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Quick synthesis of fluorescent nitrogen-doped carbon nanoparticles for selective and sensitive Fe(III) detection in water

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ABSTRACT

Recently, fluorescent carbon nanostructures have attracted enormous attention thanks to their excellent optical properties, low-cost, chemical inertness and stability. In this study, we demonstrated a quick, facile, environment-friendly and low-cost synthesis method for the preparation of fluorescent nitrogen-doped carbon nanoparticles (N-CNPs). Prepared N-CNPs have excitation-dependent fluorescent properties and demonstrate high selectivity towards Fe(III) ions in water. We found that prepared N-CNPs can be used for sensitive detection of Fe (III) ions in the range of 1–30 ppm. Thus, fluorescent N-CNPs can be a promising material for fast and low-cost analysis of Fe(III) ions in water.

1. Introduction

The ferric cation Fe(III) plays an indispensable role in many metabolic processes of the human body, such as oxygen transport, electron transport, and DNA synthesis [1]. Its deficiency or excess can be devastating to biological systems [1,2]. According to the World Health Organization, a safe limit for the Fe(III) ions in drinking water is 2 mg/L. In principle, atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) are suitable for Fe(III) detection. On the other hand, these methods are expensive, require time-consuming sample preparation and analysis procedures. From this point of view, the development of a low-cost, selective and sensitive nanosensor for monitoring of Fe(III) content in water is of paramount importance.

Fluorescent carbon dots (C-dots) are one of the most promising candidates for sensing applications owing to their excellent fluorescent properties, nontoxicity, and photostability [3]. To date, several types of C-dots were applied for the selective detection of certain heavy metal ions, such as Pb (II) [4], Fe(III) [5], and Hg(II) [6]. On the other hand, size-controlled synthesis of C-dots is still a challenging task. For example, the preparation process of C-dots requires long operating time (4–12 h) and the presence of some harsh reagents (bases/acids) [7,8]. These limitations inspired our group to develop fluorescent nitrogen-doped carbon nanoparticles (N-CNPs) from nontoxic precursors using a fast and green hydrothermal method. We showed that prepared N-CNPs have excitation-dependent fluorescent properties and can be utilized for selective and sensitive Fe(III) sensing in water.

2. Materials and methods

2.1. Synthesis

Dextrose (≥99.5%), urea (99.0–100.5%), NaCl (≥99.5%), KCl (≥99.0%), $CaCl_2$ (≥97.0%), $MgCl_2$ (≥98.0%), $Al(NO_3)_3 \times 9H_2O$ (≥98.0%), $ZnCl_2$ (≥98.0%), $CuCl_2 \times 2H_2O$ (≥99.0%), $SnCl_2$ (98.0%), $FeCl_2$ (98.0%), $FeCl_3$ (97.0%), and $Pb(NO_3)_2$ (≥99.0%) were ordered from Sigma-Aldrich and used as received. For the preparation of N-CNPs, 1 g of dextrose and 0.1 g of urea were dissolved in 30 mL of deionized (DI) water. Prepared mixture was heated to 200 °C under vigorous stirring for 1 h in Erlenmeyer flask with a screw cap. The

