trend from the first to the last cycle visible in Figure 5.1(b) leads to a shift towards smaller λ_{res} over time, causing both branches in the dCPV not to be symmetric around the zero line (dashed line in Figure 5.3(d)). In region V, the hydrogen evolution seems to shift the plasmonic resonance towards higher values. However, close to the turning points of the forward and backward scans, i.e., the left part of region II and the right part of region V, the curves are a convolution of the data and an artifact stemming from the smoothing, as discussed at the end of the previous section.

Different Smoothing Levels

Data smoothing is a necessary treatment that removes noise but also flattens out features. In this section, the ideal balance between those two aspects will be assessed. Figure 5.4 shows an exemplary dCPV but with different smoothing levels n (i.e., window lengths). For small smoothing levels, the curves show a significant noise modulation, which gets removed for higher n , but at the cost of slightly broader peaks, e.g., the gold reduction peak broadens. In general, noise suppression is more important than broadening features, which is why the smoothing level in this chapter is set to $n = 301$ for scans recorded with a scan speed of $\nu = 2.5 \text{ mV s}^{-1}$. For CPVs, as shown in Chapter 6, smaller levels of smoothing can be chosen, as no differentiation is desired.

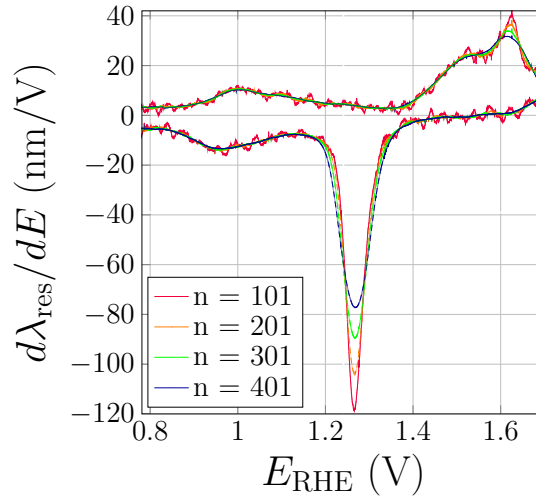


Figure 5.4.: dCPV scan with different smoothing ranges n . Scanrate $\nu = 2.5 \text{ mV s}^{-1}$, Electrolyte = $120 \text{ mM H}_3\text{PO}_4 + 180 \text{ mM KOH}$

Alternative Treatment Methods

In the literature, two other ways of recording Plasco-Voltammetry data exist: single wavelength intensity and maximum intensity methods [99, 100, 101]. The former excites the plasmons with a small bandwidth, i.e., single wavelength, and records the corresponding reflected intensity, while the latter illuminates the sample with a broad light spectrum and records the reflected spectrum in order to extract the maximum intensity thereof. For comparison, the dCPV method basically extracts the peak position, but in order to reduce noise and extract

5. differential Cyclic Plasm-Voltammetry

further information, this is done via a fit, as detailed in section 5.2.3. The advantage of single wavelength and maximum intensity measurements is the low computational requirement of the data treatment, which leads to faster data processing. In Figure 5.5, corresponding evaluations of the measured data underlying Figure 5.3 are depicted. For extracting the single wavelength spectroscopy representation, the probing wavelength had to be selected first, as this data set was measured using broadband illumination. The probing wavelengths in Figure 5.5 are 650 nm, 850 nm and 755 nm, which are red-shifted to, blue-shifted to and approximately in the resonance of the plasmons excited in this experiment. This is done in order to show the impact of the probing wavelength selection on the resulting (d)CPV. The overall progression of all graphs is similar to the one shown in Figure 5.3(d), but although the same smoothing window ($n = 31$) was used, the graphs have a lower signal-to-noise ratio such that essentially only Au oxidation and reduction are discernible. Note that in the case of the single wavelength recording at $\lambda = 850$ nm, the responses to Au oxidation/reduction are inverted compared to the recordings at the other two wavelengths as this probing wavelength lies on the other side of the maximum. In contrast to Au oxidation/reduction, anion ad-/desorption and double layer charging are completely masked by noise. This is in stark contrast to the dCPV plot shown in Figure 5.3(d).

Overall, the data treatment method presented in section 5.2.3 leads to considerably more information about the electrode/electrolyte interface than the single wavelength and maximum intensity methods. In this thesis, this will be preferred over the faster data acquisition.

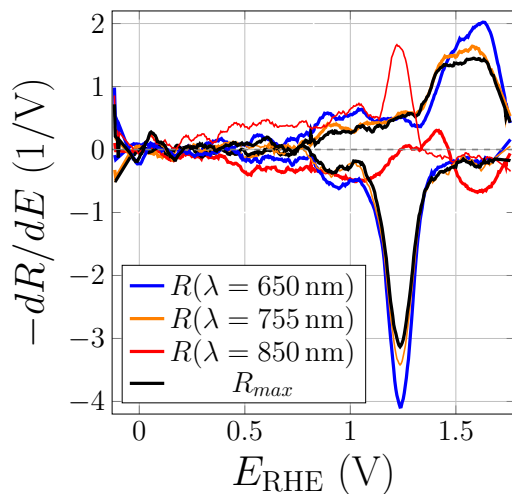


Figure 5.5.: Same data set as in Figure 5.3 but only the reflectivity at specific wavelengths λ , as given in the inset, or the maximum reflectivity were used as input for the dCPV data treatment. Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

5.3. Investigation of the Au/Electrolyte Interface

5.3.1. Different Scan Rates

The impact of the potential scan rate on the dCPV reveals important properties of the relation between CVs and dCPVs. Figure 5.6 shows dCPVs for three different scan rates (a) and the corresponding CVs (b) for Au NP electrodes in 100 mM H_2SO_4 . In contrast to the well-

established scan rate dependence of cyclic potential scans, the values of the dCPVs recorded at different scan rates are all comparable in size. Furthermore, the regions discussed above, i.e., Au oxidation/reduction, anion ad-/desorption, and double layer charging, are clearly distinguishable, independently of the scan rate. However, there are also some notable differences between the dCPVs measured at the different scan rates: They exhibit the same potential shift of the reduction peak as the CVs, however, with the heights of the peaks inverted. Another difference is the shape of the curve resulting from Au oxidation, which is rather distorted for $\nu = 50 \text{ mV s}^{-1}$ but still replicates the main features of the CV for $\nu = 2.5 \text{ mV s}^{-1}$. This is a consequence of the limited recording speed of the spectrometer of $\delta t = 100 \text{ ms}$, which, in turn, leads to a resolution that improves for slower scan rates. Additionally, at the latter scan rate, a downward shift of the curves is visible in both forward and reverse scan directions.

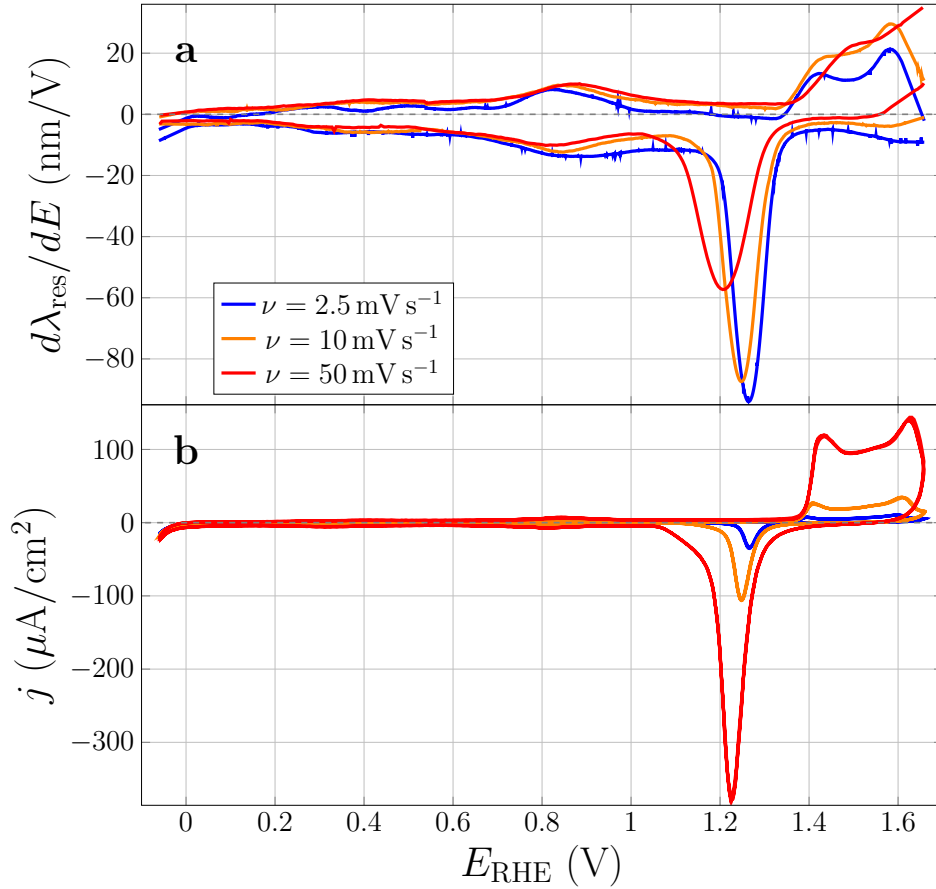


Figure 5.6.: dCPV (a) and corresponding CV (b) of a Au NP array in 100 mM H_2SO_4 (Ar purged) for different potential scan rates.

The reason for the scan rate independence of the capacitive current in a dCPV is that in a dCPV the derivative of λ_{res} , which is linked to the transferred charge Q , is taken with respect to the applied potential E and then plotted against the same E . In contrast, the current density is a derivative of Q with respect to time and plotted against the potential E . Hence, there is an intrinsic time dependence in the latter but not in the former.

This finding of scan rate-independent optical responses in the double layer region contrasts the findings of Dahlin et al. [102], who report clearly visible and scan rate-dependent hysteresis in their optical data during cyclic voltammetry. The main differences are the use of the absolute plasmonic resonance wavelength shift in contrast to our differentiated signal and

5. differential Cyclic Plasm-Voltammetry

the use of colloidal synthesis with an indium tin oxide (ITO) substrate and Cr adhesion layer. Therefore, the reason for the differences in the occurrence of a hysteresis probably lies in the presence of additional Faradaic reactions stemming from the Cr and the interaction between the annealed NPs and the ITO. In our systems, the adhesion layer and the metal-support interface are completely shielded from the electrolyte and did not require an annealing process.

We note that the observation of a clear double layer charging in the optical measurement contrasts the findings of Steinhauser et al. [103]. They used a dCPV method, but did not find capacitive features. When comparing our dCPVs with theirs (Supporting Information of Steinhauser et al. [103]), there is a weak charging effect visible in their data. The difference in the significance of this signal might be due to the level of homogeneity and control of the cleanliness of the electrochemical interface of our sample production method compared their manufacturing technique.

With the capacitive and anion adsorption signals being nearly independent of the scan rate, it is advantageous to use slow scan rates for a better signal-to-noise ratio of the dCPV.

5.3.2. Different pH Values and Ionic Species

Figure 5.7(a) shows two dCPVs of a standard Au NP array in a pH6.1 buffered electrolyte with $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ions and in a pH1 electrolyte with HSO_4^- ions, respectively. The dCPVs were recorded with a scan rate of $\nu = 2.5 \text{ mV s}^{-1}$. Both systems show the same response in the double layer region and similar overall progressions in all parts of the scan. Compared to the HSO_4^- -system, the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ -system does not exhibit a downward bending in the anodic potential range, while both systems show the same narrowing of the forward and backward branches.

Overall, the magnitude of the dCPV signal upon anion adsorption compared to the Au oxidation is only slightly smaller, which is interesting, as, due to the size of the HSO_4^- and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ -ions, the coverage is much lower than that of the gold oxide layer. One explanation might be that one sulfate ion covers multiple active sites at once and induces a change in water structure on the NP surface due to its adsorption [104].

Figure 5.7(b) shows a zoom into the anion adsorption/desorption and Au oxidation/reduction regions of Figure 5.7(a). The adsorption of the phosphate ions is clearly shifted with respect to that of the sulfate ions. A comparison with the CVs in Figure 5.7(c) shows that the resonance shift during HSO_4^- ad-/desorption closely follows the corresponding peaks in the CVs. However, the overall picture is more complicated. Observe that the increase in the current in region IV due to the start of the Au oxidation corresponds to a clear decrease of the dCPV signal. Yet, the Au oxidation by itself is expected to increase the dCPV signal. An explanation for the decrease in region IV might be the concurrent and rather sharp desorption of the phosphate/sulfate ions with the onset of Au oxidation as shown by Zhumaev et al. [105], which cannot be seen in Figure 5.7(c). Anion desorption is expected to shift the dCPV signal to lower values as it reverses the adsorption that led to an increase of the signal. Additionally, this shift is expected to be rather strong, as the desorption is quenched to a comparatively small potential range, in which the accumulated increase of the signal due to adsorption (regions II and III) has to be reversed. Overall, the dCPV signal in region IV is decreasing and thereby indicating that the proposed anion desorption overshadows the Au oxidation. This is visible in both electrolytes. The Au oxide reduction leads to a renewed concurrent adsorption of sulfate/phosphate ions, which is overshadowed by the gold reduction peak in the dCPVs.

Thus, the dCPV method can resolve the competitive adsorption of oxygen/hydroxide, here referred to as Au oxidation, and HSO_4^- and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ions on the Au NP array.

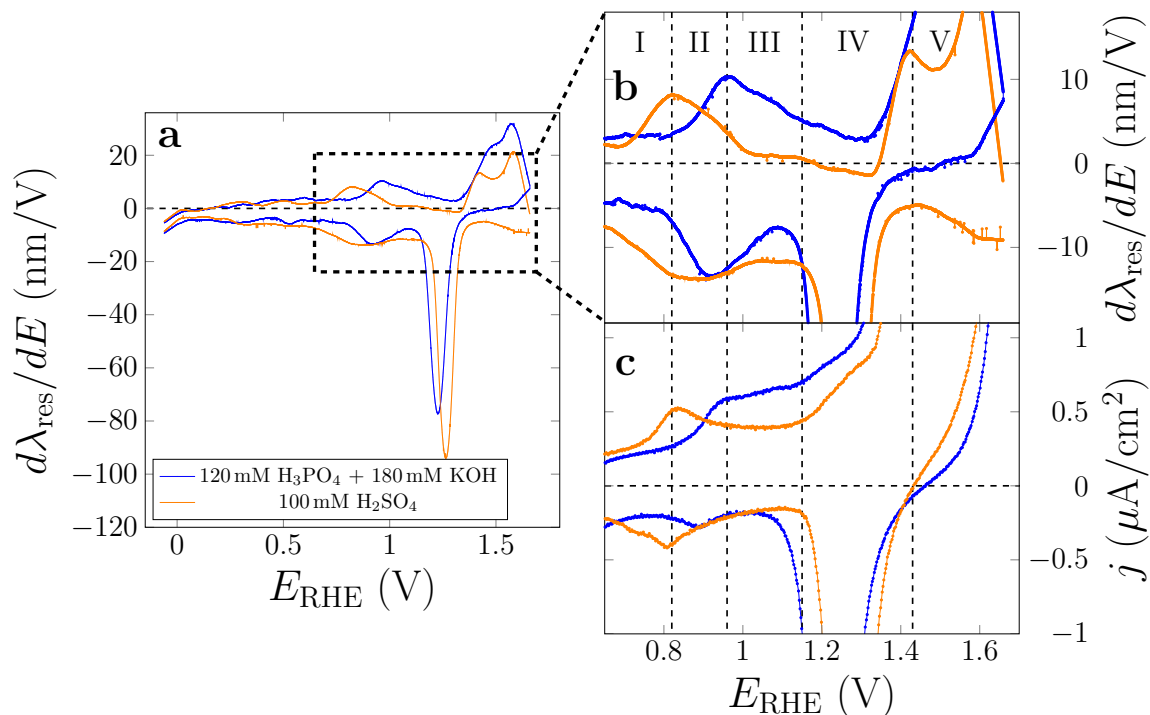


Figure 5.7.: Full dCPV (a), a zoom into the anodic region (b) and the anodic region of a CV (c) of a Au NP array in different electrolytes (Ar purged). Applied scan rate was 2.5 mV s^{-1} . Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

5.3.3. Copper UPD and OPD on Au

In Figure 5.8 (a)-(c), the dCPV, the differential plasmonic width voltammogram, and the corresponding CV of Cu underpotential deposition (UPD)/stripping and sulfate adsorption/desorption are shown. Cu UPD on gold surfaces in sulfate containing electrolytes generally undergoes three stages, visible as three peaks in the CV (c.f. Figure 5.8(c)): random adsorption of Cu ions (P), a sulfate-induced hexagonal ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ overstructure (S) and a full monolayer coverage (1x1) (M) [106, 107, 108, 109, 110]. The underpotential stripping exhibits the respective counter processes M^{I} , S^{I} and P^{I} .

On plain monocrystalline (111) Au surfaces, peaks $\text{S}/\text{S}^{\text{I}}$ and $\text{M}/\text{M}^{\text{I}}$ are pronounced while $\text{P}/\text{P}^{\text{I}}$ is nearly completely suppressed. In contrast, on polycrystalline Au surfaces the peak-pair $\text{P}/\text{P}^{\text{I}}$ is the dominating one [106]. As all three peak pairs are visible in the CV of our nanostructured Au electrodes (c.f. Figure 5.8(c)), we can assume that the surface of the NP arrays has a polycrystalline character with a large fraction of Au (111) grains.

Starting from the orange circle in the cathodic direction, the dCPV (Figure 5.8(a)) exhibits a broad minimum, which corresponds to sulfate desorption. With the onset of the Cu UPD, the dCPV signal increases and exhibits a maximum around the start of region III. The backscan, starting at the cathodic side of the blue curve, exhibits a minimum during the Cu stripping (region V), before the signal increases again and undergoes another maximum, which corresponds to the sulfate adsorption. We conclude that the Cu UPD and stripping behave similarly to adsorption and desorption of anions, as both UPD and adsorption exhibit maxima and Cu stripping/anion desorption exhibit minima.

This finding stands in full agreement with the findings shown above. However, if one takes

5. differential Cyclic Plasto-Voltammetry

a closer look at the features in dCPV and differential plasmonic width voltammogram, a more detailed picture of Cu UPD emerges.

Starting in cathodic direction at the beginning of region I, the deposition current decreases down to a minimum (P) and the dCPV increases up to a small plateau. At the interface, both Cu and sulfate ions adsorb randomly on the gold surface, which both leads to an increase in λ_{res} and W ($FWHM$), due to an increasing number of isolated Au-adsorbate interactions inducing CID. The plateau coinciding with peak P means that the impact of randomly adsorbed ions has reached its maximum, and any further ions do not change the electronic interface states as much.

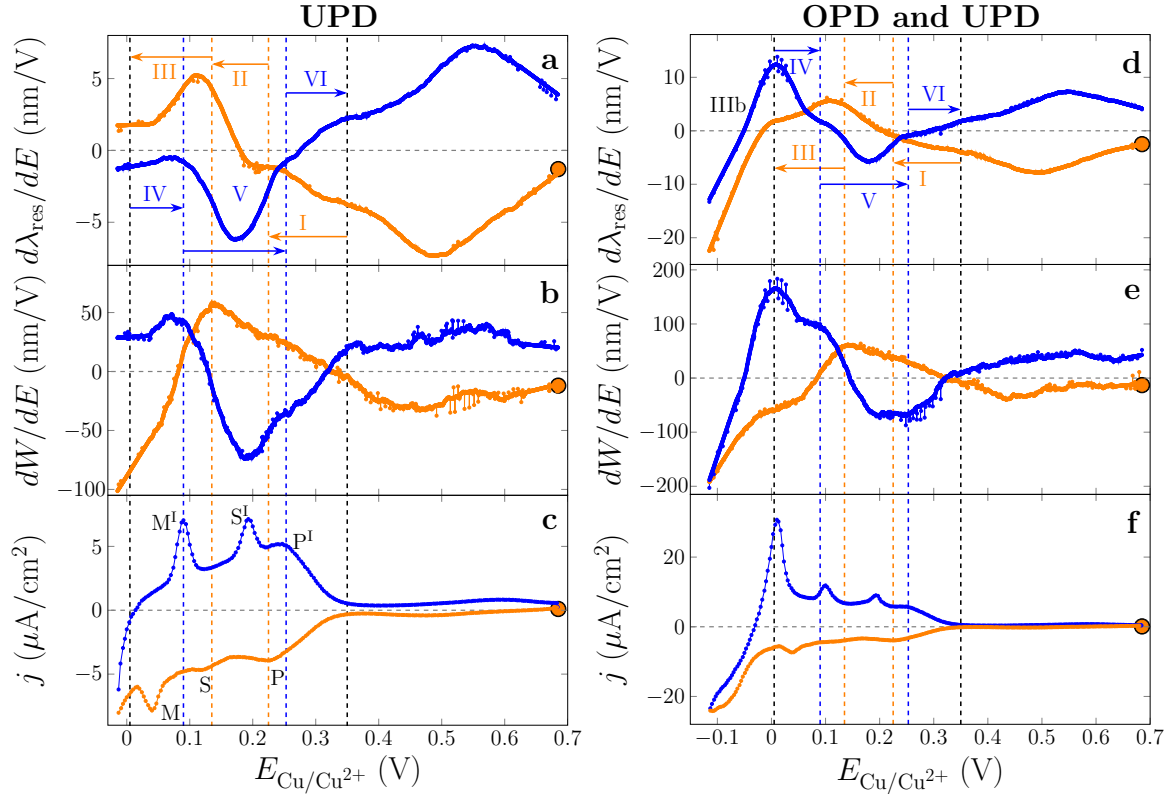


Figure 5.8.: (a) dCPV, (b) differential plasmonic width voltammogram and the corresponding CV (c) for Cu underpotential deposition (UPD) and dCPV (d), differential plasmonic width voltammogram (e) and CV (f) for Cu overpotential deposition (OPD) on Au NP arrays in 100 mM H_2SO_4 + 0.1 mM Cu_2SO_4 (Ar purged). The scans start at the orange circle toward more cathodic potentials. Forward scans are depicted orange and backward scans are colored blue, while specific regions (I-VI) of the UPD are marked with dashed lines in the color of the branch that they belong to. The positions of the dashed lines are the same in both plots (a)-(c) and (d)-(f). Cu UPD current peaks are labeled with P, S, M and their corresponding stripping peaks are labeled with P^1 , S^1 , M^1 accordingly. The scan rate was set to 2.5 mV s^{-1} . Reprinted with permission from [64]. Copyright 2025 American Chemical Society.

In both region II and region III, the transition from random adsorption to a sulfate-induced $(\sqrt{3} \times \sqrt{3})R30^\circ$ Cu layer decreases the current to peak (S) and increases the width W to a maximum between regions II and III, before steeply decreasing in region III. Following the CID dependence on the availability of local energy levels, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ covered surface is

most likely the configuration with most of these, as the Cu is more or less evenly distributed on the gold surface but does not exhibit a clear metal-metal interface, as a monolayer does. Additionally, in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ configuration, the presence of co-adsorbed sulfate ions could impact the width as well. Further deposition of Cu in region III is known to fill the gaps in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ coverage ultimately leading to a full (1x1) monolayer. One reason for the stark decrease of the plasmonic width upon the monolayer completion might be the establishment of an atomically uniform interface which is expected to act less as a multitude of single adsorption bands than as a clear metal-metal interface. This in turn should then have a smaller CID-effect, thus leading to a sharper plasmonic resonance, i.e., smaller W . Another reason might be the weakened impact of the adsorbed sulfate-ions, which are expected to impact the plasmonic resonance less through a full Cu monolayer, in turn leading to a quasi-desorption feature in the dCPV, i.e., a decrease in width and resonance position. In region III, the current peaks once more (M), marking the completion of the monolayer and the UPD transitions to the OPD at the cathodic border (black dashed line) of this region.

The dCPV in regions II and III is seemingly not impacted by the change in surface configuration, as it exhibits an adsorption peak as seen for sulfate in the sections above. Consequently, the resonance position λ_{res} depends more on the overall change in (electro-) chemical surroundings, similar to an effective medium sensor.

The backscan begins with the stripping peak M^I , at which the Cu coverage transitions back to the sulfate induced $(\sqrt{3}\times\sqrt{3})R30^\circ$ Cu layer, which itself transitions to random adsorption at S^I . Apart from the CV, the Cu underpotential stripping also exhibits the inverted features of the UPD for both dCPV and differential plasmonic width voltammogram. While the UPD goes along with a maximum of λ_{res} in regions II and III, the stripping exhibits a minimum in the corresponding region V. Peak S^I coincides with a peak in the width W and peak P^I coincides with a plateau of the latter, just as for peaks S and P, respectively. The overall potential shift between each corresponding peak-pairs is due to the slower kinetics of the deposition compared to the stripping of Cu on Au.

Figure 5.8(d)-(f) shows the CV, dCPV and differential plasmonic width voltammogram of a measurement that included both Cu UPD and OPD. All of the regions and markings are the same as in Figure 5.8(a) and the region IIIb shows the Cu OPD. Here, the deposition current decreases sharply and remains negative on the backscan up to -0.05 V. At the border between regions IIIb and IV, the Cu-bulk stripping manifests itself in a sharp current maximum while both dCPV and differential plasmonic width voltammogram decrease with the Cu-bulk deposition and increase during Cu-bulk stripping. Interestingly, the dCPV signal shows the opposite behavior for Cu UPD and OPD, i.e., a positive signal for UPD corresponds to a negative signal for the OPD and vice versa. This suggests that the monolayer deposited during UPD changes the interface states similarly to the adsorption of anions via CID while the OPD increases the bulk part of the deposited copper, which can be regarded as a change in dielectric environment, rather than a process that is directly impacting the NP/electrolyte interface. As stated above, the sign of the CID in the dCPV is independent of the charge of the adsorbate in question.

5.4. Model Features of Plasmonic Sensing

Differential Cyclic Plasmovoltammetry on well-defined nanoarrays serves as a useful platform for investigating processes on the electrified NP/electrolyte interface, providing information beyond that provided by cyclic voltammetry. The capacitive charging of the NPs, the ad-

5. differential Cyclic Plasm-Voltammetry

/desorption of anions, and gold oxidation/reduction can be clearly detected, and all their dCPV signals are of the same order of magnitude, which enabled the observation of competitive adsorption of sulfate/phosphate ions and gold oxidation. In addition, the sensitivity of this technique to surface effects has been demonstrated by the clear distinction between Cu UPD and OPD on Au and between different deposition steps during UPD. The quality and cleanliness of the interface from stabilizing (linker) molecules is of great importance in this context to ensure clear visibility of and differentiation between the various contributions.