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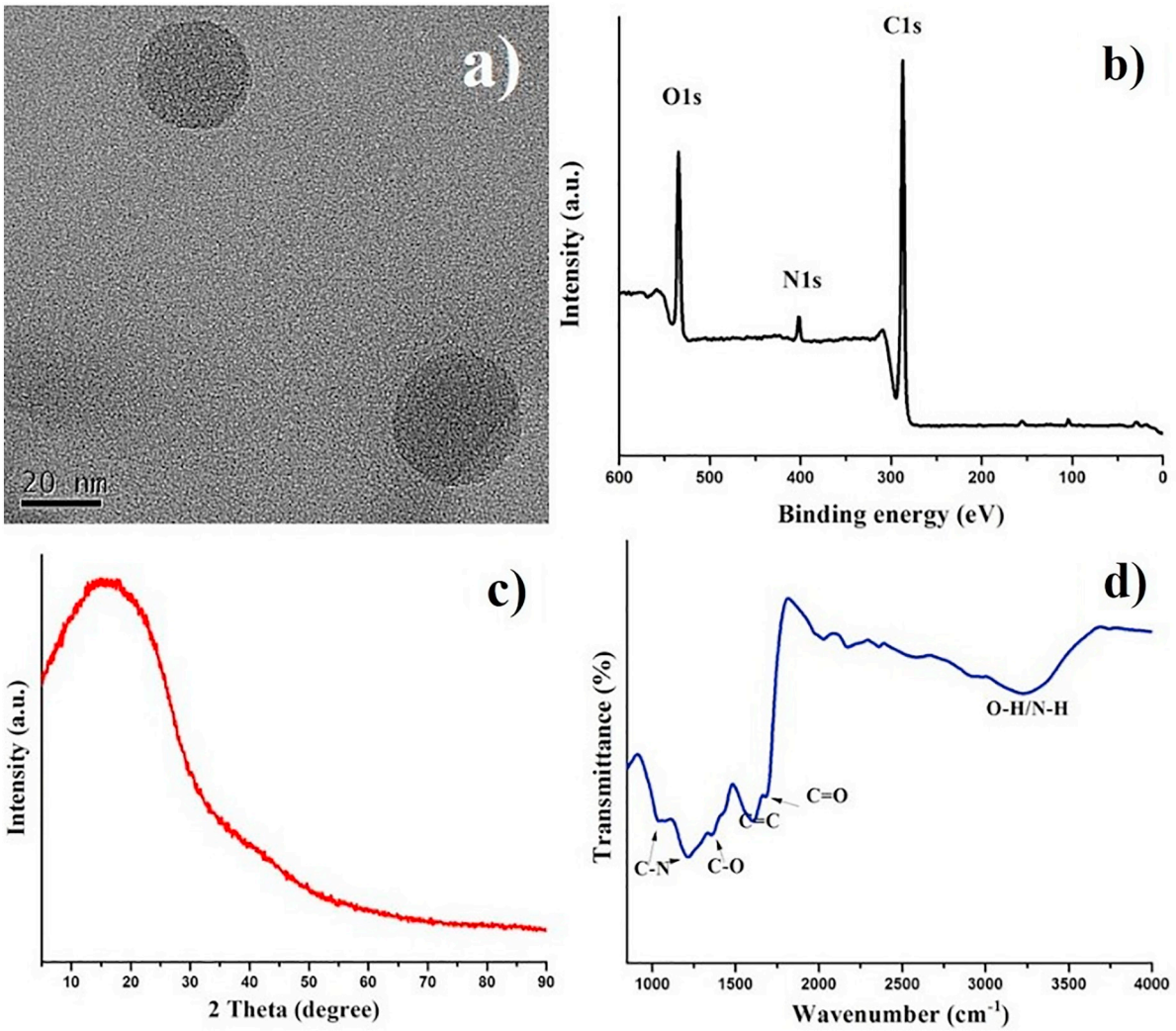

Fig. 1. (a) TEM, (b) XPS, (c) XRD, and (d) FTIR analysis of prepared N-CNPs.

obtained dark-brown solution was filtered through the syringe filter (0.1 μm) to remove large aggregates. N-CNPs were collected, washed several times with DI water and dried. For sensing measurements, 200 μL of N-CNPs aqueous solution (0.01 g per 5 mL of H_2O) was added to 2 mL of aqueous solution of metal ions with a known concentration.

2.2. Characterization

The morphology of N-CNPs was studied using the transmission electron microscope (TEM, JEM2010F). X-ray photoelectron spectroscopy (XPS) analysis was carried out on Versa Probe. X-ray diffraction (XRD) measurements were conducted using a Rigaku SmartLab X-ray Diffractometer with Cu Kα radiation source. IR transmission measurements were carried out using a Fourier-transform infrared spectrometer (FTIR, Nicolet iS5). Quantum yield (QY) was measured by C9920–02 Hamamatsu absolute quantum yield measurement system. The optical properties of nanoprobes were examined using a fluorescence spectrophotometer (FS, Agilent Cary Eclipse).

3. Results and discussion

TEM, XPS, XRD, and FTIR were employed for analysis of synthesized N-CNPs. Fig. 1a shows that prepared N-CNPs have a spherical morphology and mean diameter of 31 ± 5 nm. The wide-range XPS spectrum (Fig. 1b) obtained from the surface of N-CNPs exhibited the characteristic peaks corresponding to the presence of carbon (287.8 eV), oxygen (535 eV) and nitrogen (402.4 eV). The atomic % was estimated to be 87, 8.1, and 4.9 for carbon, nitrogen, and oxygen elements, respectively. These results suggest that nitrogen element was introduced into the structure of carbon nanoparticles during the synthesis process. A typical XRD analysis (Fig. 2c) reveals that prepared N-CNPs are amorphous. FTIR analysis (Fig. 2d) was further used to