Finally, as Faradaic reactions do not contribute to a change of the dCPV signal, dCPV provides a means to probe adsorption and morphology changes covered in the CV by high current densities. In the following chapter, this will be employed to discover new insights into the Au/aqueous electrolyte interface. Before this, it seems instructive to summarize the basic features of dCPV and CPV, namely double layer charging, ad-/and desorption of cat- and anions, and irreversibilities.

Charging

Increasing/decreasing the electron density inside the NPs will blue/red-shift the resonance position. Figure 5.9(a),(b) shows a model dCPV and CPV of the charging effect. In the dCPV, the pure charging effect consists of two parallel branches, which is very similar to the CV. The lower branch (orange) symbolizes the cathodic scan, which increases the electron density on the NPs and decreases the resonance position (i.e., blue-shift). The anodic branch (blue) means a reduction of electron density and a red-shift. In general, a dCPV is the differentiated CPV, hence a CPV can be obtained by integrating a dCPV. This is usually not necessary, as the CPV is calculated first from the measurements, but it is deemed instructive for this section, as only dCPVs have been discussed in this chapter so far. The CPV, therefore, consists of two sloped lines, which are exactly parallel and start and end at the same value.

Irreversibilities

Independent of the origin, irreversibilities occur as asymmetries with respect to 0 in the dCPV, as for a totally reversible dCPV, any blue-shift is compensated by a red-shift. While those shifts do not need to occur at the same potential, they must occur within the same cycle for reversible systems. In Figure 5.9(c), the irreversibility is visible as a down-bending of both charging branches for $E < -0.5$. Similarly, in the CPV (Figure 5.9(d)), the irreversibility is visible as a shift between the starting- and end points of the cycle.

Ad- and Desorption

Adsorption of chemical species red-shifts the resonance position as the newly formed bonds at the nanoparticle surface introduce CID. Desorption reverses this shift back to the original position if no irreversibilities are present. In Figure 5.10, adsorption of anions (a),(b), and cations (c),(d) is shown in superposition with a charging effect. The relative positions of the ad- and desorption features in the dCPV and the occurrence of a hysteresis in the CPV depend of the ratio between ad-/desorption kinetics and scan rate. If the latter is very fast and the scan rate slow, there would be no hysteresis in the CPV, and the ad-/desorption features in the dCPV would be at the exact same potential.

Anion adsorption in the form shown here and investigated in this thesis occurs at anodic scans (orange) and desorptions at slightly more negative potentials during cathodic scans (blue). For cations, the situation is inverted, with adsorption on the cathodic branch and

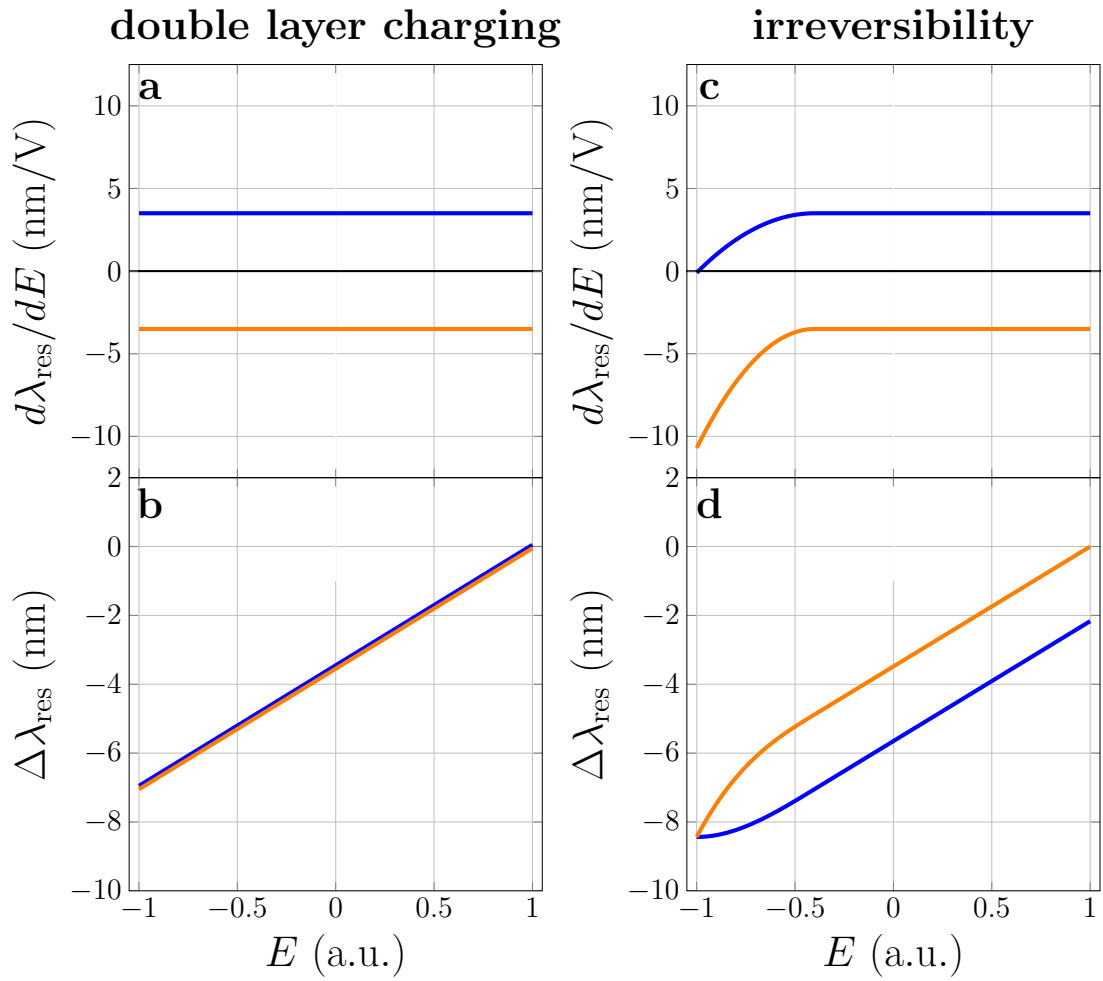


Figure 5.9.: Schematic dCPVs (a), (c) and CPVs (b), (d) for charging effects (a), (b) and the occurrence of irreversibilities (c), (d).

5. differential Cyclic Plasco-Voltammetry

desorption at slightly more positive potentials during the anodic scan. The shape of the adsorption feature in the dCPV and CPV depends, of course, on the exact reaction occurring at these potentials and can range from near-gaussian shapes (cf. Figure 5.7(b)) to very complex multistep processes (cf. Figure 5.8).

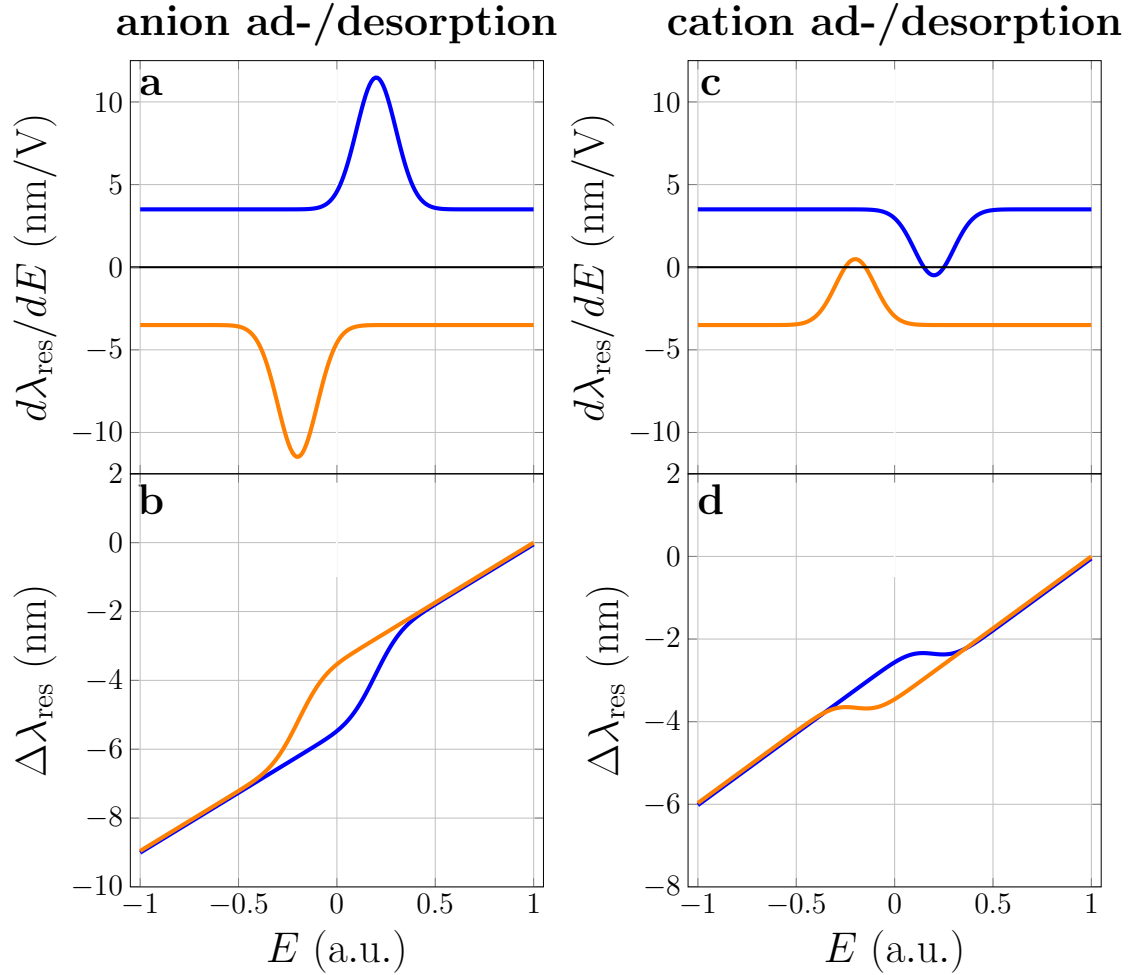


Figure 5.10.: Schematic dCPVs (a), (c) and CPVs (b), (d) for anion adsorption (a), (b) and cation adsorption (c), (d).

6. Stability of the Au/Electrolyte Interface

In the previous chapter, there have been multiple indications of irreversibilities during electrochemical treatments in the form of down bending of dCPVs (cf. Figures 5.6 and 5.7) and continuous blue-shifts of consecutive CPVs (cf. Figure 5.1(a) and (b)). In this chapter, an in-depth analysis of the underlying effects, namely morphological changes and the interaction of gold and hydrogen, will be conducted. This chapter closely follows the paper “Stability of the Au / electrolyte interface during hydrogen evolution: A Cyclic Plasmo-Voltammetry study” by M.J. Feil et al. [62].

6.1. Introduction

A central quantity for the stability of an electrified metal surface is the mobility of the surface atoms, i.e., the tendency of surface atoms to change their position on the lattice. Dona et al. investigated the mobility of Au adatoms in contact with an electrolytic solution [111, 112]. They showed that the mobility depends on the applied potential, with a higher mobility for potentials positive of the potential of zero charge (PZC). This was related to the stronger interaction between Au surface atoms and water molecules for more anodic potentials, which in turn weakens the Au/Au interaction strength, thus increasing ad-atom mobility [111, 112]. Moreover, electrochemical annealing studies showed that type and concentration of ions in solution, e.g., Cl^- , significantly affect the mobility of Au [113], which was attributed to the stronger anion/Au interaction compared to the water/Au interaction.

These observations hold as long as the Au surface is not oxidized. When investigating the stability at higher potentials, inductive plasma coupled mass spectroscopy [114] and rotating ring disk electrode experiments [115] revealed that reduction of the Au oxide is accompanied by Au dissolution and thus a degradation of the surface. Again, the dissolution is faster in more acidic electrolyte and in the presence of strongly interacting anions [116]. Au dissolution during Au oxide reduction was attributed to the exposure and subsequent dissolution of Au^{3+} ions [114].

Another degradation process of Au electrodes is cathodic corrosion [117, 118, 119]. Cathodic corrosion is an etching process that occurs at highly negative surface charges and in strongly alkaline solutions. It causes significant structural changes to the electrode and leads to the formation of metal nanoparticles in solution. It is assumed that the dissolution process is accompanied by the formation of ternary metal hydrides [118]. In contrast, Au/electrolyte interfaces are considered quite stable at weak cathodic potentials near the onset of hydrogen evolution, especially in neutral or acidic electrolytes, but degradation studies under such conditions are rare. Also, only a few experimental investigations on the adsorption of hydrogen on Au exist, mainly due to a lack of experimental in situ methods that can probe submonolayer coverages of hydrogen. Most of what is known on the interaction between hydrogen and Au comes from ultra-high vacuum experiments [120, 121, 122, 123, 124, 125, 126, 127].

In this chapter, we investigate the stability of the Au/electrolyte interface close to the onset of hydrogen evolution under mild electrochemical conditions, as typically used in fundamental studies on hydrogen evolution reaction (HER) kinetics, with Cyclic Plasmo-Voltammetry (CPV) and differential CPV (dCPV). Compared to the previous chapter, the potential range

6. Stability of the Au/Electrolyte Interface

is extended to the HER region, and morphological changes and degradation is monitored in long-time studies. The interpretation of the morphological changes from the CPV data is supported by AFM measurements and simulations. We will demonstrate that morphological changes occur much faster in the HER region than during Au surface oxidation/reduction and are more pronounced in acidic electrolytes than in neutral electrolytes.

6.2. Stability Measurements of the NP Array under Various Conditions

6.2.1. Stability in the Double Layer Regime

We start our investigations in the double layer region of Au, which is well characterized in the literature. Figure 6.1 shows in plate (a) CPVs of the nanostructured Au WEs in an acidic electrolyte (red to orange lines) and a neutral electrolyte (dark to light blue lines) and in plate (b) the corresponding CVs. This type of representation is chosen because absolute changes in λ_{res} are better visualized compared to dCPV. Clearly, in both electrolytes λ_{res} decreases during the cathodic scan and increases during the anodic scan. These changes reflect the change in electron density of the Au nanostructures with potential. As mentioned above, the higher the electron density, the more blue-shifted the plasmonic resonance. In addition, an extended hysteresis in the neutral system is observed, which deviates from the progression of Figure 5.10(b) in the sense, that cathodic and anodic branches do not fall together at all. This is not expected for a single ad-/desorption peak-pair. To better understand the adsorption processes, a dCPV of the neutral CPV is shown in Figure 6.2. The dCPV clearly shows two peak pairs, corresponding to the ad- and desorption of H_2PO_4^- and of HPO_4^{2-} , which is known in the literature for phosphate anions in neutral pH [128]. As seen from Figure 5.10(b), anion adsorption, where ad- and desorption do not occur on the same potential, creates an extended hysteresis. An additional pair of adsorbing ionic species (H_2PO_4^-) at more cathodic potentials would extend the hysteresis of the other ionic species (HPO_4^{2-}) and thus resulting in the hysteresis observed in the neutral system of Figure 6.1(a).

In sulfuric acid electrolyte (pH1), such a second hysteresis is not expected, as there is one anion dominating (HSO_4^-). On top of this, there is a more important difference between these measurements: For the neutral electrolyte, the resonance position ends at the same value at which it started, while in the acidic electrolyte, a drop in the resonance wavelength of 2 nm occurs at the end of the potential cycle. This indicates an irreversible change of the Au/acidic electrolyte interface, which is superimposed to the reversible change in electron density.

6.2.2. Stability during the Au Oxidation/Reduction Reaction

The differences in the optical response of the Au electrode in neutral and acidic electrolytes become even more pronounced when cycling the potential in the Au oxidation/reduction region. As can be seen in Figure 6.1(c), λ_{res} increases strongly during the anodic scan, which parallels the formation of Au oxide, as confirmed by comparison with the CVs in Figure 6.1(d). After the reversal of the potential scan, λ_{res} stays approximately constant until Au oxide reduction sets in, which causes a steep decrease of λ_{res} (light blue and orange lines). However, while in the neutral electrolyte, λ_{res} of the cathodic scan traces the curve in the double layer region of the anodic scan before the oxidation, it drops considerably further in the acidic electrolyte and declines faster in the subsequent double layer region than without the oxidation/reduction cycle, up to a total drop of 6 nm. Most of this change can be related to Au dissolution and increased mobility of Au surface atoms, as will be discussed below.

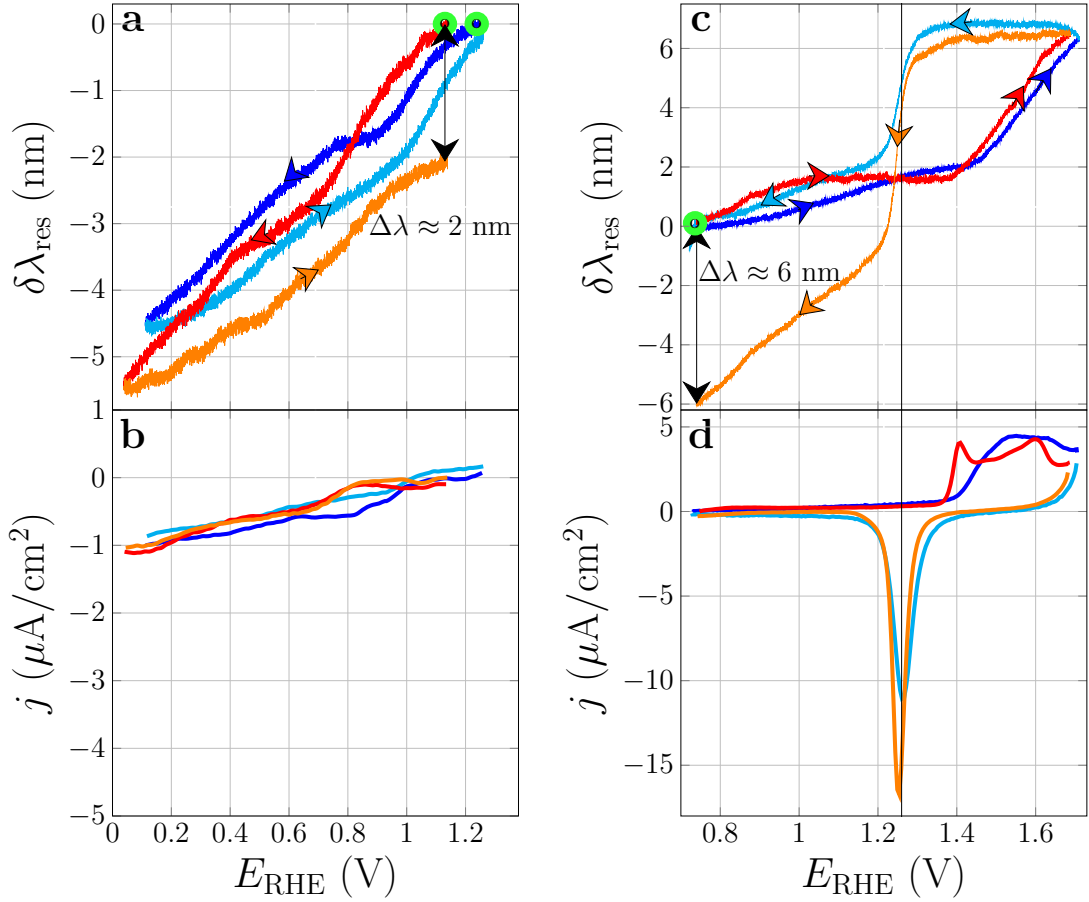


Figure 6.1.: Cyclic Plasmo-Voltammetry (a and c) and corresponding CV scans (b and d) of Au NP arrays in Ar saturated pH1 100 mM H_2SO_4 (red, orange) and Ar saturated pH7 120 mM $\text{H}_3\text{PO}_4 + 180$ mM KOH (blue, cyan) at scan speed $\nu = 2.5 \text{ mV s}^{-1}$. (a) and (b) show the double layer region, (c) and (d) show the Au oxidation/reduction region. (b) and (d) show the corresponding CVs to the CPV shown in (a) and (b), respectively. For the $\delta\lambda_{\text{res}}$ -axis, $\delta\lambda_{\text{res}}$ at the starting point (green circle) was used as a reference (i.e., has been set to 0).

6.2.3. Stability in the Hydrogen Adsorption Region

Having found irreversible changes in the anodic potential region for acidic electrolytes, we now extend the potential region slightly more cathodic in the neutral environment to get a first idea of changes of the Au/electrolyte interface during the HER for different cations in solution. Figures 6.3(a) and (b) show dCPVs and CVs of several measurements of the same Au nanodisk array in different neutral electrolytes. The experimental setup was kept identical for all measurements and there were no other hydrogen evolving measurements in between those depicted here. For all potential cycles, the Au oxidation/reduction reaction (region I), as well as sulfate adsorption (region II) and double layer charging/discharging (region III), lead to the same overall progression independent of the cation species. Note that all 4 cycles performed are shown for every measurement. The symmetrical progression of the cathodic and anodic branches around zero in regions II and III reflects that λ_{res} shifts are reversible, and thus, the samples are stable in these potential regions.

6. Stability of the Au/Electrolyte Interface

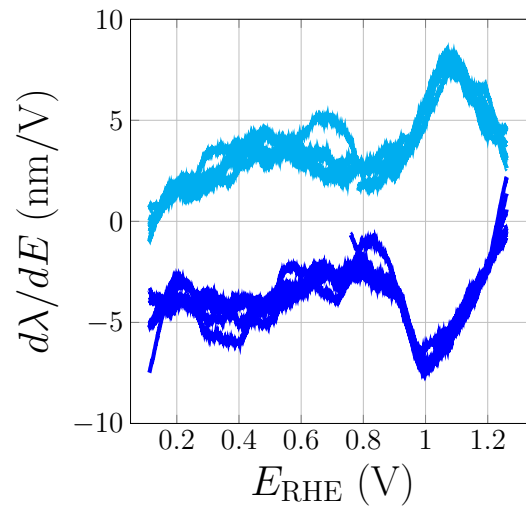


Figure 6.2.: dCPV of the double layer measurement (neutral system) shown in Figure 6.1(a).

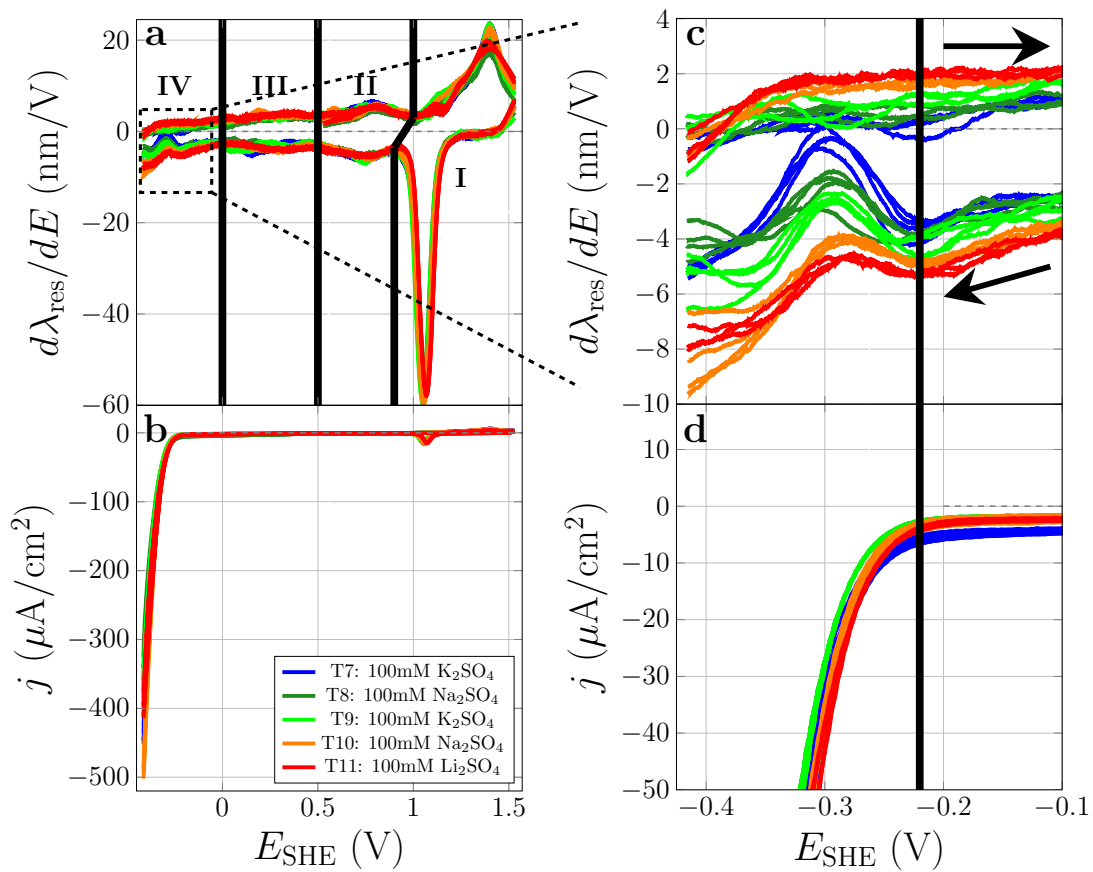


Figure 6.3.: (a), (c) dCPVs and (b), (d) CVs of Au NP arrays in Ar saturated 100 mM M_2SO_4 , with $M = K, Na, Li$ (cf. inset in b) at scan speed $\nu = 2.5 \text{ mV s}^{-1}$. (c) and (d) represent a zoom into the region indicated in (a). These measurements were part of treatments T8-T11 (c.f. Figure 6.5).

6.2. Stability Measurements of the NP Array under Various Conditions

Figures 6.3(c) and (d) represent a zoom into the potential region (IV). It can be seen that a maximum occurs in the cathodic branch of the dCPV signal, where HER currents are already considerable. The onset of the peak around $E_{\text{SHE}} \approx -220 \text{ mV}$ coincides with a discernable HER current. We associate this peak with hydrogen adsorption onto the Au surface, as adsorption processes manifest themselves in a redshift of $\delta\lambda_{\text{res}}$, and thus in an upward peak in a dCPV, as, e.g., also reported for sulfate adsorption [64]. In contrast to the sulfate adsorption, there is no desorption peak visible with the exception of the first anodic branch of the dark blue scan where the dCPV shows a shallow minimum at $E_{\text{SHE}} \approx -220 \text{ mV}$. This observation will be discussed in more detail further below. Within one measurement, the maxima of the dCPV curves are similarly high, but decrease from measurement to measurement, parallel to an increasing downward bending of the cathodic branch to more negative dCPV values, which is accompanied by a steeper change on the anodic branch, showing at least partial reversibility. However, the average value of both branches is shifted significantly to negative values in all measurements, indicating an overall irreversible change of the Au/electrolyte interface induced by the HER. Note that these measurements were conducted on the same sample, but they represent only a part of the full treatments done, as will be highlighted below (cf. Figure 6.5). In contrast to the neutral measurement shown in Figure 6.1, these electrolytes were not buffered to prevent multiple adsorption processes.

6.2.4. Stability in the HER Regime

Having seen hydrogen adsorption and slight irreversible changes close to the onset of the HER, we extend our study once again to more negative potential values and now compare again the behavior in acidic and buffered neutral electrolytes. As can be seen in Figure 6.4(a), the CPVs are approximately on top of each other at the beginning of the measurements in the double layer region at 1.2 V vs. RHE and show an almost constant decrease until approximately 0 V vs. RHE, which reflects the increasing charge density, as also observed in the measurements described above (cf. Figure 6.1). With the onset of the hydrogen evolution, the CPV curves become significantly different. In the neutral electrolyte, the decrease of λ_{res} is weakened and remains essentially constant for an extended amount of time after reversal of the scan direction. It is only after $\Delta t \approx 200 \text{ s}$ that the expected increase of λ_{res} due to anodic charging sets in, thus the overall λ_{res} is reduced by 2 nm during one full cycle. Note that the HER current density of this measurement, as shown in Figure 6.4(b), exceeds the HER current density in Figure 6.3 threefold. In the acidic system, λ_{res} decreases significantly faster with the HER onset, and this trend continues even after the turnaround of the potential sweep direction. Only when the acidic system stops evolving hydrogen, so does the rapid decrease of λ_{res} , which reverts instantly to the double layer behavior with an increase of λ_{res} with approximately the same magnitude of the slope as observed during the cathodic scan in this potential region. Overall λ_{res} drops $\approx 8.6 \text{ nm}$ during one full cycle, 7 nm of which is lost in the HER region. The CPVs indicate that the Au structures undergo morphological changes and degradation in the HER region, however, of strongly differing impact in neutral and acidic electrolytes. The possible origin of these differences will be discussed below.

6.2.5. Long Term Stability

So far, we have seen multiple indications of anodic and cathodic degradation of the Au electrode arrays under various conditions, but each time only for a few consecutive cycles. In order to understand the impact of degradation on the interfacial properties over longer periods of time, we show in Figure 6.5 how λ_{res} changes with time over a large number of measurements done with one particular Au nanostructure array. We refer to the different measurements with

6. Stability of the Au/Electrolyte Interface

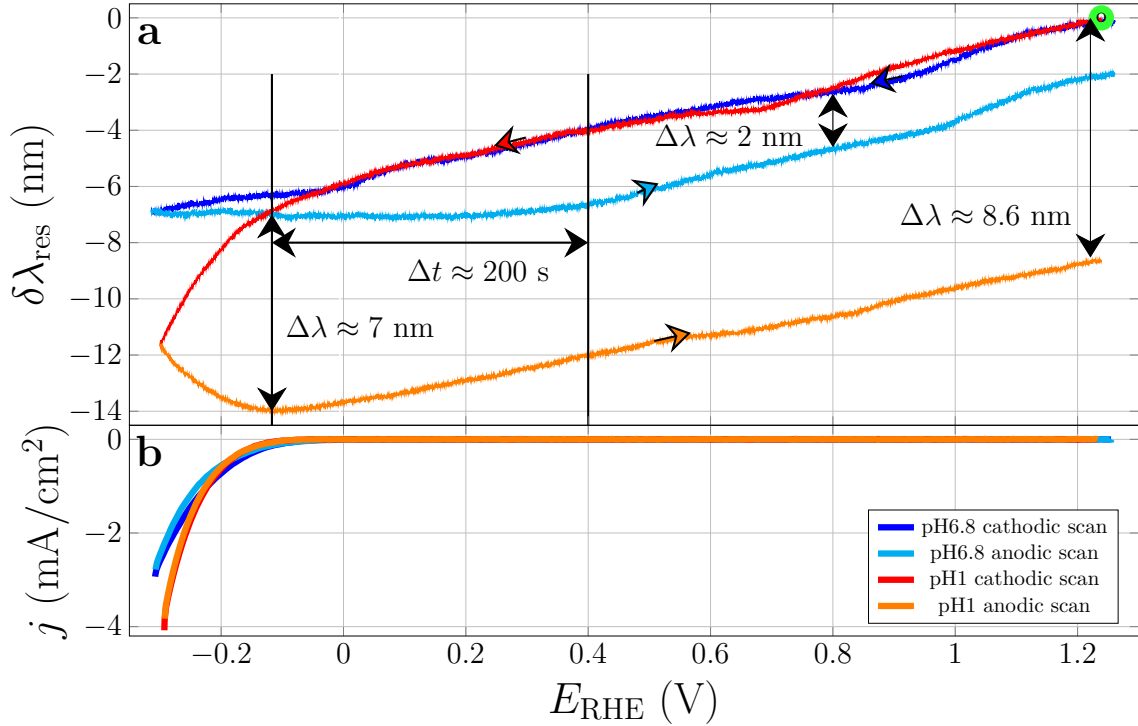


Figure 6.4.: Cyclic Plasmo-Voltammetry (CPV) (a) and CV scans (b) of Au NP arrays in Ar saturated 100 mM H_2SO_4 (red, orange) and Ar saturated 120 mM H_3PO_4 +180 mM KOH (blue, cyan) in the double layer and the hydrogen evolution region. Scan speed $\nu = 2.5 \text{ mV s}^{-1}$. For the $\delta\lambda_{\text{res}}$ -axis, $\delta\lambda_{\text{res}}$ at the starting point (green circle) was used as a reference (i.e., has been set to 0).

the same Au array electrode as treatments T. Between two treatments were at least 12 h, and the system was thoroughly cleaned between treatments as described in the section 3.3. Note that in Figure 6.5, the idle times without measurements were subtracted, so the measurements appear as if they were taken continuously. Within individual treatments, several voltage cycles of different ranges and scan speeds were applied, and electrochemical impedance spectroscopy measurements were carried out. The specific electrochemical procedures for every treatment T1-T11 are detailed in section A.2.1 of the appendix, with the treatments during which the CV was extended into the HER region being highlighted in light blue. AFM data of the Au nanodisks recorded ex-situ in between measurement days are depicted as insets with an arrow pointing to their respective position in the measurement progression. A more detailed view of the AFM images in Figure 6.5 is shown in section A.2.2 of the appendix.

Starting from approximately 800 nm, the plasmonic resonance wavelength decreased over the course of the different treatments until it reached 630 nm after ≈ 61 h of measurements. This resonance wavelength represents the lower limit that allows the asymmetric Breit-Wigner function to be fitted to the data with sufficient accuracy (cf. section 4.3.2). It can be clearly seen that the largest shift of λ_{res} occurs during T1, and the changes of T2-T5 become continuously smaller. Comparing the 2D representation of the AFM pictures taken after T1 and T4, a clear change in morphology can be observed. While in the AFM image obtained after T1, asymmetric features and a ring structure can be seen, the structures in the image measured after T4 seem to be much more homogeneous and symmetric. In addition, the diameter of

the nanodisks seems to have decreased.

During T6, which includes the first CV extending into the HER region, an enhanced decrease of λ_{res} is visible. The greater decrease persists in all subsequent treatments T7-11, where the potential was also scanned into the hydrogen evolution region. Comparing the AFM picture taken after T11 with the one taken after T4, a clear trend towards even smaller and more homogeneous structures is apparent.

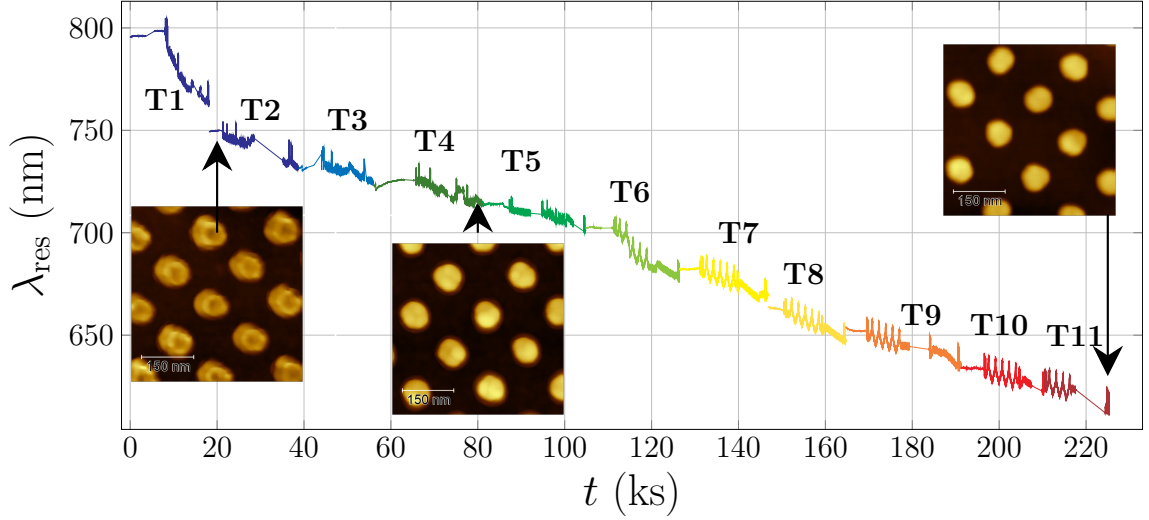


Figure 6.5.: $\lambda_{\text{res}} - t$ progression of all electrochemical measurements on one sample. Each individual measurement day is labeled with T1-11, during which multiple cyclic voltammograms and impedance spectra were conducted. All individual days were shifted in time to appear, as if they had been recorded directly after one another, and while the order of labeling is chronological, there were different time skips in between the individual days, which have been omitted for readability reasons. Pretreated AFM data sets of the sample are shown with indications of when they have been recorded. The electrolytes were 100 mM K_2SO_4 , for T1, T4, T7, T9; 100 mM Na_2SO_4 for T2, T6, T8, T10; 100 mM Li_2SO_4 for T3, T11; 100 mM Cs_2SO_4 for T5.

6.2.6. (d)CPV as a Proxy for Morphology Changes

Evidently, all treatments T1 - T11 show a decrease in λ_{res} , accompanied by some structural changes of the Au nanodisks as observed in the AFM images, indicating a form of irreversible degradation. In general, plasmonic resonances strongly depend on the geometry of the corresponding nanostructures, so a correlation between morphology and λ_{res} is expected. To further relate optical and structural changes, we perform a combined AFM-FDTD simulation study. For this purpose, we extract the average profile of the nanodisks from the AFM images and use this as the base geometry in an FDTD simulation, in which the reflectivity of the nanostructures is calculated numerically.

Figure 6.6(a) shows mean radial profiles obtained by averaging over radial profiles of all nanodisks depicted in the AFM images of Figure 6.5, where r refers to the radius of the profile and h to its height. The standard deviation of the profiles is shown as a halo around the lines. The two bumps of the first profile stem from the crown-like elevations of the production procedure (cf. Figure 3.1) and can be clearly seen to merge for longer measurement times

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while the diameter of the nanodisks becomes smaller and their height increases. Note that the profiles are only measured for $r > 0$ but have been mirrored to give the impression of a cross-section. Such measurements were done for multiple nanoparticle array batches, all showing a similar qualitative behavior (cf. section A.2.3 of the appendix). Using the radial profile, the relative volume change of the particles can be estimated. Although the area of the cross-section of the aged "after T11" particles in Figure 6.6(a) appears to be larger than the "after T1" profile, the volume calculation, in which the height of the profile is scaled with the square of the radius r , yields a continuous decrease over time. It follows that there is Au dissolution alongside the morphological change. It is worth noting that these processes are not induced or altered by the use of illumination during the experiments, as shown in section A.2.4 of the appendix, where the initial and final profiles of two samples subject to identical potential protocols are compared, where one sample was continuously illuminated for the recording of CPVs and the other one kept in the dark. This confirms that (d)CPV is a non-invasive in situ technique.

As AFM images suffer from the broadening of features on the horizontal scale, a specific treatment is necessary to approximate the real radial profile of the nanodisks for the FDTD simulation. The AFM profiles in Figure 6.6 appear to have a radius of up to 60 nm, which is however not the actual radius. The latter was determined to be around 37.5 nm from SEM measurements. To account for this, a rescaling factor is obtained from the first AFM profile (after T1) to scale it to 37.5 nm. The other profiles were scaled with the same factor. Apart from the increase in radius, the AFM measurement cannot resolve the region of contact between Au and SiO₂ well, as it measures a tail, where a clear corner should be. Hence, in a second step, these smooth tails are cut off to ensure a sharp profile. The corrections map the profiles in Figure 6.6(a) to those shown in Figure 6.6(b) which were used in the simulations.

Figure 6.6(c) depicts selected measured reflectance spectra of the sample at different stages of degradation. All of these spectra were taken with respect to the same reference (cf. section 3.4.2) and exhibit an asymmetric Breit-Wigner-type resonance behavior. It can be seen that the spectra continuously shift toward smaller resonance wavelengths while, at the same time also, intensity and FWHM decrease. The difference between the green and the red curves is especially significant due to the number of treatments between these measurements.

Figure 6.6(d) shows simulated spectra using the profiles from Figure 6.6(b). For a comparison of experimental and simulated reflectance spectra, it is important to be aware that there are two major differences between simulations and experiments: First, the way R is calculated in the simulations and the experiments. In the simulation, the reflected intensity is taken with respect to the incoming intensity, i.e., the absorbed/transmitted intensity is taken into account, thus decreasing the overall reflectance well below 100%. For the measurements, the reflectance of the samples are taken with respect to the reflectivity of a reference sample, which accounts for absorbance and transmission effects. Consequently, experimental reflectivity is expected to be around 100%, with the resonance peak above and the resonance tails below this value. Once the sample starts to decrease in diameter, the coverage of the sample and the reference do not match anymore, which results in an overall decrease in intensity. Second, all solid/solid interfaces, namely Au/Ti, Ti/TiO_x, TiO_x/SiO₂, have been assumed to be perfectly smooth in the simulations, but the real interfaces exhibit a certain roughness and any kind of roughness changes the plasmonic resonance position. Yet, all solid/solid interfaces are not in contact with the electrolyte and, hence, not expected to change during the measurements. We therefore conclude that we cannot quantitatively compare simulations and experimental data, but we can draw conclusions from a comparison of the qualitative trends.

From Figures 6.6(c) and (d) it is apparent that the simulated spectra match the overall progression of the experimental ones fairly well, in particular both data sets exhibit a decrease

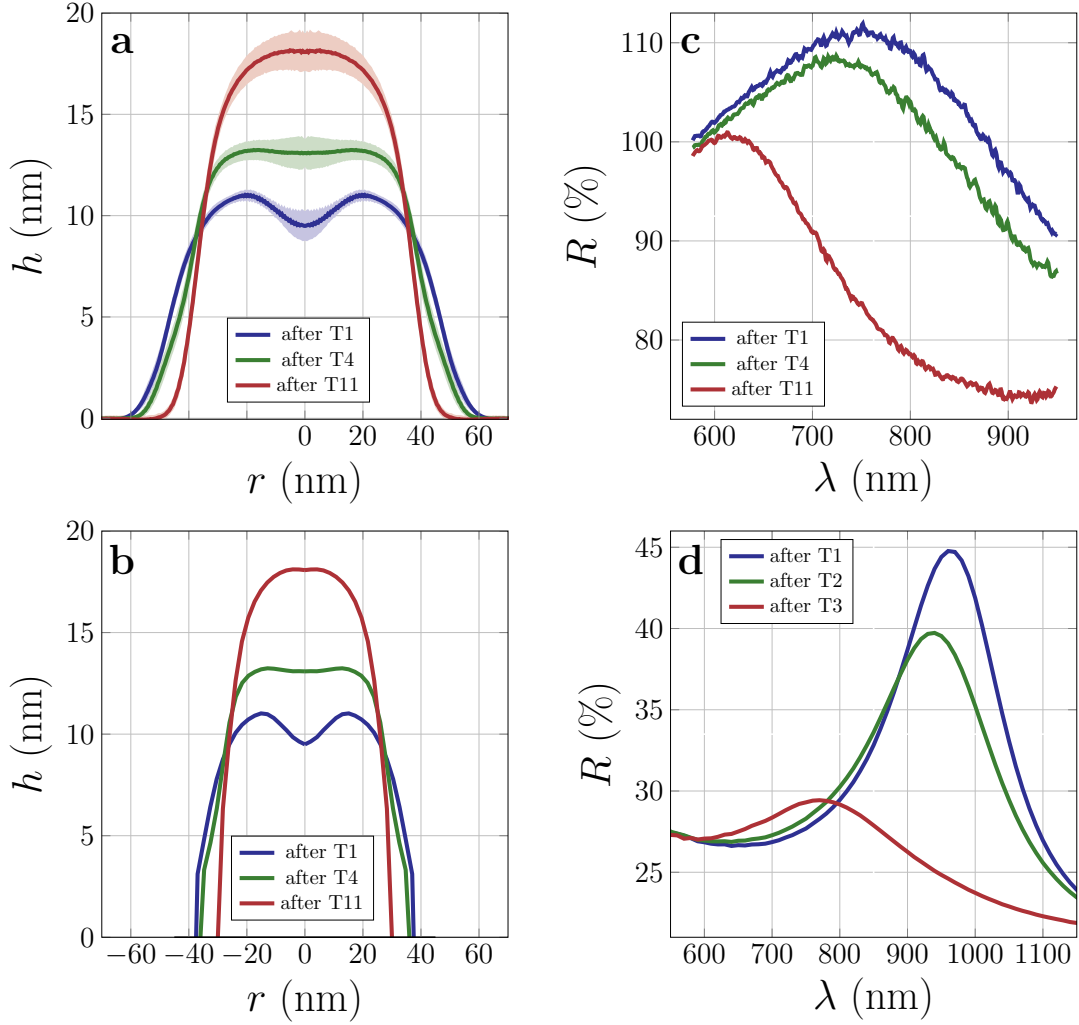


Figure 6.6.: Opto-morphological analysis of a Au NP array. The sample was subjected to CV programs for multiple different electrolytes (Ar saturated 100 mM M_2SO_4 , with $M = K, Na, Li$) on different days (T1-T11 c.f. Figure 6.5). (a) radial AFM profiles of the NPs for different stages of degradation, (b) radial profiles used for FDTD simulation adapted from the AFM measurements, (c) spectroscopic data of different days at open circuit potential, (d) simulated spectra for the particle geometries as shown in (b).

and blueshift of the reflection maxima as the initial two maxima of the crown-like structure merge, and the nanodisks shrink in diameter and increase in height. These trends are seen for all samples (cf. section A.2.3 of the appendix). We thus conclude that we can indeed use the change in plasmonic resonances as an indication of a morphology change of the Au nanodisks.

6.2.7. Degradation of a Pristine Sample

The bumps in Figure 6.6(a) stem from the production process and are expected to (1) contribute strongly to the resonance position of the pristine sample and (2) degrade very easily. A first indication of this can be seen in T1 of Figure 6.5, during which λ_{res} decreases much more rapidly than during any of the other treatments, even though there was no hydrogen

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evolved. Therefore, it is worth investigating the degradation behavior of a pristine sample under HER.

Figures 6.7 (a) and (b) show the dCPVs and CVs of the first three potential cycles reaching into the HER region of an as-produced Au nanostructure array. Previous to this measurement, only a cleaning CV was performed in the potential region where no hydrogen is evolved. Overall, it can be seen that the dCPV signals of all three cycles show only minor deviations compared to each other and are mostly congruent, except for the hydrogen evolution region, where in the first two cycles, negative peaks in the dCPV are observed. A detailed depiction of this region is given in Figure 6.7 (c) and (d). Here, it is apparent that the first cathodic scan (blue) shows a significant blueshift in the resonance position for both the cathodic and anodic scan direction that starts with the onset of the HER and is comparable to the shift observed during Au oxidation/reduction. Both cathodic and anodic scans of the second cycle (orange) show a similar trend but do not drop as far to negative values as the first cycle. The cathodic and the anodic scans of the third cycle barely show any drop at all. Instead, a hydrogen adsorption peak is clearly visible in the cathodic branch, and a corresponding, though weaker, desorption peak in the anodic branch, similar to the behavior depicted in Figure 6.3.

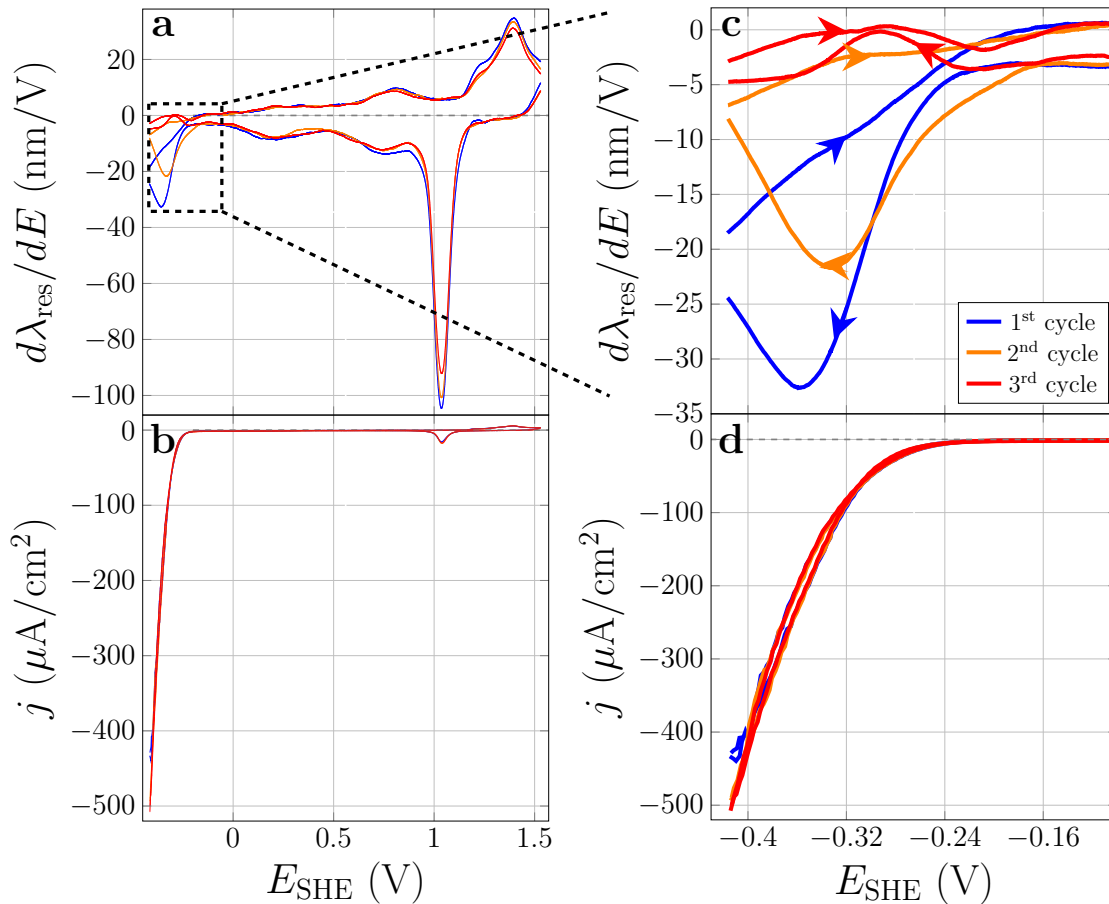


Figure 6.7.: (a), (c) dCPVs and (b), (d) CVs of Au NP-arrays in 100 mM K_2SO_4 at scan speed $\nu = 2.5 \text{ mV s}^{-1}$. (c) and (d) represent a zoom into the marked region of (a). The arrows indicate the scan direction.

6.3. Discussion on the Stability of the Au/Aqueous Electrolyte Interface

To summarize our results, we have shown that irreversible shifts of the plasmonic resonance correlate with morphological changes of the polycrystalline Au nanostructures, which we measured for different potential regions and electrolyte compositions. The results thus give insight into the stability of polycrystalline Au/electrolyte interfaces and the mobility of Au adatoms.

In the following, we discriminate between three potential ranges: (a) the double layer region (ca. 0 V - 1 V vs. RHE), (b) the Au oxidation/reduction region (ca. 1 V to 1.7 V vs. RHE) and (c) the HER potential region (< 0 V vs. RHE). The stability differed drastically in the three potential regions, being highest in the double layer region and lowest in the HER region. Furthermore, in all three potential regions, the Au/electrolyte interface was considerably more stable in neutral than in acidic electrolytes. The mechanisms responsible for the structural changes are likely to be different in the three potential regions and are discussed in turn below.

6.3.1. Mobility of Au Adatoms in the Double Layer Region

In the double layer region, any structural changes occur due to surface mobility of Au atoms [33, 111, 112]. In 1M HClO₄, the surface diffusion coefficient of Au atoms was found to increase exponentially with potentials positive to the point of zero charge (pzc) [111]. The enhanced mobility at more positive potentials is explained by stronger interactions of water molecules and anions with Au surface atoms at a more positive surface charge density. Diffusion of surface atoms might lead, e.g., to a decreased roughness, i.e., 'electrochemical annealing' [111, 112] or to surface reconstruction [33, 129]. For our polycrystalline disk-like nanostructures, we observe changes in their morphology, however, only in acidic, not in neutral electrolyte. Given the dependence of the diffusion coefficient on the surface charge, a likely explanation for the lower mobility in neutral electrolytes is that the double layer region is shifted towards more negative potentials with respect to the pzc. For polycrystalline Au $E_{\text{pzc}} \approx 330 \text{ mV} - 510 \text{ mV}$ vs. SHE [80, 130] so that the overall charge density in the double layer region of the Au/neutral electrolyte interface is less positive than in an acidic electrolyte.