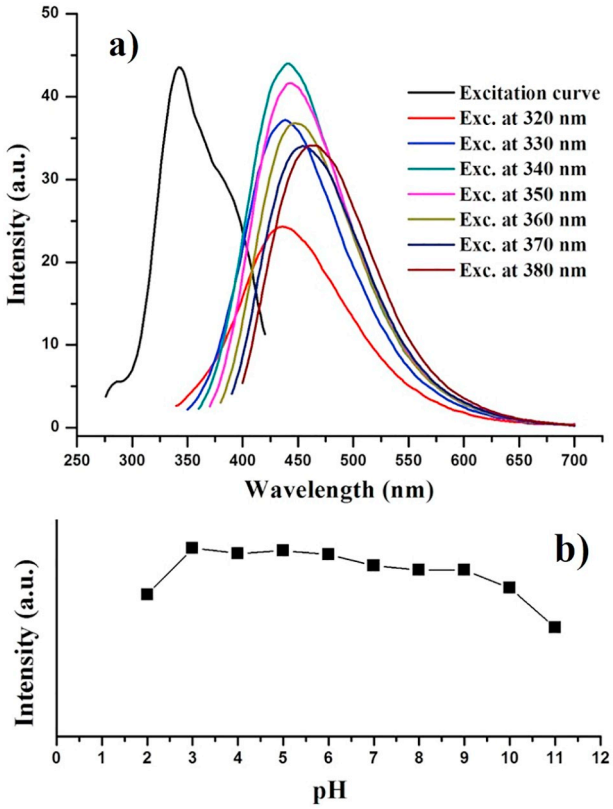

Fig. 2. (a) Excitation and excitation-dependent emission curves, (b) pH stability of prepared N-CNPs.

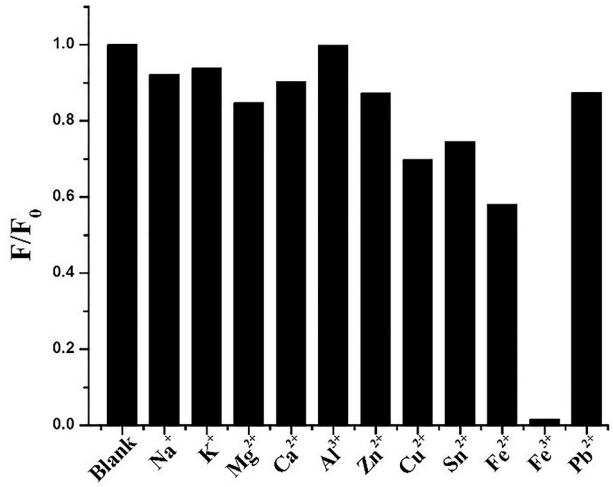

Fig. 3. Selectivity of N-CNPs towards different metal ions.

investigate the functional groups at the surface of N-CNPs. Analysis of FTIR spectrum indicates the presence of −NH group at around 3221 cm^{-1}, which may also indicate the presence of moisture or −OH groups. The presence of C═O and C═C bonds was identified from the peaks around 1683 and 1606 cm^{-1}, respectively. The stretching vibrations of the primary and tertiary amine C−N bonds at about 1036 and 1214 cm^{-1} also confirm the presence of nitrogen element in a sample [9].

FS spectroscopy was used to study the optical properties of prepared N-CNPs in water solution. Fig. 2a shows a typical excitation curve and excitation-dependent emission spectra of the N-CNPs. One can easily see that emission peaks of N-CNPs shifted to longer wavelengths upon increasing the excitation wavelengths. The maximum emission signal was detected at 443 nm under 342 nm excitation which is in a good agreement with the excitation curve. The absolute quantum yield of N-CNPs was found to be 6.17%. The effects of pH on the PL stability of the N-CNPs was investigated and dependence curve is depicted in Fig. 2b. One can see that no significant changes in fluorescence intensity (monitored at 443 nm) were observed over a wide range of pH 3–10, indicating that these N-CNPs are optically stable in the harsh environment.

The selectivity of the N-CNPs was investigated through observation of emission intensity change with addition of certain metal ions (namely, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, Fe^{2+}, Cu^{2+}, Sn^{2+} at a concentration of 150 ppm). The changes in the fluorescence intensity of emission spectra were monitored at 443 nm. Fig. 3 shows that Fe^{3+} ion caused a strong fluorescence quenching of the N-CNPs compared to other metal ions. Thus, the prepared N-CNPs exhibit high selectivity to Fe^{3+} ions. Several reports suggested that the observed fluorescence quenching might be due to the nonradiative recombination of excited electrons of N-CNPs with unpaired d electrons of Fe(III) [5,10].

The feasibility of the N-CNPs for sensitive Fe(III) ions detection in water was investigated further. Fig. 4a shows the fluorescence response of N-CNPs to various concentrations of Fe(III) ions in water. One can observe that fluorescence intensity decreases with the increase of the Fe (III) concentration from 0 to 110 ppm. However, no shift of peak positions at the maximum (443 nm) observed. Fig. 4b shows the relationship between F/F_0 *vs.* Fe(III) concentration, where F is the intensity at 443 nm in the presence of Fe(III), and F_0 is the intensity at 443 nm of the blank solution.