6.3.2. Structural Changes in the Au Oxidation/Reduction Region

In acidic electrolyte, the reduction of a monolayer Au oxide leads to an irreversible change in the resonance frequency that is much larger than the one observed in the double layer region. Thus, the stability of the Au nanostructures is considerably lowered when performing potential sweeps up to the surface oxidation region. This is in line with inductively coupled plasma-mass spectrometry (ICP-MS) studies by Cherevko et al. [114] and rotating ring disk electrode (RRDE) studies by Vesztergom et al. [115] who showed that Au dissolution takes place upon reduction of Au oxide even when the upper potential limit is kept well below the onset of oxygen evolution and Au dissolution. In [114], the authors explain Au dissolution on the cathodic sweep by assuming that the oxidation of Au occurs through concomitant O(H) adsorption and place exchange between adsorbed O(H) species and Au atoms. Furthermore, Au³⁺ ions might form in the surface near Au matrix, which are, however, at anodic potentials protected from dissolution by passivating Au oxide. During the reduction of the Au oxide, the Au³⁺ ions might become exposed to the electrolyte and either lead to readsorption of OH/O by water discharge or to their dissolution into the electrolyte. Furthermore, the relative rates of these two processes depend on pH and are shifted towards readsorption with larger pH

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values. This is again in line with our observation that no structural changes can be detected during Au oxide reduction in neutral electrolyte.

In acidic electrolytes, the decrease of the resonance wavelength extends far beyond the Au oxide reduction region (cf. Figure 6.1(c)), which indicates that during reduction, a large number of under-coordinated, highly mobile Au adatoms are formed that subsequently diffuse on the surface to form more stable configurations. The fact that this enhanced restructuring in the double layer region is not seen after Au oxide reduction in the neutral electrolyte makes it likely that either most of these mobile adatoms stem from redeposition of the dissolved Au^{3+} ions or the additional dissolution of Au that leads to much rougher surfaces. If it stemmed from subsurface oxide switching back to the surface, some irreversible changes should also be visible in the neutral electrolyte.

While in the neutral electrolyte, the Au nanostructures were stable for the duration of one cycle, over a longer timescale of measurements, morphological changes still occurred (cf. Figure 6.5). Only for the case of an open circuit, i.e., no potentials applied, is the morphology preserved, as can be seen in Figure 6.5 in the horizontal lines at the beginning and the end of the treatments, during which no potential was applied, but the sample was already/still in contact with the electrolyte. Additionally, from T1 to T5, the overall change in $\lambda_{\text{res}} - t$ seems to slow down, which could be associated with the particles approaching more stable structures and facets.

6.3.3. Stability of the Au/Electrolyte Interface in the HER Region

Potentials negative of -0.2 V versus RHE induced the strongest structural changes in our Au nanostructures in both acidic and neutral electrolytes, with changes in acidic solutions again being much more pronounced than in neutral ones, as apparent from Figure 6.4. Both measurements started at 1.25 V versus RHE, and the negative slopes of the CPV curves are essentially identical up to -0.1 V versus RHE and stem from the increasing electron density in the nanostructures, the slightly wavy character being related to reversible ad- and desorption of anions. Negative of -0.1 V , the slope of the CPV obtained in the acidic electrolyte strongly increases and keeps on increasing after reversal of the potential. In contrast, the slope measured in the neutral electrolyte decreases and stays approximately constant upon reversal of the potential for about 200 s.

As we will demonstrate below, this behavior is consistent with the following hypotheses: Once the HER starts, hydrogen adsorbs on the surface and as subsurface hydrogen (Step II of Figure 6.8). This assumption is supported by density functional theory (DFT) calculations, which showed that tetrahedrally coordinated subsurface hydrogen in the first two subsurface layers of Au(111) surface are stable [131]. Furthermore, AuH_2^- ions were shown to be stable in DFT calculations, in contrast to the neutral Au dihydrides, and could be experimentally observed in matrix isolation experiments [132]. We, therefore, conjecture that the high negative surface charge density in the HER region is likely to promote partial negative electron transfer leading to $\text{AuH}_2^{\delta-}$ complexes, which are formed from a surface and subsurface hydrogen that are bound or coordinated to the same Au atom. These hydride-like Au surface species are much more weakly bound to the Au bulk than other Au surface atoms and are likely to have a high surface mobility (left side step III of Figure 6.8). They might also split off H_2 . During this process, the distance of the topmost Au atoms to the underlying Au layer becomes still larger, facilitating an enhanced restructuring of the surface (resulting in the left side step IV of Figure 6.8).

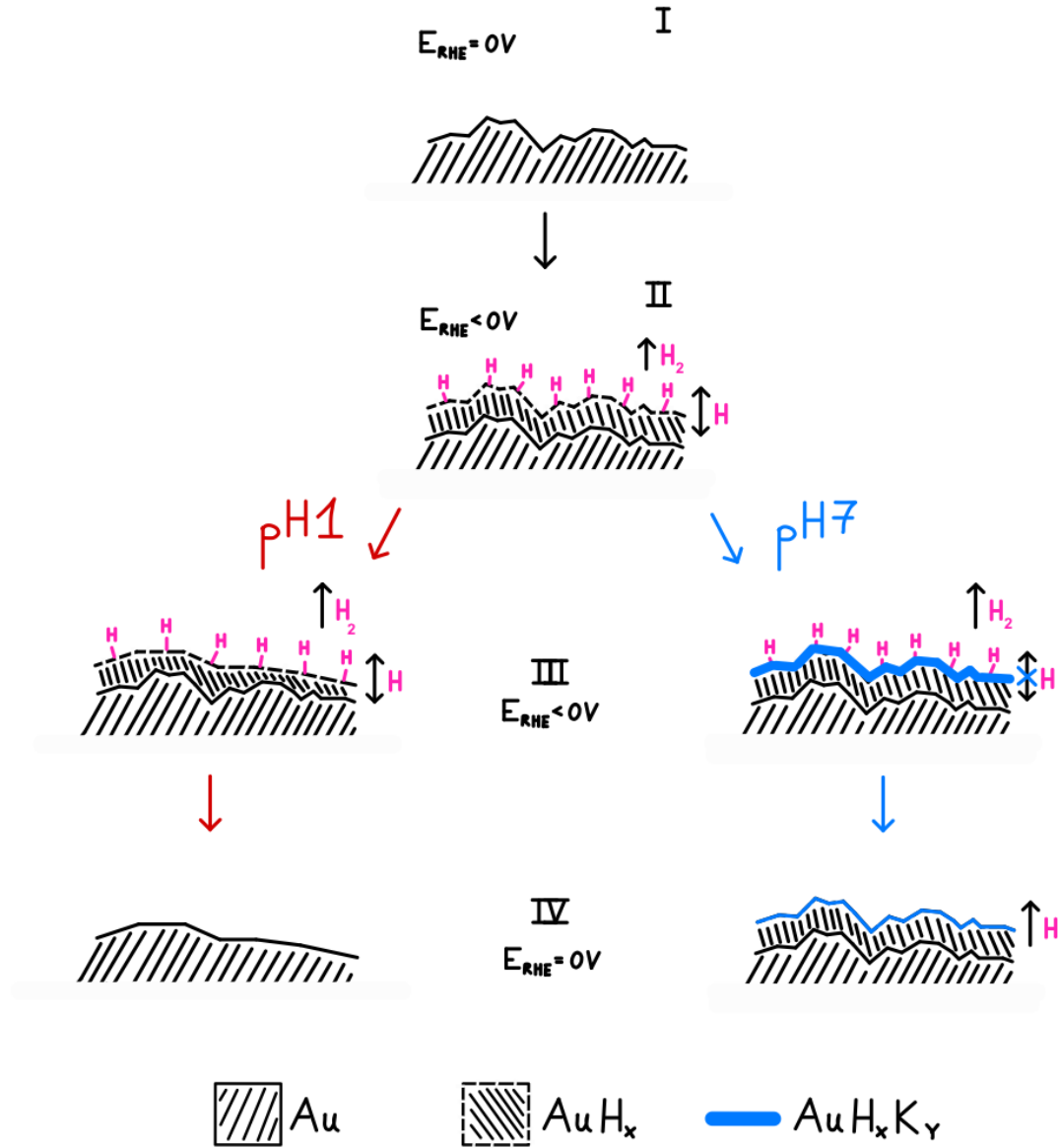


Figure 6.8.: Schematic of the stabilizing effect of ternary metal hydrides in neutral systems and the lack thereof in acidic systems. Step I represents the rough Au surface without HER. In step II, the HER begins, thus adsorbed and subsurface Au-hydride is formed. Subsurface hydrogen is denoted by AuH_x . Step III for the acidic system (pH1) involves a smoothing, i.e., degradation of the surface structure, and in step IV, the hydrogen is completely removed upon returning to $E_{RHE} = 0V$, leaving the surface in the smoothed state. Step III for the neutral system (pH7) shows the build-up of a ternary metal hydride-like layer (involving K^+ ions) covering the surface and thus preventing H from freely moving in or out of the AuH_x layer. Upon returning to $E_{RHE} = 0V$, the AuH_xK_y layer is slowly removed, but the AuH_x is not yet converted back to Au.

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This mechanism holds in acidic electrolytes where protons are the only cations in solution. In the presence of other cations, for example, alkali cations, the cations in the double layer might form ternary metal hydride surface complexes with the $\text{AuH}_2^{\delta-}$ species, which stabilize the hydrides and reduce their mobility (right side step III of Figure 6.8). Ternary metal hydride ions, dissolved in the electrolyte, are believed to be highly reactive intermediates in cathodic corrosion [118, 133, 134]. At our much lower overpotentials for HER and a much lower electrolyte pH compared to the experiments in the literature, the surface complexes are unlikely to dissolve into the electrolyte, but rather impede H_2 formation from Au hydrides and reduce the mobility of surface Au atoms (right side step IV of Figure 6.8).

We now show that we can consistently interpret our (d)CPV data with this model mechanism. Nevertheless, we would like to stress that, at this point, the mechanism remains a hypothesis. In acidic electrolyte, the strong blueshift of the CPV curve in the hydrogen evolution region results from an irreversible reorganization of the surface structure and geometry of the Au particles, possibly accompanied by minor dissolution of Au, which is enabled by subsurface H and Au dihydride formation that enhance the Au mobility. As soon as we leave the HER region again on the anodic branch, the behavior of the CPV curve is dominated by the decreasing electronic charge density in the plasmonic structures. Hence, λ_{res} experiences a redshift with approximately the same slope as during the cathodic sweep in the double layer region.

The presence of K^+ ions in the neutral electrolyte leads to the formation of ternary surface metal hydride-like structures, which suppresses the reorganization of the nanostructures to a large extent. Naively, one would then expect that in this case, the blueshift of λ_{res} seen in the double layer region also continues in the hydrogen region. However, the observed blueshift is less pronounced. At this point, it is important to remember that the plasmonic resonance depends on the dielectric properties of the immediate surroundings of the plasmonic structure. If the surface is chemically altered, the effective metallic nanostructure becomes smaller and is covered by another species, which leads to a redshift of λ_{res} . When we assume that the formation of ternary surface metal hydrides acts like a partial non-metallic skin, the weaker decrease we observe in the CPV between approximately 0.1 V vs. RHE and the cathodic turning point can be explained from the superposition of a blueshift due to increasing electronic density and slow structural changes and a redshift due to the formation of a partial dielectric skin. Note that the chemical alteration of the surface also leads to a lower sensitivity of the resonance on electronic or morphological changes. After switching the sweep direction to positive potentials, the resonance wavelength stays approximately constant, which can again be explained from a superposition of the three factors: change in electron density, which now leads to a redshift, slow geometric or morphological changes, and a (partial) dielectric skin, accompanied by decreased sensitivity. The resonance wavelength stays nearly constant, even positive of the onset of hydrogen evolution. Only 200 seconds later, at approximately 0.4 V vs. RHE, does the slope of the curve attain its value which is characteristic for the double layer region. The retarded onset of the double layer region behavior indicates that the postulated ternary metal-hydride-type species are quite stable and only slowly oxidized. To further support our hypothesis that the smaller degradation rate of the nanostructures in neutral electrolyte is due to the formation of ternary surface metal hydrides that stabilize the surface, we conducted a control experiment in which we added potassium sulfate to a sulfuric acid electrolyte and compared the dCPVs before and after the salt addition. We observed indeed that the degradation in the presence of potassium ions was slowed down (cf. section A.2.5 of the appendix).

In the transition between T5 and T6 of Figure 6.5, it can be seen that the morphological changes induced by HER decrease the resonance wavelength significantly. However, the sample

had already been subjected to potential cycling in the double layer and Au oxide formation regions for approximately a full day. This underlines once more that the morphological changes in the HER region are much more pronounced than during oxide reduction. An even stronger indication for this conclusion is the strong restructuring of the pristine sample shown in Figure 6.7. The blue CV is the first one that was driven into the HER region, which means the progression between the different scans shows the behavior of the initial degradation of the nanoparticles illustrated in Figure 6.5 for a different sample. As hydrogen adsorption is already visible after the third cycle, the degradation is much faster compared to T1-T5. The samples produced by LO-NIL are expected to incorporate several crystal defects and exhibit 'crown-like structures', as detailed in section 3.1. Therefore, the first time that Au surface atoms experience an increase in mobility, a massive structural change is expected. Note that the CVs are essentially identical as the total surface area stays approximately the same (the reduction peak of the Au oxide monolayer has basically the same area for all three cycles). It is also expected that the initial morphological change weakens for the consecutive cycles as the morphology comes closer to the stable configuration of the Au/electrolyte interface. This can be seen rather well in the increase of the dCPV signal in the HER region for later cycles in Figure 6.7(c). Note that although hydrogen adsorption occurs in all three cycles, as it is widely accepted as one crucial step in the H_2 formation process, it can only be seen in the dCPV after the initial morphology change has happened. This would explain why hydrogen adsorption was only observed for neutral electrolytes, as their degradation is much weaker than that of the nanostructures in acidic systems, where a drop of the dCPV signal is always observed and does not seem to weaken even with time.

The down bending and the weaker hydrogen adsorption feature in Figure 6.3(c), which both scale with the aging of the sample, lead to conclusions about the structural evolution of the nanostructures. The weakening of the hydrogen adsorption peak does not correlate with the current, which is roughly the same for all CVs. A reasonable explanation seems to be to assume that the number of sites on which strong hydrogen adsorption is possible decreases with time. In fact, Bus et al. [126] suggest that hydrogen adsorbs strongly on undercoordinated Au sites, such as corners and step edges, which will be depleted first during the restructuring of the surface.

Regarding the lack of desorption peaks, it is assumed that the subsurface hydrogen formation stretches the desorption peak, and the formation of (ternary) Au hydrides suppresses it. A weak desorption peak is discernible in the first anodic scan of Figure 6.3(c) (dark blue minimum at the HER onset) but can not be observed at all in the consecutive scans.

7. Double Layer Behavior under Dynamic Conditions

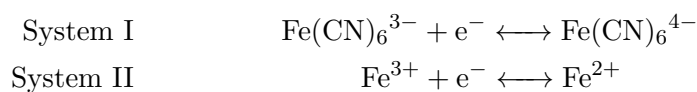
In this chapter, the behavior of the double layer under strong faradaic currents of non-adsorbing species will be investigated using dCPV. To resolve these otherwise elusive effects, measurement protocols have to be adapted, and data treatment has to be optimized. This chapter will serve as a step toward more applied systems, thus showing the limits and potentials for dCPV as an analytical method.

7.1. Introduction

Understanding the double layer behavior of electrochemical systems under dynamic conditions, i.e., under finite faradaic current, is imperative to formulating more accurate models of reaction and mass transport kinetics. The most common and universal method to do this is electrochemical impedance spectroscopy (cf. section 3.3.3), which has been successfully applied to characterize electrochemical systems for several decades [67]. However, when it comes to the analysis of dynamic systems, i.e., large faradaic currents, several papers suggest that there are limits to the applicability of EIS due to the coupling of faradaic and charging currents [135, 136, 137]. Both currents are assumed to be independent of one another in standard textbooks. However, Wu et al. [137] show numerical evidence in line with the arguments of Delahay et al. [136] and Nisancioglu et al. [135] that the flux of reactants due to faradaic currents does affect the charging current and, hence, the modeled capacitance. One possible interaction between faradaic current and charging of the interface was described by Aoki et al. [138]. They found via EIS that with increasing faradaic current, the capacitance dropped, and this was explained by introducing mirror-image surface charges to their equations, which counteract the capacitive charging.

With the literature in disagreement over the correct way to model the double layer in EIS measurements under dynamic conditions, it is instructive to use a complementary method to provide insights into what this behavior could look like.

In previous chapters, dCPV has been shown to reproducibly measure the double layer behavior, i.e., charging and discharging, of plasmonic working electrodes with high precision. Additionally, it has been assumed that faradaic currents do not affect the overall charging state of the NP appreciably, which is not generally the case. To investigate the dynamic double layer behavior, dCPV is employed to monitor the charging and discharging of a metal NP/electrolyte interface under the following faradaic reactions:



Each redox pair is well-researched and will be introduced in the following sections before the experimental results are discussed.

7.2. $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ Redox Couple

In the literature, the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (ferro/ferricyanide) redox couple is generally thought of as undergoing an outer-sphere reaction [139, 140]. However, several studies have shown a more complex electrochemical behavior. For once, its reaction rates are heavily impacted by the choice of the counter cations ($\text{Li}^+ < \text{Na}^+ < \text{K}^+$) [141]. Additionally, the addition of Na^+ ions leads to the decomposition of ferricyanide, which in turn leads to the formation of Prussian Blue [142]. The latter complex blocks the surface and inhibits the reaction rate [143]. Moreover, the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ions interact with adsorbed species on the electrode surface, thus impacting the adsorption isotherms [144]. With this, as well as increased electrode corrosion, using EIS measurements to investigate such systems is challenging [145]. Hence, dCPV will be employed to investigate the double layer behavior during faradaic reactions as well as the interaction between $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ions and other adsorbed species.

7.2.1. Experimental Results

The first step in analyzing the behavior of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple is by comparing it to a known reference system. In this case, the pH7 180 mM KOH + 120 mM H_3PO_4 buffer solution was used in order to prevent the formation of cyanide, which happens in more acidic pHs.

Figures 7.1(a) and (b) show one dCPV and CV of a Au NP array in the pH7 buffer solution (blue line) and one dCPV with an additional 4 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and 4 mM $\text{K}_3\text{Fe}(\text{CN})_6$ (orange line). While the dCPV curve of the former replicates measurements already shown in previous chapters, with the two phosphate ad-/desorption peak pairs I/I_b and II/II_b (cf. Figure 6.2), the latter exhibits only one such peak pair III/III_b which is shifted by $\Delta E \approx 180$ mV with respect to the peak pair II/II_b. Apart from being shifted, the absolute peak values of peak pair III/III_b are smaller than those of II/II_b. Additionally, the phosphate ad-/desorption peak pair I/I_b is missing, and instead for $E_{\text{RHE}} < 0.7$ V, the dCPV signal decreases to values far below the double layer values. The current of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox reactions (orange line in (b)) exceeds the double layer current of the reference measurement (blue line) by several orders of magnitude. However, there is no apparent relation between the features of the dCPV and the progression of the current.

In order to get a more detailed image of the impact of only the $\text{Fe}(\text{CN})_6^{3-}$ species on the dCPV, multiple measurements for different concentrations of these species have been performed. They are shown in Figure 7.1(c) and (d). For the control measurement with no additional ferro/ferricyanide species (blue line), only one phosphate peak pair is visible, as the potential window does not reach the potential values of the peak pair I/I_b. This was chosen to avoid creating too much $\text{Fe}(\text{CN})_6^{4-}$. When increasing the concentration, a double peak pair emerges (green line), where the more anodic peak is shifted by $\Delta E \approx 180$ mV to the reference measurement. Increasing the concentration further reduces the cathodic peak and increases the anodic peak pair (orange line) until the progression of 7.1(a) with only one peak pair is retained (red line).

7.2.2. Discussion

In the experiments, two main features were observed. The first was the occurrence of two peak pairs due to the adsorbing phosphate, which was impacted by the presence of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ species. The second was the greatly suppressed dCPV signal around

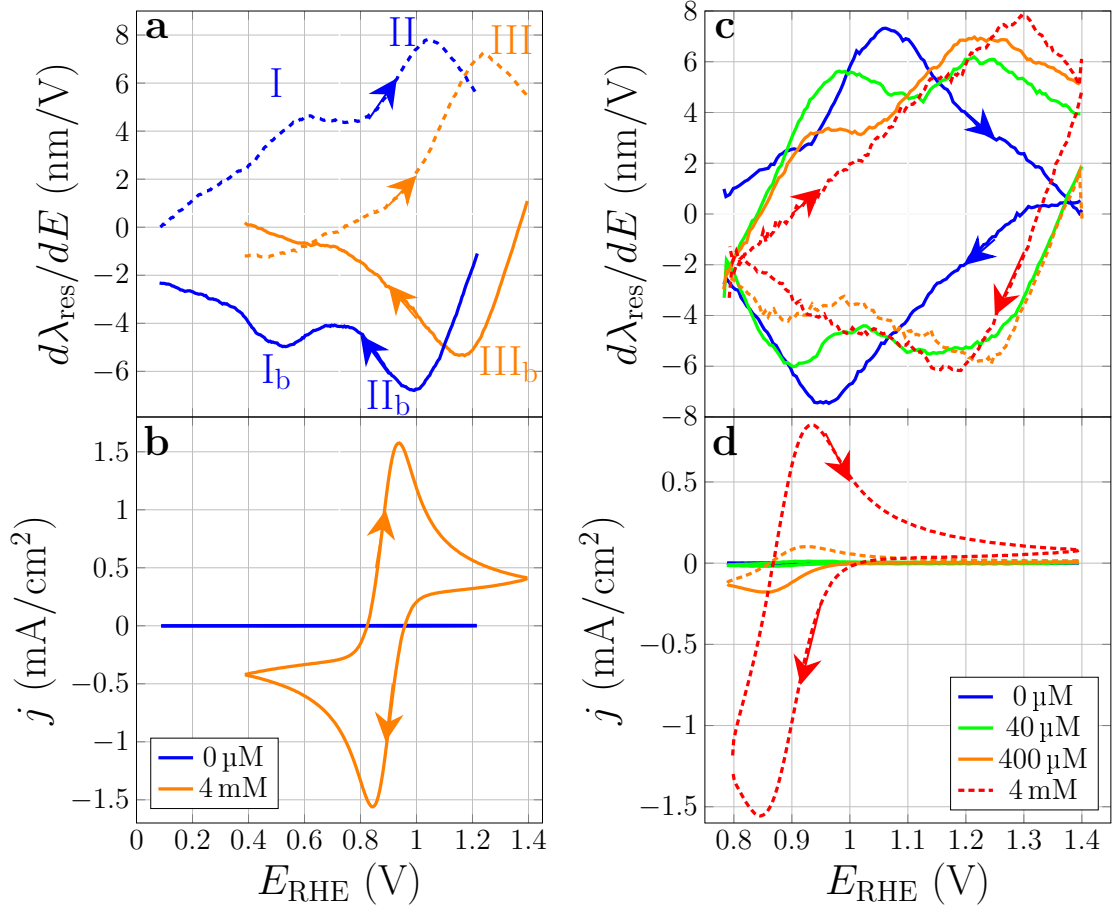


Figure 7.1.: dCPV (a) and CV (b) of a Au NP array in pH7 180 mM KOH + 120 mM H_3PO_4 buffer solution with (a),(b) 4 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 4 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and with (c),(d) varying concentrations of 4 mM $\text{K}_4\text{Fe}(\text{CN})_6$ as indicated by the legend. Scan rate $\nu = 50 \text{ mV s}^{-1}$.

the double layer potential region. Both of these were hinted at in the literature and are discussed in the following.

The potential shift of the more anodic peak pair (II/II_b) could be due to the adsorption of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ species on the electrode surface at OCP ($E_{\text{RHE}} = 903 \text{ mV}$) [140], which then have to be removed, before the phosphate species can adsorb, thus shifting them to more anodic potentials. At the same time, such desorption of ferro/ferricyanide is expected to be seen in the dCPV, which is not apparent in Figure 7.1. A reason for this could be that ferro/ferricyanide does not adsorb strong enough to impact the plasmonic resonance while still affecting the other anions. Moreover, for the case of small concentration (green and orange lines in Figure 7.1(c)), the occurrence of the second peak pair can be explained by the cathodic peak being shifted to more anodic potentials and thus reaching the scanned potential range of the measurement shown in 7.1(c),(d). Hence, it is assumed that this peak pair is equivalent to I/I_b. The phosphate peak pair I/I_b was due to the presence of another phosphate species at pH7 and seems to be suppressed with increasing concentration of the $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ salts in solution. In both cases of maximal concentration (4 mM) the peak pair is completely suppressed. Note that the pH does not change upon adding ferro/ferricyanide.

For $E_{\text{RHE}} < 0.7 \text{ V}$, the dCPV in Figure 7.1(a) shows a significant narrowing compared to

7. Double Layer Behavior under Dynamic Conditions

the reference measurement, which indicates that there is a negative differential capacitance during this part of the potential scan. This is, however, not reflected in the corresponding EIS data (cf. section A.3). The decreased prominence of the remaining peak pair III/III_b in Figure 7.1(a) could also be due to a suppressed charging which would result in an apparent decrease of the dCPV signals. In turn, this would mean that the overall number of adsorbed phosphate molecules is not changed by the ferro/ferricyanide ions, which are completely removed upon the adsorption of the former.

This depolarization could be due to a constant stream of oxidized/reduced ions from the surface into the solution during the oxidation/reduction. In the case of an anodic sweep, the surface is more positively charged, and at the same time, the electrolyte close to the surface is more positively charged due to the species created at the surface. Hence, it should be expected that there is a depolarizing repulsive force acting on the charges at the surface. This argument holds, independently of the absolute charge state of the surface and of the charge of the reduced/oxidized species, as only the change in charge is relevant. Both ferro/ferricyanide are negatively charged, but the overall charge in the electrolyte is neutral before reactions are forced due to the counter cations in the solution. Consequently, the bulk electrolyte close to the electrode will be positively charged if $\text{Fe}(\text{CN})_6^{4-}$ ions are replaced by $\text{Fe}(\text{CN})_6^{3-}$ ions due to oxidation. Ferro/ferricyanide species have been described as complex-forming, especially with the potential to form Prussian Blue, which is unlikely in this case, as Prussian Blue is expected to completely block the surface, thus diminishing the phosphate adsorption peak over time, which is not seen for either measurement.

7.3. $\text{Fe}^{3+}/\text{Fe}^{2+}$ Redox Couple

Similar to ferro/ferricyanide, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is referred to as undergoing an outer sphere redox reaction [146]. However, this redox reaction seems to be greatly impacted by the presence of anions, especially sulfate species. It is hypothesized that the sulfate ions form complexes with the hydrated $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions, which enables an anion-bridged charge transfer mechanism that is akin to an inner sphere reaction. This effect is also seen for trace amounts of Cl^- ions in a HClO_4 electrolyte [147, 148].

In the following, the double layer charging and the adsorption of ions on the Au electrode surface in pH1 100 mM H_2SO_4 base electrolyte with varying concentrations of $\text{Fe}_2(\text{SO}_4)_3/\text{FeSO}_4$ will be probed. With an excess amount of $\text{HSO}_4^-/\text{SO}_4^{2-}$, any complex formation is expected to be visible alongside the dynamic double layer behavior.

7.3.1. Experimental Results

Figure 7.2 shows dCPVs and the corresponding CVs of an Au NP array in sulfuric acid with different concentrations of $\text{Fe}_2(\text{SO}_4)_3/\text{FeSO}_4$. The concentrations of both species are the same in each individual measurement and are given in the legend. In Figure 7.2(a), it can be seen that the overall progression of the dCPV is very similar to previous measurements (cf. the 50 mV s^{-1} curve of Figure 5.6) and independent of the $\text{Fe}_2(\text{SO}_4)_3/\text{FeSO}_4$ concentration and the faradaic current resulting from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox reaction. The largest deviation is found at the Au oxidation/reduction reaction, which yields a lower absolute signal for larger faradaic currents. Note that the current (Figure 7.2(b)) increases approximately proportional to the increase in concentration (by a factor of ten for every step) and its features are not replicated in the dCPV graphs. The capacitance data of this system, as measured by EIS, exhibits similar behavior in that it is small for values of small currents and gets larger for larger absolute currents (cf. section A.3). Figures 7.2(b) and (c) show a zoom in Figure 7.2(a) (indicated by

the dashed box). There, a difference between the increasing concentrations becomes apparent: Both branches of the dCPV signal in the double layer potential region are continually shifted to absolute smaller values for increasing concentration of $\text{Fe}_2(\text{SO}_4)_3/\text{FeSO}_4$. The shift seems to be larger around the sulfate ad-/desorption peaks ($E_{\text{RHE}} \approx 0.8 \text{ V}$) and decreases for more cathodic potentials. The shift is largest for the smallest concentration changes, i.e., the shift is about $+2 \text{ nm V}^{-1}$ for the cathodic branch when the concentration is changed from $< 25 \mu\text{M}$ to $40 \mu\text{M}$ and barely visible for the change from $400 \mu\text{M}$ to 4 mM .

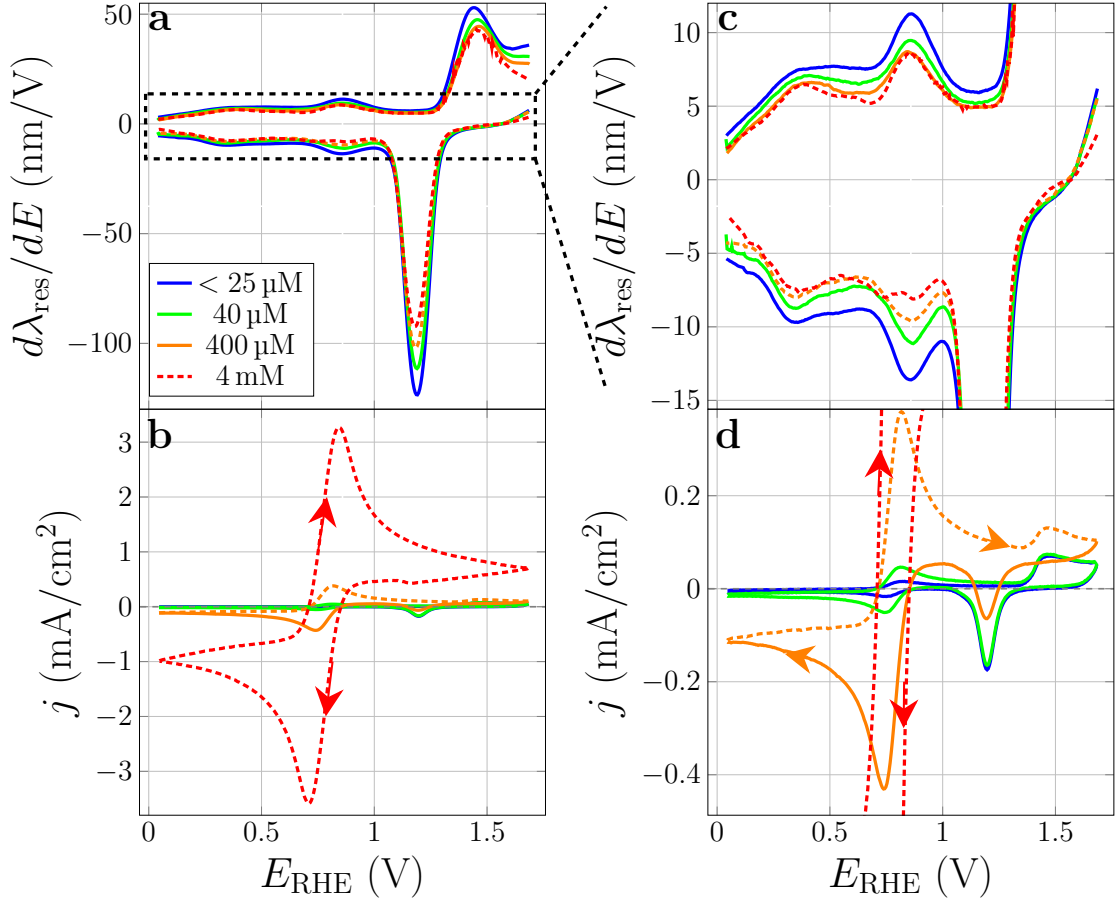


Figure 7.2.: dCPV (a) and CV (b) of a Au NP array in pH1 100 mM H_2SO_4 with varying concentrations of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ as indicated by the legend. Zoom in into the double layer region of the dCPV (c) and the CV (d). Scan rate $\nu = 50 \text{ mV s}^{-1}$.

7.3.2. Discussion

The electrolyte composition was chosen in a way that the change in sulfate concentration by adding $\text{Fe}_2(\text{SO}_4)_3/\text{FeSO}_4$ is not expected to impact the electrochemical response in a relevant magnitude. For the largest $\text{Fe}_2(\text{SO}_4)_3/\text{FeSO}_4$ concentration, the sulfate concentration increase is just 8% and much lower for all the other cases. The pH is also not impacted.

The apparent double-peak structure in Figure 7.2(c) is not expected to originate from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions in solution, as a similar change in dCPV progression has been observed in this potential region for multiple 50 mV s^{-1} measurements without these additional ions (cf. the bump at 0.45 V in Figure 5.3(d)).

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Regarding the observed changes in the double layer region, there are two effects to be considered: First, the depolarization of the double layer due to the faradaic reaction occurring at the interface, and second, the interaction of adsorbed sulfate species with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions. Both effects would result in a decrease of the dCPV values in the double layer potential region; the former because of inhibited charging and the latter because of decreased sensitivity due to the adsorbate layer on its surface (cf. the argument made in section 6.3.3 regarding the stagnant behavior of the neutral CPV in the HER region).

Compared to the ferro/ferricyanide reaction, the current density of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ is twice as large, and there are fewer ions in the solution. The overall concentration of ions is expected to contribute to a stronger screening of excess charge, which, if at all, reduces the depolarizing capability of the charges produced by the redox reaction. However, the shift of the dCPV branches towards zero is comparatively small. Contrary to this, the decline in the shift from the sulfate adsorption region to more cathodic potentials coincides with the decrease of the current of the $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$ reduction current. This would indicate the dynamic depolarization mechanism stated in the previous section. The difference in effect strength compared to the ferro/ferricyanide measurements could be due to the difference in ion size and their screening close to the surface, as hydrated $\text{Fe}(\text{CN})_6^{3-/4-}$ ions are expected to be larger than hydrated $\text{Fe}^{3+/2+}$ [149, 150].

To conclude, we have shown via dCPV that dynamic depolarization occurs under $\text{Fe}^{3+/2+} / \text{Fe}(\text{CN})_6^{3-/4-}$ redox reaction conditions. This was seen as a narrowing of the dCPV value in the double layer region with increasing concentration of these ions. Also, several indications regarding interactions between these redox pairs and the other anions of the solution have been noted, which need to be confirmed with additional measurement techniques that resolve the adsorbed molecules.

The next step is to repeat these measurements with ions that do not adsorb, such as HClO_4 , and further well-known outer sphere reactions, such as $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ [151]. Without adsorption processes present in the dCPV data, the change in the dis-/charging should be clear enough to be able to compare the impact of different redox pairs and buffer solution ions.

8. Surface Modification of Plain Cu Electrodes during Stepped Potential Programms

Up to this point, all samples used in this thesis have been designed for the process of plasmonic sensing during electrochemical measurements on model systems. This enabled the development of dCPV, which led to several interesting findings regarding the fundamental interactions of Au, H, and ions and fundamental properties of the double layer region. However, if this method were to be employed on more applied systems, e.g., catalysis on less defined but scalable electrodes, several challenges must be addressed in the setup and the data treatment. In this chapter, we will try to apply dCPV to track the formation of Cu NPs on mechanically polished plain Cu electrodes under gas-evolving conditions as a first step toward more applied systems. This system is used to analyze catalytic mechanisms of the CO₂ reduction reaction on Cu, which is applied in the sense of a simple and scalable electrode (mechanically polished Cu-slabs), large currents, and significant gas evolution. Thereby, the main challenges to the optical analysis are (I) the gas evolution, which distorts the optical spectra, and (II) the transient unknown change in the chemical composition of the Cu electrode parallel to the formation of (III) highly irregular NPs.

We will begin this chapter by introducing the surface morphology of the Cu samples after using different electrochemical protocols. In the following section, the treatments of the spectroscopic data will be discussed and compared to simulated spectra. It is not obvious that the measured spectroscopic features of NPs on plain copper are indeed plasmonic resonances, which is why they will not be referred to as such. Similarly, dCPV will be called “differential treatment” if it is applied to non-plasmonic optical data. The results of this chapter were obtained in cooperation with Hagen Übele.

8.1. Nanoparticle Formation on Plain Cu Electrodes

Cu oxidation and subsequent NP formation from plain Cu sheets is a well-known phenomenon in the literature [152, 153, 154] in part due to its relevance in industrial processes involving copper and its oxidized forms [155, 156]. Recently, such NP formation has also been addressed in the field of carbon-to-fuel research, where the NPs are formed during stepped potential CO₂ reduction reaction (CO₂RR) protocols. Here, we will also examine Cu surfaces during stepped potential programs, an example of which is shown in Figure 8.1. “Stepped” in this context refers to a periodic switching between an anodic potential $E_{\text{RHE,a}} = 0.7 \text{ V}$ and a cathodic potential $E_{\text{RHE,c}} = -1.1 \text{ V}$ which are applied for times t_a and t_c respectively. Understanding how to control the NP formation is thought to help design systems with a significant increase of the selectivity toward higher-order carbon chains. For example, it has been shown that the adsorption of specific species (e.g., CO and bicarbonate) hinders NP formation, while the role of metallic cations is still under debate [157, 158, 159, 160].

To illustrate the NP formation in our system, AFM images have been recorded ex situ for different states of the Cu/Cu oxide surface and are shown in Figures 8.2. One additional AFM image is shown in section A.4 of the appendix. All of those samples were polished, subjected

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to some specific treatment, and then transported to the AFM, during which they were stored in deionized water (≈ 12 min) and then in air during the AFM measurement (≈ 2 min). Some additional oxidation cannot be ruled out, which is why these AFM images are only used for a qualitative comparison.

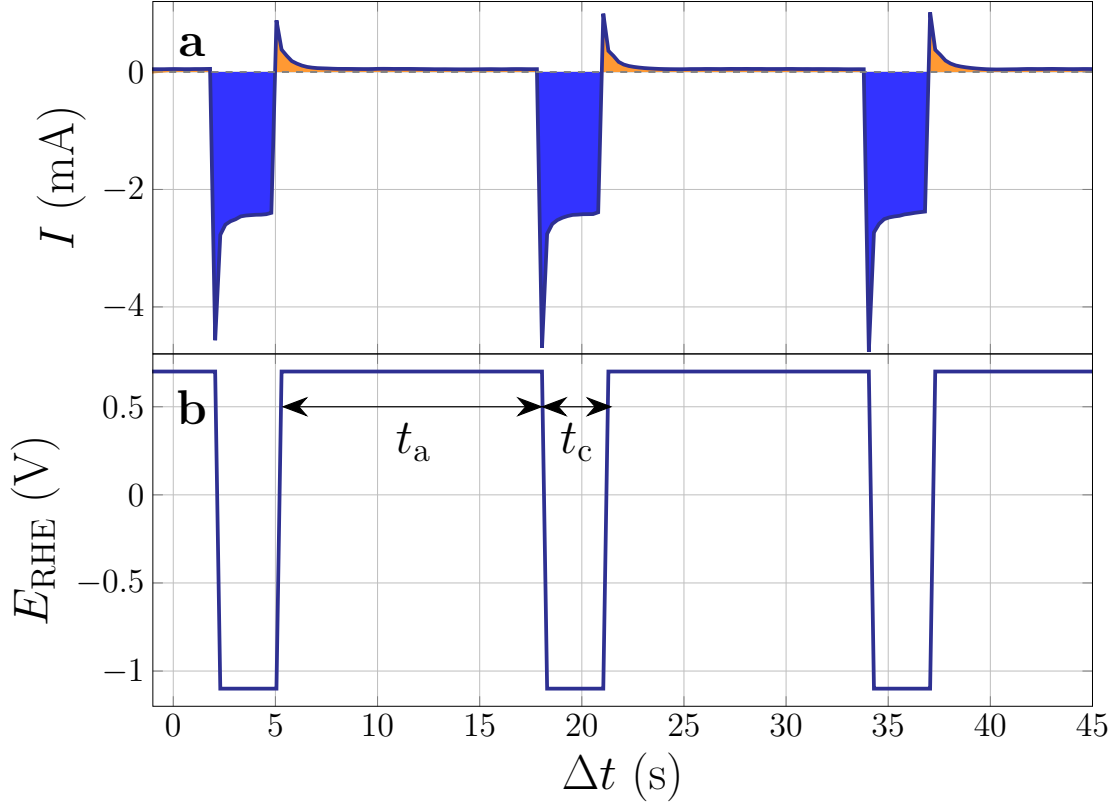


Figure 8.1.: Current-time curves for a small cutout from the step potential measurement shown in Figure 8.6. The reductive charge (at $E_{\text{RHE},c} = -1.1$ V) is marked blue and the oxidative charge ($E_{\text{RHE},a} = 0.7$ V) is marked orange. t_a and t_c are the times of the anodic and cathodic pulses. The electrolyte was 100 mM KHCO_3 (CO_2 saturated, pH7).

The AFM image of Figure 8.2(a) shows a Cu sample that has been subjected to a constant and slightly oxidizing potential ($E_{\text{RHE}} = 0.7$ V) for 30 min. Most of the visible surface consists of small flat grains (diameter ≈ 60 nm) and some deviations from a perfectly flat surface (e.g., dent in the lower corner). The latter is expected from the mechanical pre-polishing treatment, which is done by hand. In comparison, the sample shown in Figure 8.2(b) exhibits a higher roughness with grains extending to around 120 nm in three dimensions. Also, these grains have visible edges, which is why they are considered pyramid or cube-shaped nanoparticles. This sample was subjected to 30 min of constant reduction potential ($E_{\text{RHE},c} = -1.1$ V) and 1 h of stepped potentials between $E_{\text{RHE},a} = 0.7$ V for $t_a = 6$ s and $E_{\text{RHE},c} = -1.1$ V for $t_c = 6$ s. The largest structures have been observed in Figure 8.2(c) where a Cu sample has been put in 100 mM KHCO_3 (air saturated) after being polished and kept there for approximately 12 h. The surface is covered by microscopic particles of side lengths up to $0.5 \mu\text{m}$, which exhibit a morphology indicating highly ordered crystal facets. It has to be noted that the chemical composition of none of these sample surfaces is known, nor is it known how they grew into these particular shapes.

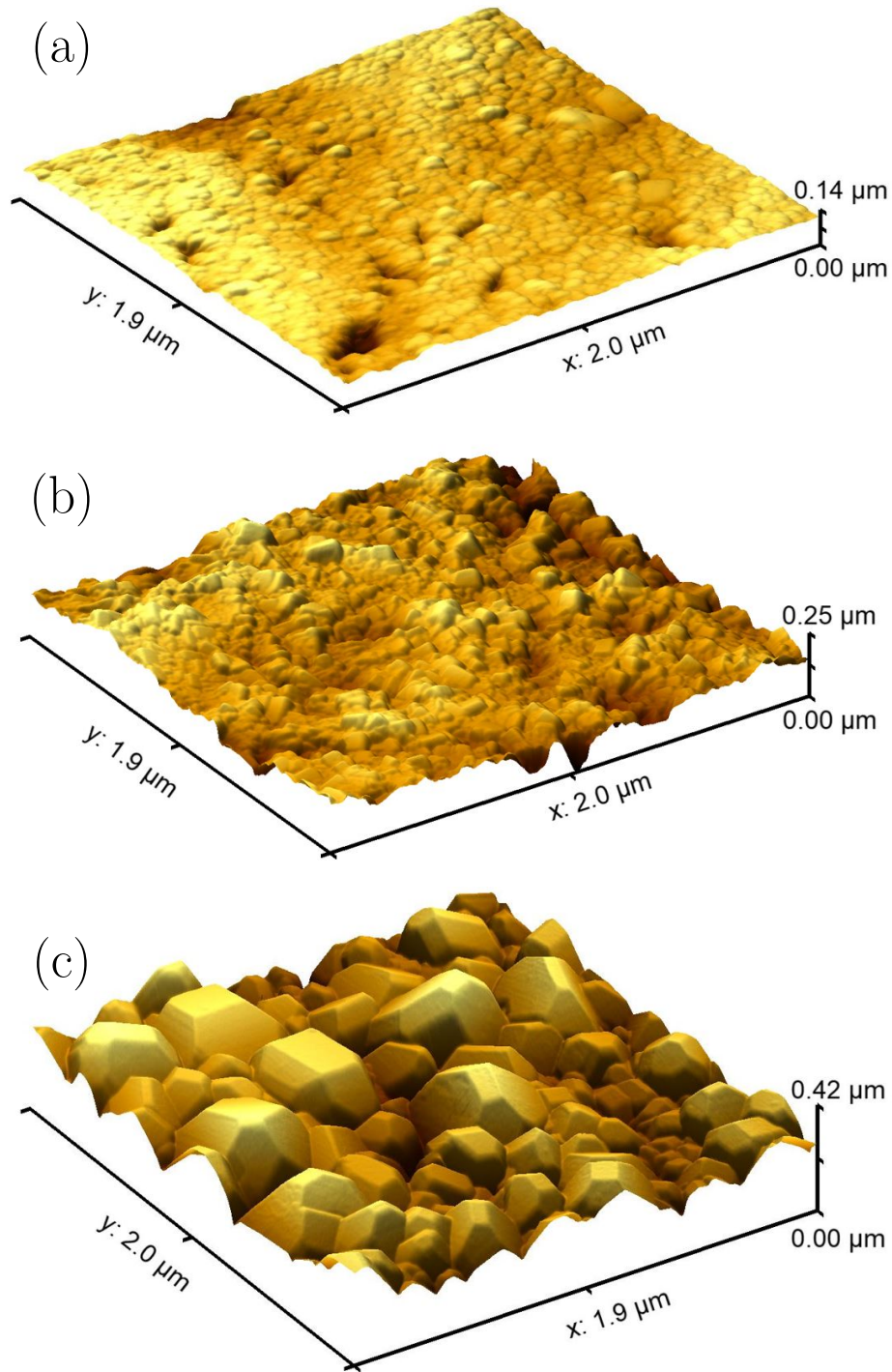


Figure 8.2.: AFM data of plain mechanically polished Cu electrodes after (a) 30 min of slightly oxidizing potential ($E_{\text{RHE}} = 0.7 \text{ V}$), (b) 30 min of constant reduction potential and 1 h of stepped potentials (oxidizing puls $E_{\text{RHE,a}} = 0.7 \text{ V}$ for $t_a = 6 \text{ s}$ and reductive puls $E_{\text{RHE,c}} = -1.1 \text{ V}$ for $t_c = 6 \text{ s}$), (c) 12 h resting in 100 mM KHCO_3 (air saturated). For (a) and (b), the electrolyte was pH7 100 mM KHCO_3 (CO_2 saturated). The x-, y-, and z-axis have the same scale. The minimal z-value is set to 0.

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Especially the structures in Figure 8.2(b) exhibit particles of sizes that could potentially be plasmonically active, as particles of similar size and morphology have been used in plasmonic studies [99]. A spectroscopic investigation is, therefore, worthwhile and conducted in the next section.

8.2. Spectroscopy of Gas Evolving Cu Electrodes

The optical setup and the data acquisition for analyzing the Cu NP are identical to the method used on the Au NP arrays, as shown in section 3.3.1. A picture of the setup in operation is shown in Figure 8.3.

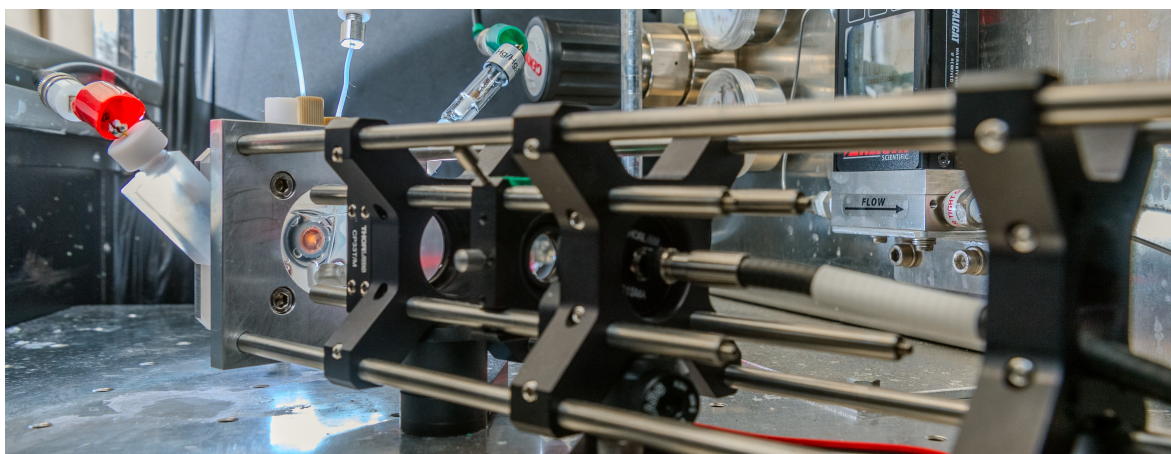


Figure 8.3.: Electrochemical and optical measurement setup of CO₂RR on Cu electrodes during operation. Copyright Andreas Heddergott.

To illustrate the shape of the initial Cu samples, several initial spectra are shown in Figure 8.4 alongside a COMSOL simulated plain Cu spectrum. The reference spectrum used to calculate these reflectance spectra (cf. equation 3.11) was recorded beforehand with a finely polished Ag sample as a reflecting mirror in the same electrolyte to acquire the reflectivities of the system, e.g., the shutter, the glass fiber ends, and the glass window of the cell. The characteristic drop around 550 nm can be seen for all samples and is indicative of the red color of Cu, as blue and green are not reflected as much as red. The features in the region $900\text{ nm} < \lambda$ stem from the use of Ag as reference, the water, and the spectrum of the white light source. The drop for $\lambda < 400\text{ nm}$ is an artifact introduced by the spectrometer but is of no significance to the subsequent data treatment.

8.2.1. Selection of the Reference Spectra

One of the core aspects of reflectance spectroscopy is the selection of a suitable reference spectrum. For the well-defined Au NP arrays, a similar sample with its plasmonic resonance far outside the visible spectrum was chosen. The polished silver reference was used to obtain the real spectrum of Cu, which in turn was used to determine the quality of the polishing treatment. This was necessary as every newly polished Cu electrode exhibited different spectral features, which also prevented using the spectrum of one individual polished Cu sample as the initial reference. Once a sample is deemed acceptable for further treatment, its initial spectrum is used as the initial reference spectrum (cf. Figure 8.4). However, during the electrochemical procedures that lead to structures, as shown in Figure 8.2(b), large amounts of

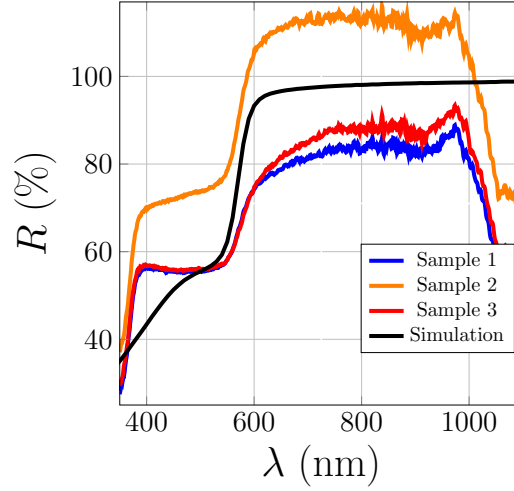


Figure 8.4.: Initial spectra of three different polished Cu samples in water compared to the simulated flat Cu surface.

gas bubbles are evolved as shown in Figure 8.5(a). These gas bubbles are moved erratically through the main compartment due to the convective current introduced by the magnetic stirring rod, which impacts the spectrum. In order to quantify the impact of the gas bubbles on the optical spectra, a measurement is conducted with a constant reductive potential ($E_{\text{RHE,c}} = -1.1 \text{ V}$) applied for 30 min to a freshly polished Cu sample. A selection of the recorded spectra are shown in Figure 8.5(b). There, several spectra with respect to the initial reference and for different levels of gas bubble impact are shown. The initial spectrum is also shown for comparability reasons, and as it is effectively divided by itself (the initial reference), it occurs as a straight line (dark blue) at $\Delta R = 100\%$. At $E_{\text{RHE,c}} = -1.1 \text{ V}$, gas evolution occurs, but nanoparticle formation is expected to be suppressed. Hence, the spectra are only affected by gas bubble formation, which manifests in the following two aspects:

- (1) Light gets scattered by gas bubbles, which decreases the total amount of light going back to the detector. Hence, compared to the initial reference, the spectra will be shifted to lower reflectivities proportionally to the number of gas bubbles in the light path. This impact will be wavelength dependent, as the reflected light contains more “red” ($\lambda > 550 \text{ nm}$) than “blue” ($\lambda < 550 \text{ nm}$) photons (cf. Figure 8.4). As those are scattered as well, more “red” photons are effectively scattered than “blue” photons. This means that with respect to the initial reference, the part $\lambda < 550 \text{ nm}$ of the spectrum should be less shifted downwards than the part $\lambda > 550 \text{ nm}$. Both of these effects can be seen in Figure 8.5(b).
- (2) Without gas bubbles, the light would need to go through $\approx 10 \text{ mm}$ of water (back and forth), which absorbs light in the near-infrared region ($925 \text{ nm} < \lambda < 1040 \text{ nm}$). With gas bubbles in the light path, the effective pathway consists of less water compared to the previous case (which is replaced by the gas of the bubble), and compared to the initial reference, there is less absorption by water. Hence, the reflectivity in this region is expected to exhibit a higher reflectivity than before, barring the shift described in (1), which is seen in Figure 8.5(b).