One can observe that F/F_0 plot *vs.* Fe(III) (Fig. 4b) demonstrates some linear regression region. Typically, the fluorescence intensity in the region of 1–30 ppm decreased linearly with increasing Fe(III) concentration (Fig. 5). The correlation coefficient $R^2 = 0.9945$ indicates that the N-CNPs have a very high sensitivity towards Fe(III) ions. Fe(III) sensing with N-CNPs was tested several times and only negligible deviations ($\leq$ 4%) were observed. Thus, prepared N-CNPs can be used as a selective and sensitive nanoprobe for Fe(III) ions detection in the range of 1–30 ppm. It should be noted, that this method is easier, cheaper and more energy-efficient compared to the traditional methods.

4. Conclusion

In summary, fluorescent N-CNPs were utilized for selective and sensitive Fe(III) sensing in water in the range of 1–30 ppm. Prepared N-CNPs are highly fluorescent and have sizes in the range of 31 ± 5 nm.

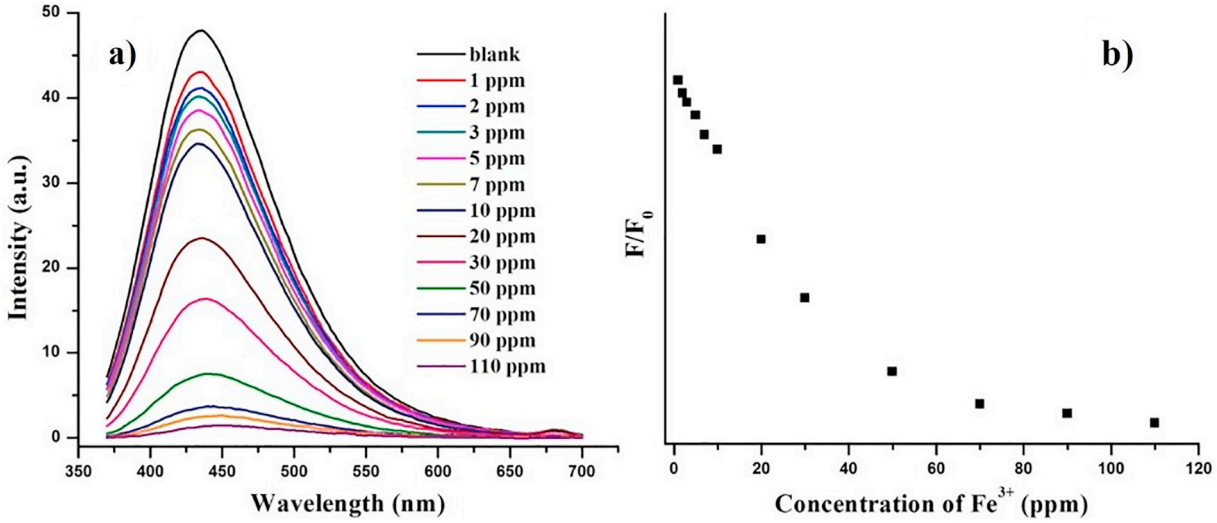

Fig. 4. (a) Emission and (b) F/F_0 plot *vs.* Fe(III) concentration.

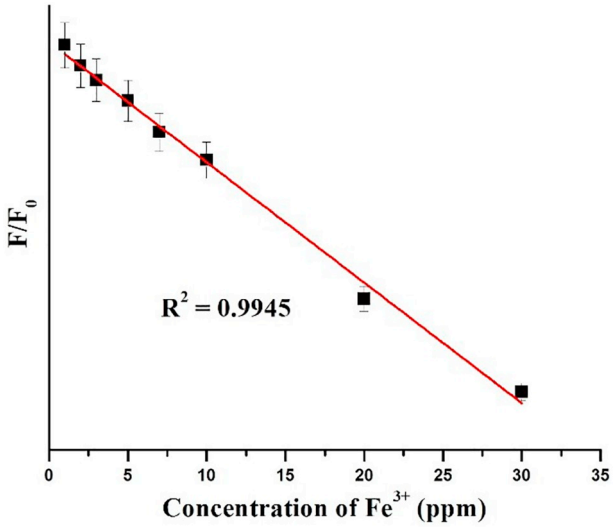

Fig. 5. F/F_0 plot *vs.* Fe(III) at concentrations in the range of 1–30 ppm.

We showed that prepared N-CNPs are selective to the Fe(III) ions in aqueous solution. The analysis reveals that fluorescence quenching at low concentrations (1–30 ppm) has a linear trend and can be utilized for low-cost detection of Fe(III) ions in water.

Declarations of interest

None.

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