From these two aspects, it is obvious that the spectra have to be treated with another

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reference, than the initial one, as these impacts mask any plasmonic effect. As the measurement has been conducted in a way that mitigates the formation of nanoparticles, these spectra themselves can be used as the new family of reference curves. With all spectra being subjected to different levels of gas bubble formation, a selection process has to be employed to choose the correct reference spectrum from the family.

The selection will be made by the value of each individual spectrum during the main treatment (with respect to the initial) at the wavelengths $1040 \text{ nm} < \lambda < 1080 \text{ nm}$, as indicated by the dashed lines in Figure 8.5(b), and matched with the reference curve of the same value at that range. The physical motivation behind this choice is that this wavelength range is not expected to be influenced by the spectroscopic changes of the sample and only by vertical shifts due to the gas bubbles. Hence, this value range can be seen as a direct descriptor for the level of gas bubble impact.

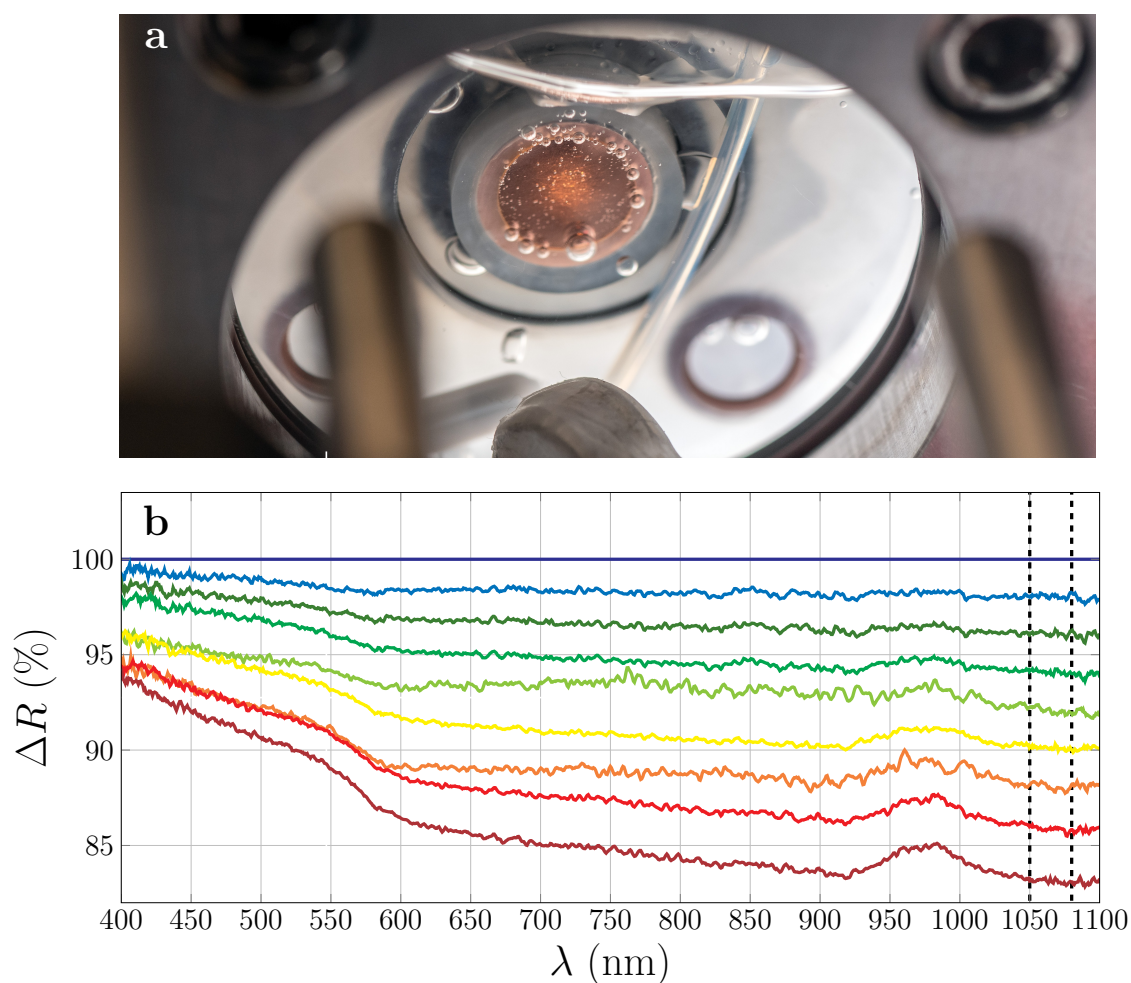


Figure 8.5.: (a) Gas evolution on a Cu electrode during operation. Copyright Andreas Hedergott. (b) Example spectra recorded during 30 min of chronoamperometry at $E_{\text{RHE}} = -1.1 \text{ V}$ in 100 mM KHCO_3 (CO_2 saturated, pH7). The colors of the individual spectra indicate the level of gas bubble impact on them. Dark blue is recorded without gas bubbles, while dark red was recorded for the system with the largest amount of gas bubbles.

8.2.2. Tracking Spectroscopic Features

After selecting and applying the references, the spectra look like those shown in Figure 8.6(a) (solid lines). Due to the choice of reference, all spectra converge to $\Delta R = 100\%$ at $\lambda = 1060$ nm. All of these curves exhibit a similar resonance-like feature around $\lambda = 570$ nm, which will be the focus of the following data treatment. A suitable fit function has to be selected to extract the resonance-like features from these curves. An asymmetric Breit-Wigner function does not yield good results, as it requires a very specific curve shape to work properly (cf. Figure 4.8(b)). In this case, a Gaussian function on top of a third-degree polynomial (parameters a, b, c , and d)

$$R = A \cdot e^{\frac{(\lambda - \lambda_{\text{center}})^2}{2\gamma}} + a\lambda^3 + b\lambda^2 + c\lambda + d \quad (8.1)$$

was selected as the most reliable fit function. λ_{center} is the center position of the Gaussian peak, γ is a descriptor for the width, and the third-degree polynomial is selected to replicate the change in incline that occurs over time. A selection of these fit functions is shown as the dashed lines in Figure 8.6(a). Only the part between the dashed vertical lines in Figure 8.6(a) is fitted to exclude as many parts of the spectra that are significantly impacted by the features shown in Figure 8.5(b) as possible.

Treating the center position value of the Gaussian function in the same way as the resonance position in section 5.2.1, a time series over the complete stepped potential treatment can be plotted, as shown in Figure 8.6(b). It can be seen that the center position starts off at $\lambda_{\text{center}} = 550$ nm with high fluctuations (region I) and rises continuously while the fluctuations get smaller (region II and III) before leveling out at $\lambda_{\text{center}} \approx 590$ nm (region IV). To resolve the fine progression, which occurs on the order of seconds, a zoom into region II is shown in 8.6(c) and accompanied by the corresponding cut-out of the applied potential (Figure 8.6(d)). The center position follows the applied potential with an increase in center position for the switch to oxidative potentials and vice versa for reductive potentials. The difference in center position due to the change in potential is approximately 7 nm, and the position itself does not change during the individual pulses, which deviates from the current-time profile (cf. Figure 8.1). The thickness of the $\lambda_{\text{center}}-t$ plot in 8.6(b) (region II, III, and IV) is, therefore, an expression of the spectral reaction intensity, i.e., wider regions imply a more significant change in λ_{center} . Hence, the spectral intensity decreases during regions II and III before it increases again for region IV. Figures 8.6(e) and (f) show a zoom into region IV and the corresponding applied potential during this time. It is clearly visible that the reaction of the Gaussian resonance peak to changes in the applied potential is inverted to the reaction seen in Figure 8.6(c), which cannot be easily related to specific changes of the surface without knowing its composition.

As one single measurement exhibits features that are difficult to interpret, it is instructional to look at multiple results of the identical measurement protocol on different samples.

8.2.3. Comparability of Identical Measurement Protocols

A collection of identical stepped potential measurements ($t_a = 13$ s, $t_c = 3$ s) is shown in Figure 8.7(a). The dark blue curve is the same as in Figure 8.6. Overall, all of the curves follow a similar progression with a large fluctuation at the beginning, a consecutive narrowing for larger times, and a continuous increase in resonance position. Quantitatively, they all start at wavelengths $\lambda_{\text{center}} < 572$ nm and end up in a range of $582 \text{ nm} < \lambda_{\text{center}} < 598$ nm. A zoom into the first quarter of the measurements is shown in Figure 8.7(b) alongside the applied potential (c). The main similarity is the qualitative reaction of the peak positions to

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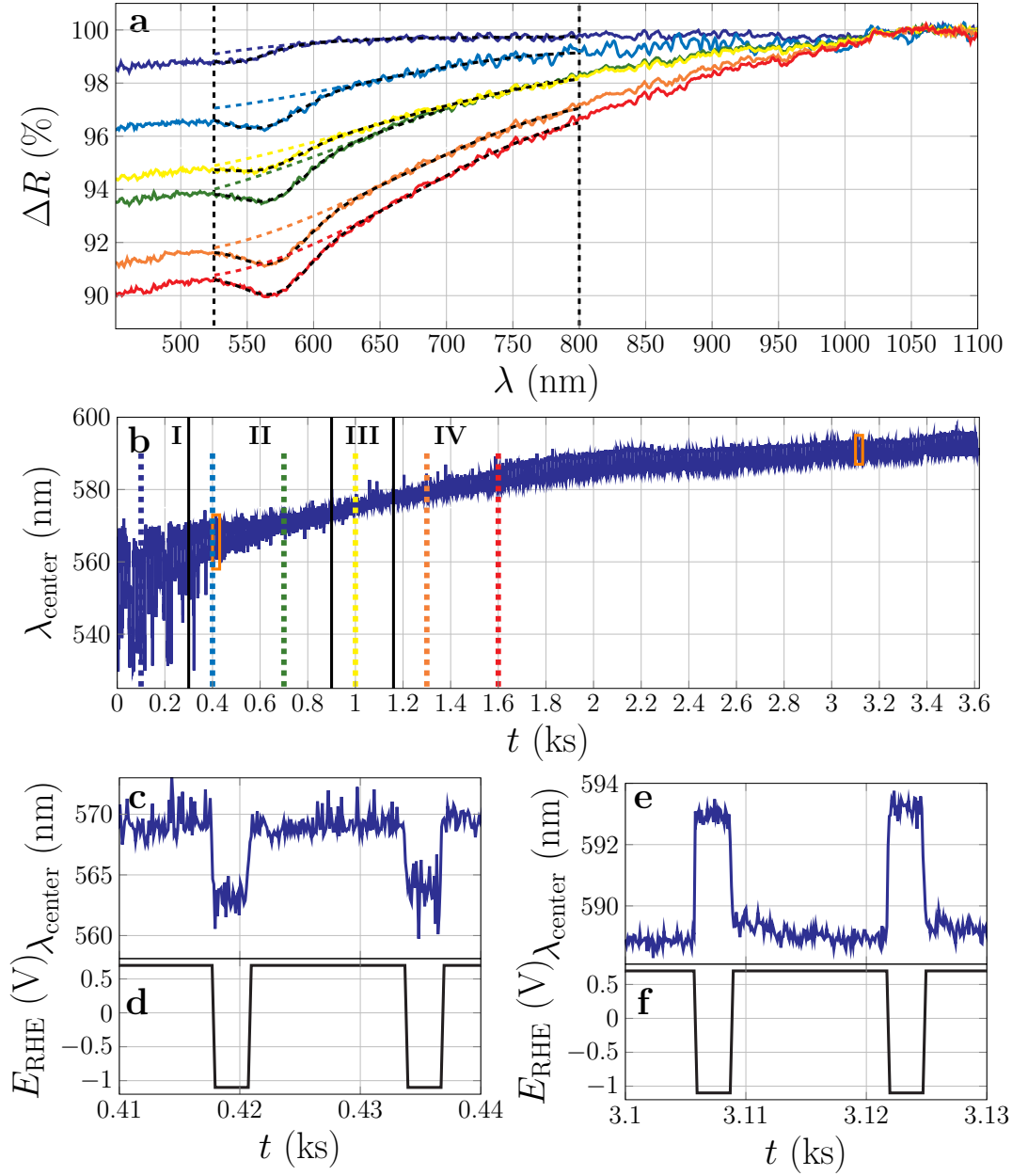


Figure 8.6.: (a) Fully treated reflectance spectra (solid) and their fit functions (dashed) during a stepped potential treatment. The colors indicate a progression over time, starting with blue and ending with red. (b) Resonance position λ_{center} of the Gaussian peak versus time during a stepped potential treatment in 100 mM KHCO_3 (CO_2 saturated, pH7). The oxidizing puls was set at $E_{\text{RHE,a}} = 0.7 \text{ V}$ for $t_a = 13 \text{ s}$ and the reductive puls was set at $E_{\text{RHE,c}} = -1.1 \text{ V}$ for $t_c = 3 \text{ s}$. (c) and (e) are cut-outs of the data in regions II and IV (marked by orange squares in (b)). (d) and (f) are potential time curves of (c) and (e) respectively. The colored dashed lines in (b) reflect the positions from which the spectra of equal color in (a) are taken.

the potential pulses. The main difference is that their change in center position between the voltage steps ranges from 4 nm (dark blue) to 30 nm (green).

So far, the spectral features measured on the Cu samples cannot be concluded to be of plasmonic origin. Hence, in the following, simulations of this system will be shown and compared to the measurements.

8.2.4. Simulation of the Plasmonic Peaks

Reflectivity simulations of the Cu NP on plain Cu have been conducted using COMSOL Multiphysics in a similar configuration as introduced for the Au NP arrays in section 3.2. The basic geometry was adapted to the size and shape of the NPs shown in Figure 8.2(b). As the surface of the substrate is fully reflective copper, each simulated spectrum will be divided by a reference spectrum of a perfectly flat Cu surface (cf. black line in Figure 8.4). The selection of the simulated geometries is shown in Figure A.7 of the appendix. As before, the geometries only mark one unit cell of a full array, which is simulated by periodic boundary conditions (cf. section 3.2.1). All of them are pyramids with different side lengths, heights, and aspect ratios. The real geometries of the NPs of interest, as seen in Figure 8.2(b), are rarely perfectly pyramid-shaped. Still, from all basic geometrical shapes, the pyramid seems to be the best fit for most of the particles. The results of this calculation are given in Figure 8.8(a). For the smallest NP (dark blue line), there is only a slight deviation from the 100% line of a flat Cu surface. With increasing NP size, the difference of the reflectivity for $\lambda < 600$ nm grows larger. The reflectivity is smaller for smaller wavelengths and even goes to zero for the largest NP (red line) for $\lambda < 400$ nm. In every progression, except for the smallest NPs (dark blue line), a local minimum around $\lambda = 550$ nm can be seen. The tip-to-tip NP distance for all simulated arrays was set to 150 nm. Hence, for the largest NPs, the simulated effective coverage was 64%, and for the smallest NPs, it was only 4%. In order to understand the impact of the effective coverage on the reflectivity profile, the NP arrays of height $h_{\text{pyr}} = 60$ nm and width $w_{\text{pyr}} = 60$ nm have been simulated with different tip-to-tip distances, which is shown in Figure 8.8(b). From this, a similar progression in the reflectivity can be seen compared to Figure 8.8(a), with the highest coverage (blue line, 64% coverage) exhibiting the smallest reflectivity and the smallest coverage (red line, 16% coverage) exhibiting the largest reflectivity.

These findings seem to reproduce the features seen in the measurements (cf. Figure 8.6) and are, therefore, indicative of plasmonics on the Cu nanostructures. To fully confirm plasmonic behavior and their use in analyzing the Cu surface, dCPV spectra should be considered, as is done in the following section.

8.2.5. Differential Treatment

Analyzing the changes in spectral features during cyclic voltammetry could provide insight into the processes on the surface and could contribute to the evaluation of whether these spectral features are of plasmonic origin.

In contrast to dCPV on Au NP arrays, not every CV can be used for a differential analysis, as the particles have to grow first. Additionally, the reflectivity of the Cu surfaces gets lower over time, and once a critical value is reached, the application of the dCPV method (cf. Chapter 5) yields no more useable data. The drop in reflectivity of Cu samples over long measurement time is illustrated in section A.4.3 of the appendix. Hence, the differential treatment shown in Figure 8.9 is taken from another measurement day than the data shown before.

Starting at $E_{\text{RHE}} = 0.2$ V and going to more anodic potentials on the blue curve, the oxidation of Cu occurs in the CV, which is replicated in the differential treatment. The subsequent reduction of Cu oxide at $E_{\text{RHE}} < 0.6$ V seems to occur in two steps in the CV: a sharp peak at $E_{\text{RHE}} = 0.58$ V and a broad peak at $E_{\text{RHE}} \approx 0.45$ V. The former is replicated

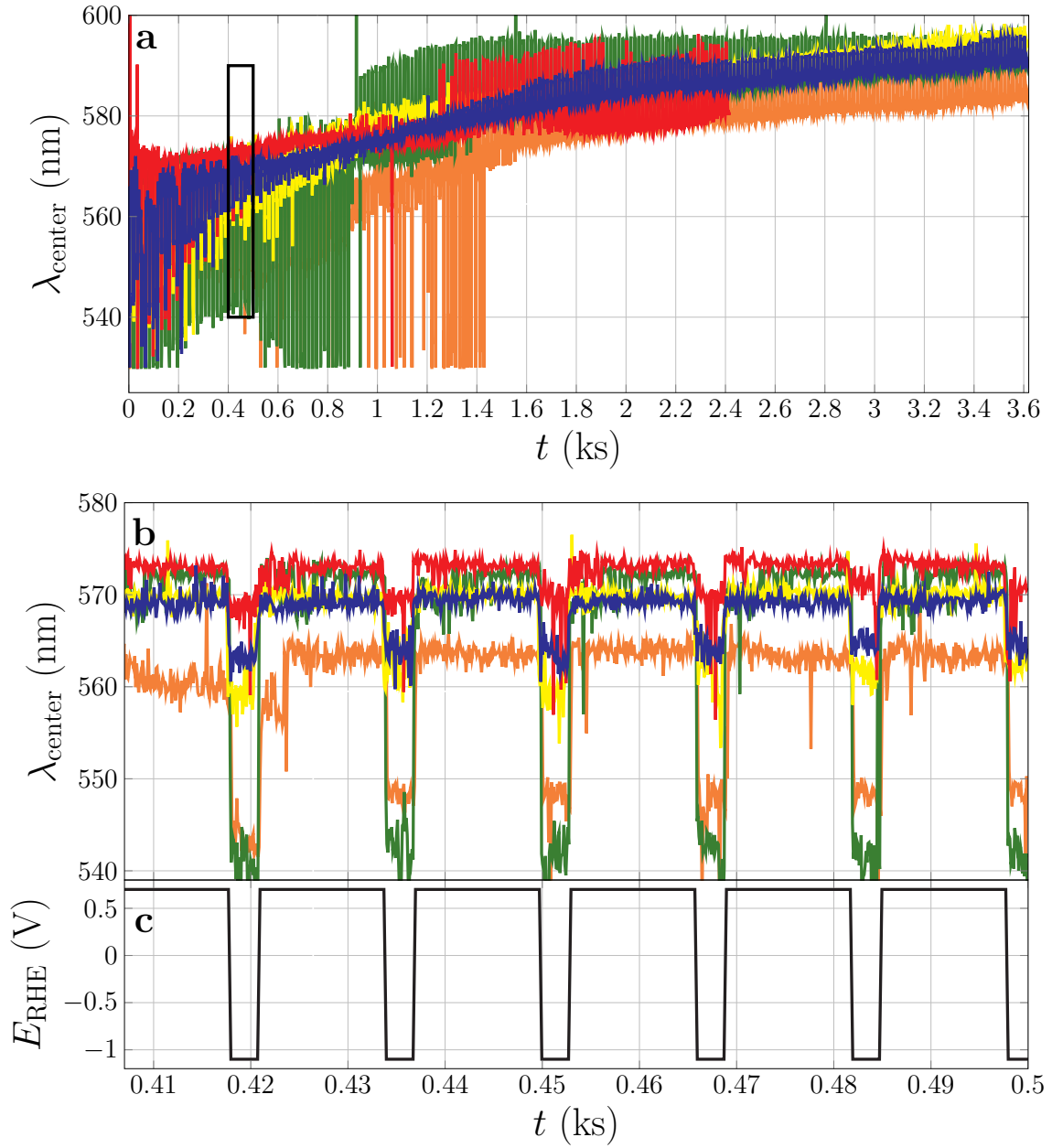


Figure 8.7.: Resonance position λ_{center} of the Gaussian peak versus time during a stepped potential treatment for several identical measurement protocols. (a) Complete time series, (b) zoom into the region marked by the black square in (a), and (c) corresponding potential progression. The electrolyte was 100mM KHCO_3 (CO_2 saturated, pH7), the oxidizing puls was set at $E_{\text{RHE,a}} = 0.7 \text{ V}$ for $t_a = 13 \text{ s}$, and the reductive puls was set at $E_{\text{RHE,c}} = -1.1 \text{ V}$ for $t_c = 3 \text{ s}$.

with a peak in the differential treatment, while the latter is replicated with a much more significant dip of the opposite sign. The CV exhibits two parallel branches for potentials $-0.3 \text{ V} < E_{\text{RHE}} < 0.3 \text{ V}$. The same region in the differential treatment is tilted but also approximately parallel. At the onset of the CO_2 reduction and hydrogen evolution reaction at $E_{\text{RHE}} < -0.3 \text{ V}$, the differential treatment exhibits a peak on the cathodic scan (orange)

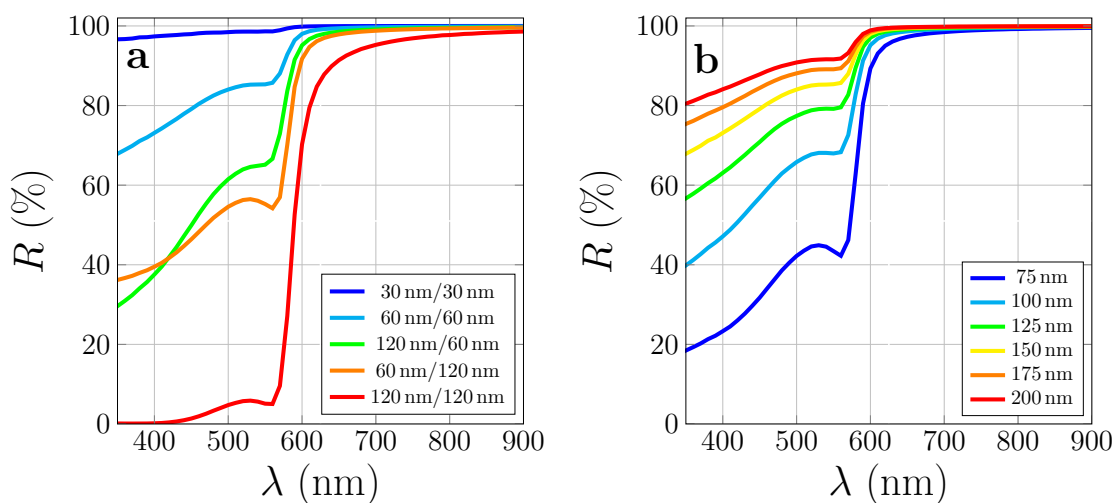


Figure 8.8.: Simulated reflectance spectra of Cu nanopyramid arrays on a Cu substrate in water. (a) Simulation of different base width and height combinations. The middle points of the individual NPs were spaced 150 nm in both x- and y-direction. The first value of the legend indicates the height of the pyramid, and the second indicates the side length of its base square. (b) Simulation of the $h_{\text{pyr}} = w_{\text{pyr}} = 60$ nm system with different NP spacings. All data shown in this Figure have been divided by the spectrum of a flat Cu (optical data from McPeak et al. [161]) surface in water (optical data from Kedenburg et al. [162]).

and a dip at the exact same potential ($E_{\text{RHE}} = -0.4$ V) on the anodic scan (blue).

Both the Cu oxidation/reduction and the CO_2 /hydrogen reduction seem to indicate adsorption/desorption and structural changes, respectively, in a way comparable to dCPV on Au NP arrays. In the following section, all findings will be summarized and discussed.

8.2.6. Discussion

Applying optical spectroscopy to in situ formed Cu NP on Cu substrates in a similar way to dCPV for Au NP arrays yields complex spectroscopic features. The first question that needs to be answered is whether these features are of a plasmonic nature. The second question is about whether the features can be used to monitor the state of the surface during electrocatalytic reactions.

Considering the AFM data, the structures obtained on the Cu surfaces are significant enough to exhibit plasmonic effects, as has been found for other roughened surfaces [163]. Moreover, the appearance of dips at around $\lambda = 570$ nm in the fully treated spectra of Figure 8.6(a) and the fact that they can be fitted rather well with a Gaussian function substantiate this interpretation. Of course, the part of the Cu spectrum (cf. Figure 8.4) that is most sensitive to any change of the surface is its edge at $\lambda = 570$ nm. Any compositional change, e.g., Cu oxide formation or increase in roughness, would result in changes at this edge. Consequently, the appearance of Gaussian-like “dips” alone is insufficient to assume plasmonics.

The simulated spectra, on the contrary, obtained peaks similar to those of the measurements while assuming only Cu on the surface. In comparison with the spectra simulated and measured on Au NP arrays (cf. Figures 4.15 and 4.7), the spectroscopic response seems to be inverted for the Cu NPs on Cu. The reason for this could be the difference in the support

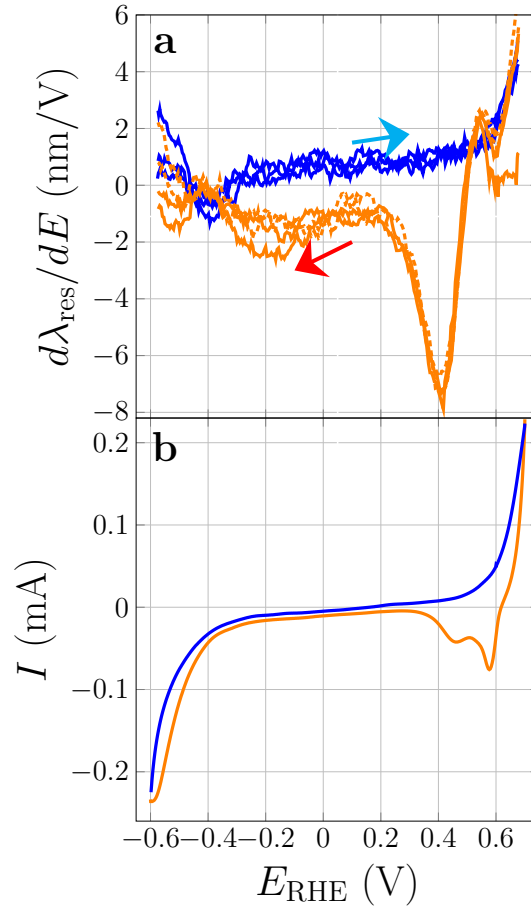


Figure 8.9.: Differential treatment of a Cu (a) surface during a CV (100 mM KHCO_3 (CO_2 saturated), 50 mV s^{-1}) (b) after stepped potential treatments.

material; while it was an oxide/semiconductor for the Au NPs, it is a metal for the Cu NPs. A plasmon excited on the former would, on average, add to the surface's reflectivity by re-emission. Given that the simulated Cu plate is perfectly flat and very reflective, a possible plasmonic excitation would, on average, dissipate energy in forms other than purely photonic re-emission, like phonon generation, thus decreasing the reflectivity.

The differential treatment in Figure 8.9(a) exhibits features that are very similar to dCPV curves obtained in previous chapters. For once, the division into two branches upon entering the double layer region follows the same pattern as for dCPVs on Au NP arrays. Additionally, the peaks around $E_{\text{RHE}} = -0.4$ V could be related to the adsorption (orange) and the desorption (blue) of molecules such as CO_2 , OH, H, during the reduction reactions. The onset of the adsorption peak coincides with the onset of the reduction current, and the existence of a subsequent desorption peak right before the reduction current subsides is akin to the behavior observed at the Au NP arrays. For the Cu oxidation/reduction reaction, the features are more complex, as we observe different signs of the peaks in the differential treatment for two reductive current peaks. Moreover, while the area under the curve of the Cu oxidation is larger than for the subsequent reduction peak, in the differential treatment, the area under the anodic scan of this potential region is dwarfed by the signal during the subsequent reduction. As has been found in the literature, the surface composition of Cu changes significantly during stepped potential programs, and hence, oxidation during a subsequent CV is expected

to drastically change the surface again. These are all strong indications of a plasmonic origin of the spectroscopic features observed in Figure 8.6. A final assessment can, however, only be given once all of the other findings regarding the analysis of the surface have been addressed.

The strongest indication that an effective optical analysis cannot be performed on these samples in this setting is the missing reproducibility of identical measurements, as shown in Figure 8.7(b). When the potentials switch from $E_{\text{RHE,a}} = 0.7 \text{ V}$ to $E_{\text{RHE,c}} = -1.1 \text{ V}$ or vice versa, the electron density and potentially the chemical composition of the surface changes rapidly, which is expected to be replicated in the spectroscopic features. If the step height of the center position $\Delta\lambda_{\text{center}}$ between the two puls potentials indicates the impact of the potential switch on the reflectance spectrum, then a spread as large as $4 \text{ nm} < \Delta\lambda_{\text{center}} < 30 \text{ nm}$ would indicate completely different surfaces.

The differences in progression and final resonance position seen in Figure 8.7(a), are not necessarily due to errors in the data treatment but might be due to differences in the development of the NPs over time. As can be seen from Figure 8.4, even the initial spectra do not look alike despite the samples having been subjected to the identical polishing treatment. Reasons for this difference might be slight variations in the polishing treatment and different states of oxidation that might affect bulk Cu even in deeper layers. There is currently no method to ensure or check for a higher level of comparability between the samples.

The drastic change in the progression of λ_{center} between Figures 8.6(c) and (e) shows that there is a significant transient change occurring on the surfaces during the measurement. This change, apart from nanoparticle formation and growth, might also affect the surface composition, which is vital to know in order to select appropriate reference spectra. Our current reference spectra include only gas evolution on basically pure Cu surfaces. If the surface were to be transiently changed, e.g., oxidized, these initial reference spectra might not be valid anymore and introduce artifacts that distort or even dominate any real features. This might be an explanation for the different behavior of Figures 8.6(c) and (e). Also, it would explain the fact that differential analysis is not possible after a certain time of potential step measurements.

All in all, it can be concluded that the spectroscopic features originate from plasmonics, but we lack enough information about the surface composition, which prevents a selection of suitable reference spectra, thus complicating the interpretation of the resulting graphs. Due to this, alternative ways of extracting optical data, not from fitting the peak but from the parameterization of the complete progression, are being explored. This intends to track all transient changes at once via machine-learning algorithms.

9. Summary and Outlook

In this thesis, plasmonic properties of Au NP arrays have been systematically utilized to develop a method for in situ sensing of properties of the electrochemical interface, such as electron density, NP morphology, and chemical composition of the surface. As this method is primarily used in parallel to cyclic voltammetry, it is called (differential) Cyclic Plasmo-Voltammetry (dCPV). Plasmonic resonances of metal NPs (also called localized surface plasmon resonances) depend on the electron density and the dielectric surrounding of the metal NPs. For example, charging the NP negatively, i.e., applying a cathodic potential, will shift the resonance position to smaller wavelengths. In contrast, the adsorption of molecules or ions will shift the resonance wavelength to larger values and increase the width of the resonance. Consequently, at the core of this method lies the reliable and constant tracking of the collective plasmonic resonance position λ_{res} of metallic NP arrays, which are subjected to electrochemical treatments, such as cyclic voltammograms. It has been shown that upon adequate data treatment, new fundamental insights about the EC interface can be gained when comparing dCPVs to the corresponding CVs. A proof of principle was done by showing the competitive adsorption of sulfate ions and oxygen on Au and differentiating the different stages of Cu underpotential deposition on Au.

In the following, (d)CPV and corresponding COMSOL simulations were used to analyze the stability of Au NPs under different pH and in various potential ranges. It was found that Au NPs undergo morphology changes from flat cylinders with a crown-like extrusion on top to higher and thinner cylinders as soon as electrochemical measurements were conducted on them. The speed of the morphological change depended thereby strongly on the potential range, with cycling in the double layer region having the least impact, cycling in the Au oxidation/reduction region having a slight impact, and evolving hydrogen having by far the strongest impact on morphological changes. Additionally, the shape change was far stronger in sulfuric acid (pH1) than it was in buffered KOH + H₃PO₄ electrolyte (pH7). A potential explanation for the difference between the shape changes in both electrolytes was a stabilizing effect by the K⁺ ion in the neutral system. It was hypothesized that without K⁺ ions present, the adsorbed hydrogen diffuses into the first few sublayers of the Au surface and thereby weakens the Au-Au bonds. Consequently, the Au atoms were much more likely to be displaced on the surface due to constant bond formation and breaking of the HER. In the neutral system, we discussed that the K⁺ ion is likely to stabilize the Au-H bonds and to form ternary-metal hydride-like complexes, which not only preserve the morphology during the HER but also during an extended amount of time later. This was, to our knowledge, the first time that the morphology of Au electrodes was tracked in situ, and hydrogen adsorption on Au was shown in situ during HER.

Apart from HER, dCPV was also applied to reactions involving Fe^{3+/2+} and Fe(CN)₆^{3-/4-}. It was shown that under high reaction currents of non/weakly adsorbing species, the capacitive charging of the surface is reduced. One hypothesis for this was the non-equilibrium condition induced by the constant stream of effectively positive/negative charges in front of the electrode, which diminished the effective counter charge on the electrolyte side. On top of that, the complex behavior of competitive interaction between Fe(CN)₆^{3-/4-} and H₂PO₄⁻/HPO₄²⁻ was shown.

In order to expand the range of application of dCPV to more applied systems, the first steps

9. Summary and Outlook

towards plasmonic spectroscopy were done for self-assembled Cu NPs on Cu plates under high currents of stepped potential programs used for experiments on CO₂RR. For this, simulations and plasmonic spectroscopy on Cu samples of different NP formation levels were conducted, indicating stable plasmons excited on these samples. During the measurements, the main challenges were the treatment of the intensive gas bubble formation and the continuous unaccounted compositional change of the Cu surface. The former challenge was addressed by designing adaptable reference spectra; the latter, however, has not yet been fully solved.

With these findings, this thesis could hopefully position dCPV as a viable and affordable interface spectroscopy method. In order for its range of applications to expand, several next steps can be taken, which are noted in the following.

In the future, the data treatment of Cu NP on plain Cu plates, and consequently, any NP formation on metallic electrodes, has to be critically evaluated and adapted. The main goal hereby is to get more insight into the compositional change of the Cu surface and use this to design suitable reference spectra. Currently, a machine-learning-based approach is being developed, where the characteristic slope at $\lambda = 550$ nm of the Cu spectrum (cf. Figure 8.4) is tracked and compared to a large database of these slopes with a multitude of potential plasmonic impacts. In short, several plasmonic resonance curves of different properties (position, width, and intensity) have been artificially added to the progression of the slope, which makes up the training dataset used to analyze the real data. Additionally, the sample preparation is adapted to be more uniform in order to be able to compare the results, which might prove possible for the first 15-30 minutes. Then, this optical data, together with the GC data, could be used to relate the NP formation (or the inhibition thereof) to the products, which will deepen our understanding of the CO₂RR on Cu.

The results on the (in)stability of Au in aqueous electrolytes under various conditions could be extended to include different pH ranges in combination with different cat- and anions. For example, several sets of 100 mM H₂SO₄ with individually added K⁺, Na⁺, Li⁺, Cs⁺ ions in concentrations ranging from 1 mM to 100 mM. The corresponding anion should be SO₄²⁻ so as not to introduce another ionic species. These results could be used to prove or adapt the current hypothesis on the exact role of the cation in stabilizing the surface. Another extension could be made by combining dCPV and fourier-transform infrared spectroscopy (FTIR). Ideally, the FTIR illuminates the sample from the back, while the dCPV illuminates the sample from the front without disturbing each other due to the difference in wavelengths and illumination angles. This has the potential to simultaneously pinpoint the exact potential window where adsorptions occur (dCPV) and measure the resulting bonds via FTIR. As bands like Au-H have not been measured so far, it is expected to be a rather small signal, which makes the information from an adjacent technique vital. This might lead to new insights into the energetics of the Au-H bond, which could prove essential in investigating details of the Au-hydrogen interaction.

Regarding the experiments on the dynamic depolarization of the double layer, it would be instructive to use electrolytes consisting of only non-adsorbing species that do not undergo complexation. Then, the changes in the dCPV could be attributed solely to the change in the charged state in the appropriate potential ranges. This, in turn, could lead to a quantitative comparison of different redox couples and new and more fundamental models of the dynamic double layer.

Finally, now that plasmonics on the Au NP arrays have been shown throughout this thesis and investigated in-depth, very accurate plasmonic catalysis experiments could be designed, as the inevitable change of the resonance position is now well known. One approach to realize this would be to combine a comparatively weak white light source with a monochromatic

laser. The laser is used to induce plasmonic catalysis, while the white light spectrum can be analyzed via dCPV to give the current position and shape of the plasmonic resonance. Although the wavelength range of the laser will distort the plasmonic spectrum on a small wavelength window, the remainder of the unaffected spectrum will most often be enough to apply dCPV to the system. Then, combined with product analysis, the catalytic impact of the plasmon, alongside degradation and adsorption, can be fully resolved. A measurement setup as such might prove able to uncover unknown mechanisms behind catalytic effects in more complex systems.

A. Appendix

A.1. List of Abbreviations

Table A.1.: List of Abbreviations

AFM	atomic force microscopy
CE	counter electrode
CID	chemical interface damping
CO ₂ RR	CO ₂ reduction reaction
CPE	constant phase element
CPV	Cyclic Plasco-Voltammetry/Voltammogram
CV	cyclic voltammetry/voltammogram
dCPV	differential Cyclic Plasco-Voltammetry/Voltammogram
DI	deionized
ECSA	electrochemical active surface area
EIS	electrochemical impedance spectroscopy
FDTD	finite difference time domain
FEM	finite element method
FWHM	full width at half maximum
HER	hydrogen evolution reaction
LO-NIL	lift-off nanoimprint lithography
LSPR	localized surface plasmon resonance
NP	nanoparticle
OCP	open circuit potential
OPD	overpotential deposition
PZC	point of zero charge
RE	reference electrode
RHE	reversible hydrogen electrode
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
UPD	underpotential deposition
WE	working electrode

A.2. Supporting Information for Chapter 6

A.2.1. Long Term Stability Measurement Details

Each treatment in Figure 6.5 consists of multiple CVs and EIS measurements. The treatments follow the protocols that are summarized in Tables A.2,A.3,A.4,A.5.

Table A.2.: Measuring protocols used in treatments T1 -T11 of Figure 6.5 of Chapter 6. If under 'Nr.' occurs a number 'x' it refers to the x^{th} potential range of Cyclic Voltammograms that were measured, where the potential range from E_{MSE}^{high} to E_{MSE}^{low} was maintained for 2-5 cycles. The number '0' refers to the cleaning cycles. EIS indicates that Electrochemical Impedance Spectroscopy (EIS) measurement were carried out. EIS data were always recorded in 50mV steps. The concentration of the electrolyte was 100mM and the salt used is shown next to the treatment number Tx. In the last column the scan rate is given. Any measurement in which hydrogen was evolved is highlighted (cyan). All potentials are given with respect to the mercury/mercurous sulfate reference electrode (MSE) $E_{SHE} = E_{MSE} + 680mV$.

	Nr.	E_{MSE}^{high} (V)	E_{MSE}^{low} (V)	ν (mV/s)
T1	K ₂ SO ₄			
	0	700	-800	50
	1	800	-850	50
	2	400	-400	10
	3	400	-400	10
	4	700	-700	50
	5	800	-700	50
	6	400	-400	5
	EIS	400	-750	
	7	800	-700	50
T2	Na ₂ SO ₄			
	0	700	-800	50
	1	800	-850	50
	2	375	-425	10
	3	800	-700	50
	4	375	-425	5
	EIS	400	-800	
	5	800	-700	50
	6	800	-700	50

Table A.3.: Continuation of Table A.2

	Nr.	E_{MSE}^{high} (V)	E_{MSE}^{low} (V)	ν (mV/s)
T4	K ₂ SO ₄			
	0	700	-800	50
	1	800	-850	50
	2	400	-400	10
	3	400	-400	10
	4	800	-700	50
	5	400	-400	5
	EIS	400	-750	
	6	800	-700	50
	7	800	-700	50
	8	400	-400	10
	EIS	400	-750	
	9	800	-700	50
T5	Cs ₂ SO ₄			
	0	700	-800	50
	1	800	-850	50
	2	800	-850	50
	3	850	-850	50
	4	500	-500	10
	5	800	-850	50
	6	500	-500	5
	EIS	500	-900	
	7	800	-850	50
T3	Li ₂ SO ₄			
	0	700	-800	50
	1	800	-850	50
	2	400	-400	10
	3	800	-700	50
	4	400	-400	5
	5	800	-700	50
	EIS	400	-750	

Table A.4.: Continuation of Table A.3

	Nr.	E_{MSE}^{high} (V)	E_{MSE}^{low} (V)	ν (mV/s)
T6	Na ₂ SO ₄			
	0	700	-800	50
	1	800	-900	50
	2	850	-1100	50
	3	850	-1100	2.5
	4	850	-1100	2.5
	EIS	400	-900	
	5	850	-1100	50
	6	850	-1100	50
T7	K ₂ SO ₄			
	0	700	-800	50
	1	800	-1000	50
	2	850	-1050	50
	3	850	-1100	2.5
	4	850	-1050	50
	EIS	400	-900	
	5	850	-1050	50
T8	Na ₂ SO ₄			
	0	700	-800	50
	1	850	-1050	50
	2	850	-1100	2.5
	3	850	-1050	50
	EIS	400	-900	
	4	850	-1050	50

Table A.5.: Continuation of Table A.4

	Nr.	E_{MSE}^{high} (V)	E_{MSE}^{low} (V)	ν (mV/s)
T9	K ₂ SO ₄			
	1	850	-1050	50
	2	850	-1100	2.5
	3	850	-1050	50
	EIS	400	-900	
	4	850	-1050	50
T10	Na ₂ SO ₄			
	1	850	-1050	50
	2	850	-1100	2.5
	EIS	0	-900	
	3	850	-1050	50
	4	850	-1050	50
T11	Li ₂ SO ₄			
	1	850	-1050	50
	2	850	-1100	2.5
	EIS	400	-900	
	3	850	-1050	50
	4	850	-1050	50

A.2.2. Change in Morphology of the AFM Insets in Figure 6.5

The change in morphology of the 2D AFM images (insets of Figure 6.5) can be seen more clearly in the zoomed-in version shown in Figure A.1.

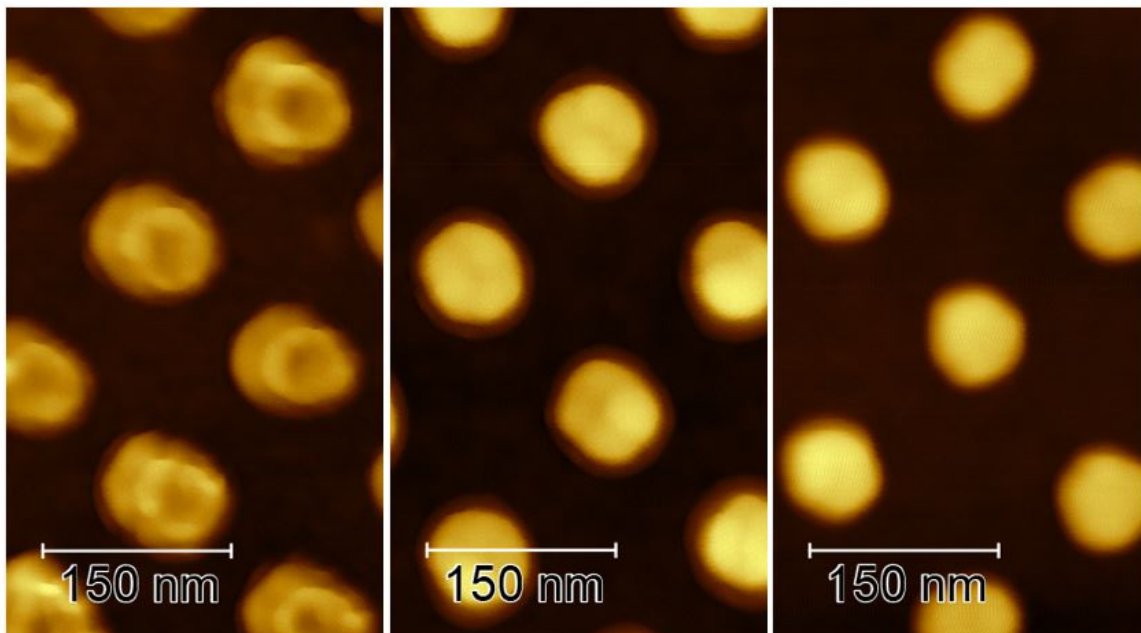


Figure A.1.: Up-scaled AFM images shown in the inset of Figure 6.5. A change in morphology is clearly visible from the left (near pristine) to the aged version in the middle and the last AFM image after all treatments T1-T11.

A.2.3. Degradation of Nanodisks via AFM Profiles

In this section, two further examples of radial AFM profiles show the different stages of degradation of the nanostructures, as shown in Figure 6.6. It can be seen that the morphological change of these samples follows the same trend towards higher and more narrow nanodisks as for the example shown in Figure 6.6.

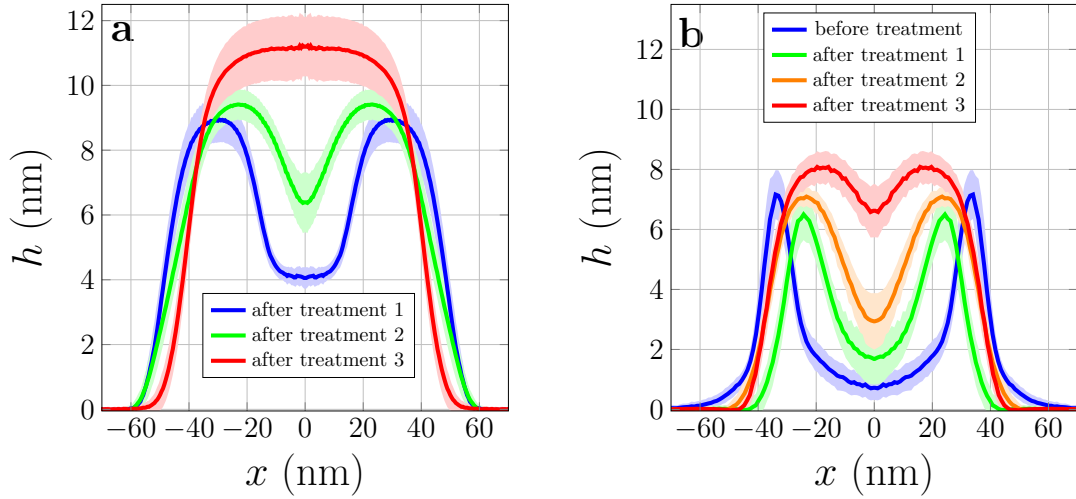


Figure A.2.: Radial AFM profiles of the nanodisks for different stages of degradation for two further samples.

A.2.4. Test of a Possible Impact of Plasmonic Excitations on the Degradation of Nanostructures

In this section, we present two measurements with two very similar nanostructured samples that were subject to identical potential protocols. One sample was illuminated during the measurement for parallel CPV recording; the other was kept in the dark, except for only a few seconds in between specific measurements (always at OCP), during which the optical spectra shown in Figure A.3b were recorded. Figure A.3a shows the corresponding AFM profiles before and after each measurement. It can be seen that apart from a general slight difference in sample geometry due to the fabrication process, the progression is very similar. It is therefore concluded that white light illumination and plasmon excitations do not change the morphology, and (d)CPV is a very sensitive, noninvasive in situ sensing technique.

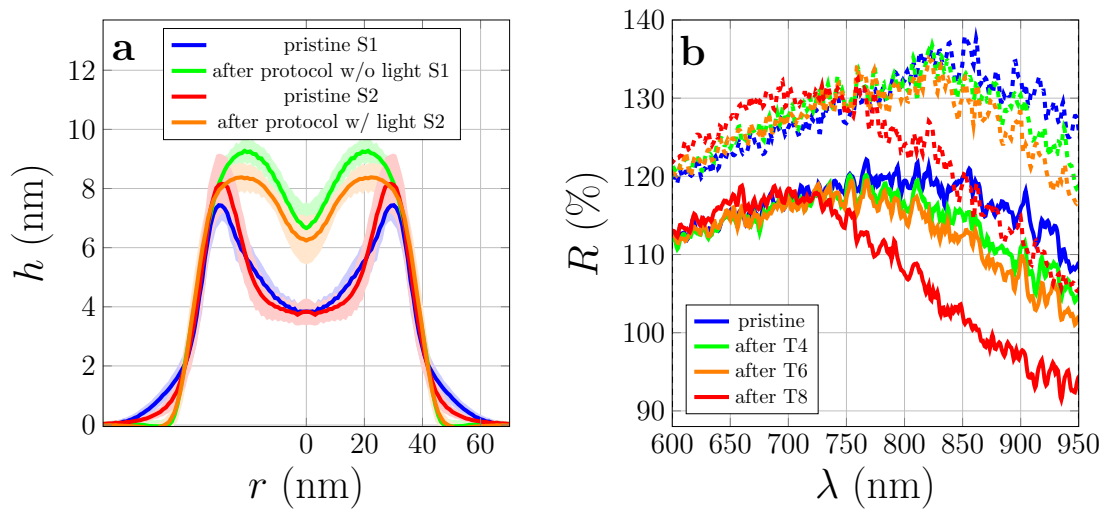


Figure A.3.: Degradation measurement assessing the impact of white light illumination and plasmon excitations on changes of the nanostructure morphology. Both samples S1 and S2 were subjected to the same measurement protocols, i.e., potential 'treatments' T1 - T9 (which were, however, not identical to those listed in Tables A.2,A.3,A.4,A.5. (a) Averaged radial profiles of AFM images before and after the entire measurement protocol. (b) Optical spectra of the plasmonic nanoparticle arrays at equivalent times of the measurement protocol.

A.2.5. dCPV of an Au NP Array in Acid with and without K^+ Ions

In section 6.3.3, we hypothesize that the lower degradation rate of the nanostructures in the neutral electrolyte is due to the formation of ternary surface metal hydrides that stabilize the surface. To substantiate this point, we conducted a control experiment in which we added potassium sulfate to a sulfuric acid electrolyte and compared the dCPVs before and after the salt addition. As can be seen in Figure A.4, the down bending in the HER region of the dCPV, which is indicative of degradation, is smaller in the presence of K^+ ions than in the absence. Though the effect is small, it shows the expected qualitative trend.

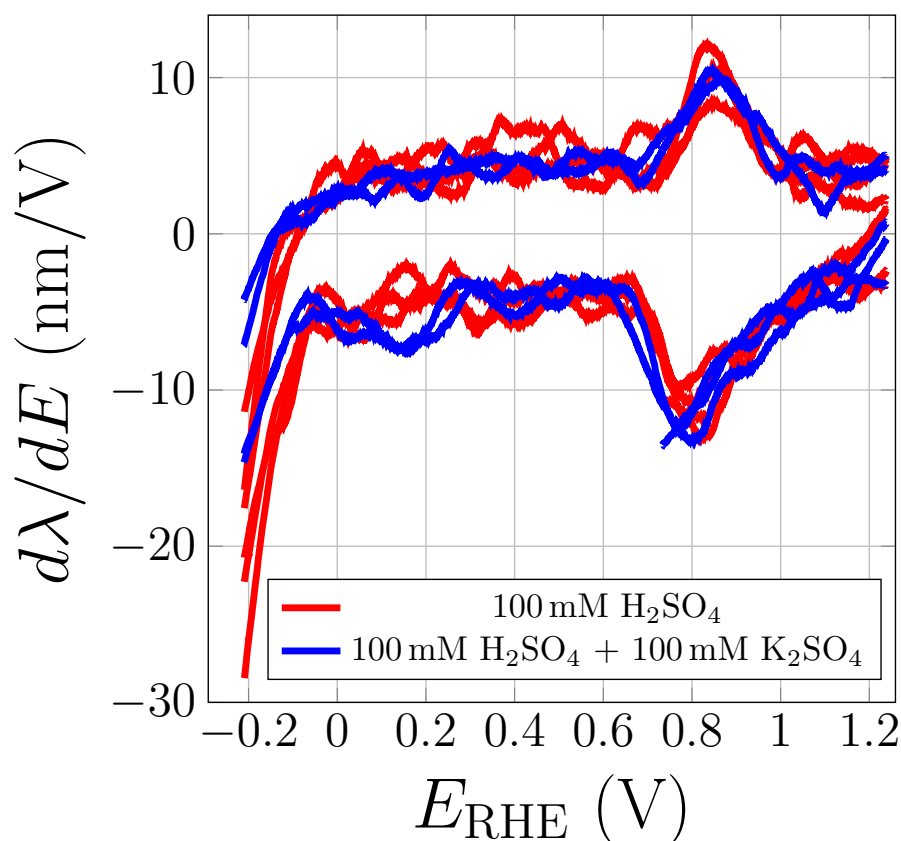


Figure A.4.: dCPV of a Au NP array cycled in the double layer and HER region with (blue) and without (red) K^+ ions. Electrolyte: 100mM H_2SO_4 (red) and 100mM H_2SO_4 + 100mM K_2SO_4 (blue)

A.3. Supporting Information for Chapter 7: EIS Data of $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Fe}^{3+/2+}$ Redox Reactions

For comparison, EIS measurements have been performed for the reference systems, the ferro/ferricyanide (System I), the $\text{Fe}^{3+/2+}$ system (System II) and are shown in Figure A.5. The measurements of the latter systems only comprise a few measurements around their respective OCP, as large currents over extended amounts of time were kept to a minimum so as not to change the ratio of the ionic species in the bulk.

It can be seen that the capacitance of System I (Figure A.5(a)) is only slightly impacted by the addition of the ferro/ferricyanide and the resulting faradaic current. The electrolyte resistance (Figure A.5(b)) is expected to be slightly lower compared to the reference solution as more ions are introduced.

The proposed depolarization mechanism should be visible in a reduction of capacitance, which is not visible in Figure A.5(a).

The capacitance of System II (orange line) is indeed lower than that of the buffer solution (blue line) around the OCP but seems to increase for increasing currents. The series resistance at and around the OCP is smaller than that of the buffer solution, which is expected as more ions are introduced. From this alone, the decrease in double layer charging cannot be explained, as the capacitance exhibits a complex behavior in the presence of faradaic currents, as explained in Chapter 7.

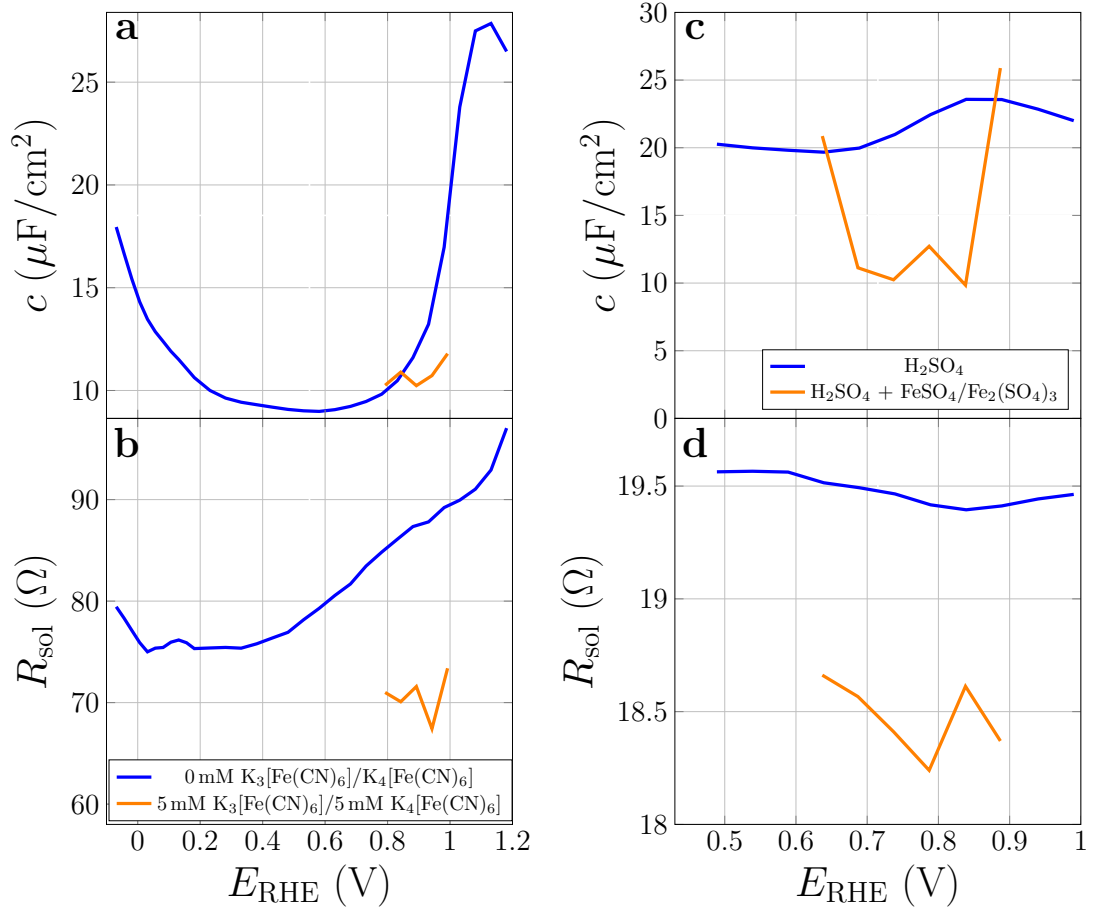


Figure A.5.: Specific capacitance c and solution resistance R_{sol} of the two outer sphere redox pairs. (a),(b): plain Au electrode in 4 mM $\text{K}_4\text{Fe}(\text{CN})_6 + 4$ mM $\text{K}_3\text{Fe}(\text{CN})_6 + 180$ mM $\text{KOH} + 120$ mM H_3PO_4 (pH 6.8). (c),(d): plain Au electrode in 4 mM $\text{FeSO}_4 + 4$ mM $\text{Fe}_2(\text{SO}_4)_3 + 100$ mM H_2SO_4 (pH 1).

A.4. Supporting Information for Chapter 8

A.4.1. Additional AFM Images of Treated Cu Surfaces

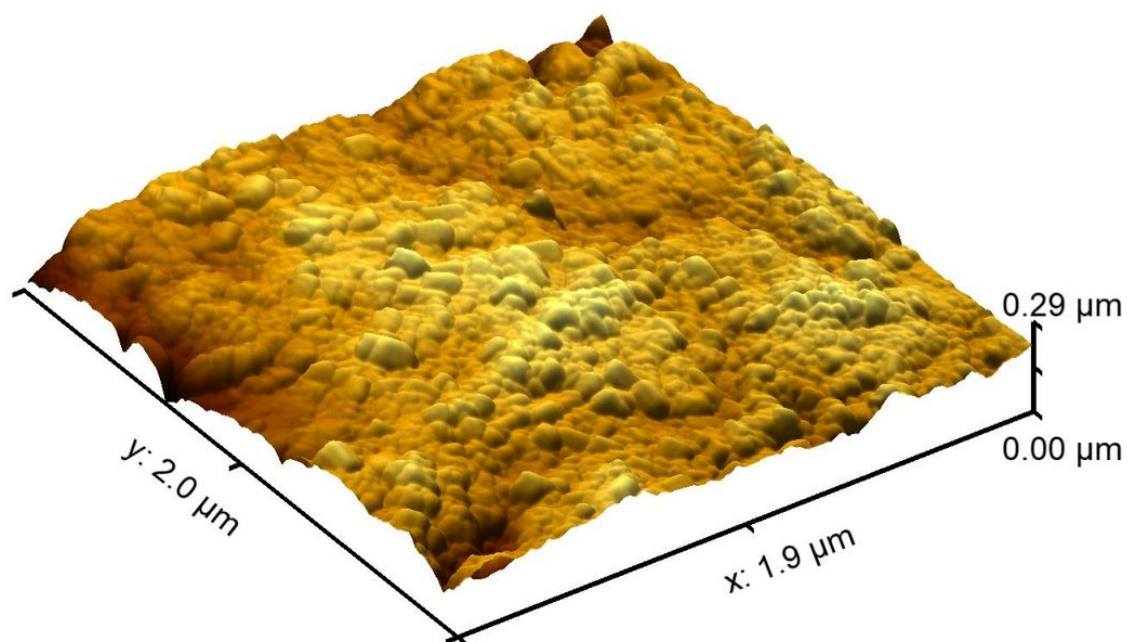


Figure A.6.: AFM data of a plain Cu electrode after 1h of stepped potentials and 30min of constant reduction potential.

A.4.2. Simulation Geometries of the Cu NPs

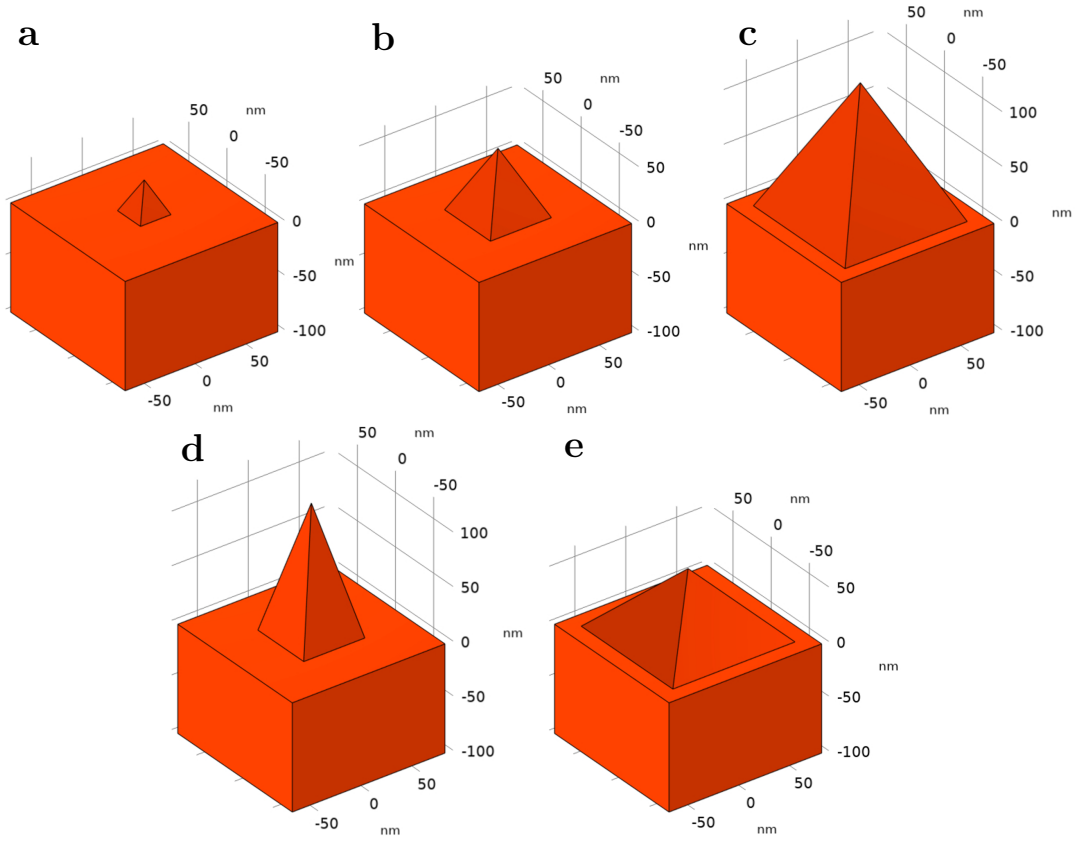


Figure A.7.: Geometries of the different nanoparticles simulated via COMSOL and shown in Figure 8.8(a). Each geometry represents one unit cell of the simulated array. The NP geometry is a pyramid of height h_{pyr} with a square base of side length w_{pyr} . The parameters were (a) $h_{\text{pyr}} = w_{\text{pyr}} = 30$ nm, (b) $h_{\text{pyr}} = w_{\text{pyr}} = 60$ nm, (c) $h_{\text{pyr}} = w_{\text{pyr}} = 120$ nm, (d) $h_{\text{pyr}} = 120$ nm, $w_{\text{pyr}} = 60$ nm, and (e) $h_{\text{pyr}} = 60$ nm, $w_{\text{pyr}} = 120$ nm. The red parts represent Cu (optical data from McPeak et al. [161]), and filling up the top part of the geometry (not shown here) is water (optical data from Kedenburg et al. [162]).

A.4.3. Long Term Measurement Protocols

Another challenge is the fact that the overall reflectivity of the samples decreases over time, as can be seen in Figure 8.6 for the first hour. As the references have been obtained from fully reflective samples and the measured reflectivity drops continuously over time, the selection of the reference spectra gets more inaccurate the longer the measurement goes on. This darkening of Cu could be due to oxidation and roughening, but the exact reason has not been verified yet. Figure A.8 shows the progression of the original spectra over time, starting with the dark blue one and continuing to the red one. The most important change here is the disappearance of the characteristic drop at 550 nm. The bottom-most curve is dominated by the reflection signal from the glass window in the EC cell, with the Cu reflectivity nearly completely suppressed to extract any usable features from it.

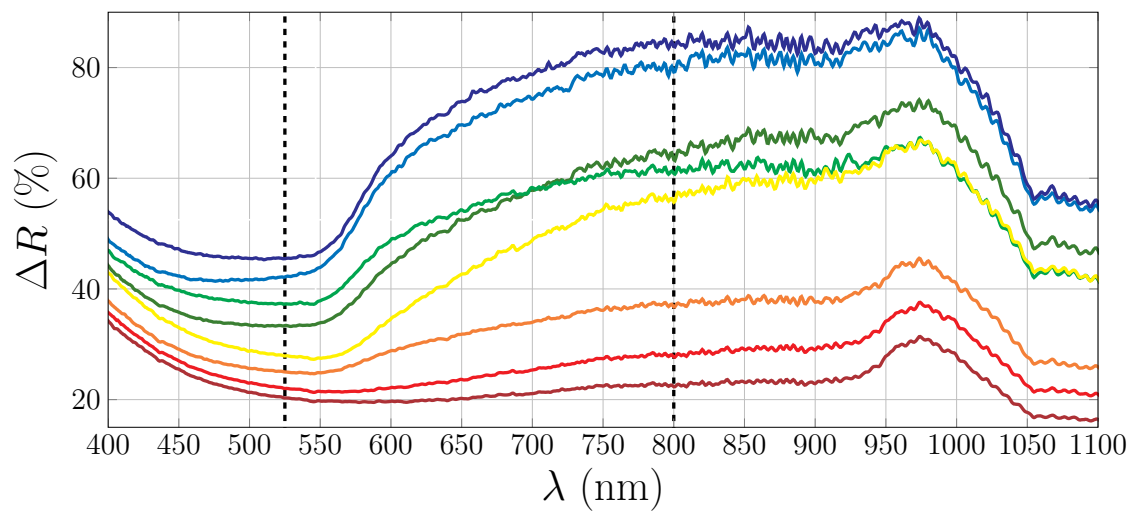


Figure A.8.: Example spectra recorded for different stages of visible oxidation and different samples. The area between the dashed lines indicates the part of the spectra that are used for fitting.

A.5. Python Code

A.5.1. Necessary Packages

```

from lmfit.models import *
import matplotlib as mpl
import glob
import numpy as np
import re
from scipy.optimize import curve_fit
import matplotlib.pyplot as plt

from mpl_toolkits.axes_grid1 import host_subplot
import mpl_toolkits.axisartist as AA

import math
from scipy.signal import savgol_filter
from scipy.signal import savgol_coeffs

from impedance import preprocessing
from impedance.models.circuits import CustomCircuit
from impedance.visualization import plot_nyquist
import pylab
from scipy.signal import find_peaks
import scipy.integrate as integrate

```

A.5.2. Removal of Outliers in Optical Datasets

```

def res_remove_outliers(res, rate):
    res_new = []
    n = 10
    for i in range(n):
        res_new.append(res[i])
    for i in range(n, len(res)):
        mean = np.mean(res[i-n:i])
        if abs(mean-res[i]) > 60*rate: #rate in V/m
            res_new.append(mean)
        else:
            res_new.append(res[i])
    return res_new

```

A.5.3. Inserting Missing Data Points

```

def time_fill(t, res):
    t_new = []
    res_new = []

```

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```
for i in range(len(t)-1):
    t_new.append(t[i])
    res_new.append(res[i])

    diff = abs(t[i+1] - t[i])
    res_slope = (res[i+1] - res[i]) / (t[i+1] - t[i])
    if diff > 0.15:
        a = int(diff / 0.1)
        for j in range(1, a):
            t_new.append(t[i] + j * 0.1)
            res_new.append(res_slope * j * 0.1 + res[i])
    else:
        pass
```

A.5.4. Removing Wrong Timestamps

```
def smoothing_time2(time_real, d_min=0.05, d_max=0.13):
# prev d_max = 0.15
    time_good = []
    time_good.append('unknown')
    for i in range(1, len(time_real)-1):
        if d_max < (time_real[i+1]-time_real[i]) or \
            (time_real[i+1]-time_real[i]) \
            < d_min or d_max < (time_real[i]-time_real[i-1]) > d_min \
            or (time_real[i]-time_real[i-1]) < d_min:
            time_good.append('unknown')
        else:
            time_good.append(time_real[i])
    time_good.append('unknown')
    a = time_good.index(next(x for x in time_good if x != 'unknown'))
    print(a)
    for i in range(0, a):
        time_good[i] = time_good[a] - (a-i)*0.10000000
    for i in range(a, len(time_good)):
        if time_good[i] == 'unknown':
            print('smoothing_time activated')
            time_good[i] = time_good[i-1] + 0.10000000
        else:
            pass
    return time_good
```

A.5.5. Manual Application of the Savitzky-Golay-Filter

```
def Filter_By_Hand(cyc, a_2_5=401, b=1, c=0.001, d=2, \
    multiplot='no', color='blue', labeladd='', remove_forward=[],
    remove_back=[], color3='blue', zoom=[], number=r'0', \
    date=r'1900-01-01', R_sol=0, a=0):
```

```

#cyc = [time, voltage_dCPV, resonance_dCPV, V_CV, I_CV,\\
        file_title, rate_CV, u_fin, res_fin, other_fin, listname, t,\\
        u_fin_IR]

c = 0.1 * cyc[6]

filen = cyc[13]

res_fin = cyc[8]
listname = cyc[10]
u_fin_IR = cyc[12]

if a == 0:
    rate = cyc[6]
    if 0.08 < rate:
        a = 21
    if 0.03 < rate < 0.08:
        a = 31
    if 0.008 < rate < 0.045:
        a = 101
    if rate < 0.007:
        a = a_2_5
    print('savgol_a = ', a)

print(c)

# smoothing the data
def Funktion(x, a, b, c):
    return a*x**2+b*x+c

# preparing the edges of the dataset
u_fin_IR_ext = []
res_fin_IR_ext = []
for i in range(len(u_fin_IR)):
    if u_fin_IR[i][0] < u_fin_IR[i][-1]:
        print("up")
        ext_lower = np.linspace(
            u_fin_IR[i][0]-(a-1)/2*c, u_fin_IR[i][0]-c,\\
            int((a-1)/2))
        ext_higher = np.linspace(
            u_fin_IR[i][-1]+c, u_fin_IR[i][-1]+(a-1)/2*c,\\
            int((a-1)/2))
        u_fin_IR_ext.append(np.concatenate(
            [ext_lower, u_fin_IR[i], ext_higher], axis=0))
# edges extension with fit function of the edge dataset
y_split = res_fin[i][0:a]
x_split = u_fin_IR[i][0:a]
popt, pcov = curve_fit(
    Funktion, x_split, y_split, p0=[1, 1, y_split[0]])

```

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```

res_e_l = [i**2*popt[0]+i*popt[1]+popt[2] for i in\\
ext_lower]

y_split = res_fin[i][-a:-1]
x_split = u_fin_IR[i][-a:-1]
popt, pcov = curve_fit(
    Funktion, x_split, y_split, p0=[1, 1, y_split[-1]])

res_e_h = [i**2*popt[0]+i*popt[1]+popt[2] for i in\\
ext_higher]

res_fin_IR_ext.append(np.concatenate(
    [res_e_l, res_fin[i], res_e_h], axis=0))
# res_e_h = [res_fin[i][-1]]*int((a-1)/2) for constant
# extension of the dataset
else:
    print("down")

ext_lower = np.linspace(
    u_fin_IR[i][-1]-c, u_fin_IR[i][-1]-(a-1)/2*c,\\
    int((a-1)/2))
ext_higher = np.linspace(
    u_fin_IR[i][0]+(a-1)/2*c, u_fin_IR[i][0]+c,\\
    int((a-1)/2))

u_fin_IR_ext.append(np.concatenate(
    [ext_higher, u_fin_IR[i], ext_lower], axis=0))

y_split = res_fin[i][-a:-1]
x_split = u_fin_IR[i][-a:-1]
popt, pcov = curve_fit(
    Funktion, x_split, y_split, p0=[1, 1, y_split[-1]])

res_e_l = [i**2*popt[0]+i*popt[1]+popt[2] for i in\\
ext_lower]

y_split = res_fin[i][0:a]
x_split = u_fin_IR[i][0:a]
popt, pcov = curve_fit(
    Funktion, x_split, y_split, p0=[1, 1, y_split[0]])

res_e_h = [i**2*popt[0]+i*popt[1]+popt[2] for i in\\
ext_higher]

res_fin_IR_ext.append(np.concatenate(
    [res_e_h, res_fin[i], res_e_l], axis=0))

```

```

y_smooth = []
x_smooth = []
y_diff = []
for j in range(len(res_fin_IR_ext)):
    y_smooth_branch = []
    x_smooth_branch = []
    y_diff_branch = []
    for i in range(int((a-1)/2), len(res_fin_IR_ext[j])-\\
int((a-1)/2)):
        y_split = res_fin_IR_ext[j][i-int((a-1)/2): i+1+\\
int((a-1)/2)]
        x_split = u_fin_IR_ext[j][i-int((a-1)/2): i+1+\\
int((a-1)/2)]
        x_split_center = [u_fin_IR_ext[j][i]-k for k in x_split]
        sigma = [gaussian(i, 0, a*c) for i in x_split_center]

        popt, pcov = curve_fit(Funktion, x_split_center, \\
y_split, p0=[1, 1, res_fin_IR_ext[j][i]], sigma=sigma)
        y_smooth_branch.append(popt[2])
        if x_split[0] < x_split[-1]:
            y_diff_branch.append(-popt[1])
        else:
            y_diff_branch.append(popt[1])

    x_smooth_branch.append(u_fin_IR_ext[j][i])

y_smooth.append(y_smooth_branch)
x_smooth.append(x_smooth_branch)
y_diff.append(y_diff_branch)

#divide in forward and backward
forward = []
forward_k = []
forward_u = []

back = []
back_k = []
back_u = []

for i in range(len(x_smooth)):
    if x_smooth[i][0]-x_smooth[i][-1] < 0:
        forward_u.append(x_smooth[i])
        forward.append(y_diff[i])
        forward_k.append(y_kernel_smooth[i])
    else:
        back_u.append(x_smooth[i])
        back.append(y_diff[i])
        back_k.append(y_kernel_smooth[i])

```

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```

for i in remove_forward:
    forward.pop(i)
    forward_u.pop(i)
    forward_k.pop(i)
for i in remove_back:
    back.pop(i)
    back_u.pop(i)
    back_k.pop(i)

# find the longest lists to orient all other lists to
# -> they have to have the same length for averaging
lenf = [len(i) for i in forward]
lenf_k = [len(i) for i in forward_k]
lenf_u = [len(i) for i in forward_u]
print(lenf, lenf_u)
# longlist_f = forward[lenf.index(max(lenf))]
longlist_u_f = forward_u[lenf.index(max(lenf))]
print(type(forward_u[0][0]))
lenb = [len(i) for i in back]
lenb_k = [len(i) for i in back_k]
# longlist_b = back[lenb.index(max(lenb))]
longlist_u_b = back_u[lenb.index(max(lenb))]

# averaging over the respective branches
# (only for those values, that are close together)
u_avg_f = []
diff_avg_f = []
diff_avg_f_k = []
for i in range(len(longlist_u_f)):
    u_mean = 0
    diff_mean = 0
    diff_k_mean = 0
    counter = 0
    for j in range(len(forward_u)):
        for k in range(len(forward_u[j])):
            if abs(longlist_u_f[i] - forward_u[j][k]) < c/2:
                u_mean += forward_u[j][k]
                diff_mean += forward[j][k]
                diff_k_mean += forward_k[j][k]
                counter += 1
            else:
                pass
    u_avg_f.append(u_mean/counter)
    diff_avg_f.append(diff_mean/counter)
    diff_avg_f_k.append(diff_k_mean/counter)

```



```

u_avg_b = []
diff_avg_b = []
diff_avg_b_k = []
for i in range(len(longlist_u_b)):
    u_mean = 0
    diff_mean = 0
    diff_k_mean = 0
    counter = 0
    for j in range(len(back_u)):
        for k in range(len(back_u[j])):
            if abs(longlist_u_b[i]-back_u[j][k]) < c/2:
                u_mean += back_u[j][k]
                diff_mean += back[j][k]
                diff_k_mean += back_k[j][k]
                counter += 1
            else:
                pass
    u_avg_b.append(u_mean/counter)
    diff_avg_b.append(diff_mean/counter)
    diff_avg_b_k.append(diff_k_mean/counter)

return u_avg_f, diff_avg_f, u_avg_b, diff_avg_b

```


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