Abstract The combination of surface science and electrochemistry is an effective method to approach a fundamental understanding of electrocatalytic systems, especially of the catalyst/support assemblies. Extrinsic chemical defects in the support can affect the performances and this topic is much investigated in recent electrocatalyst research. In this work, nitrogen functional groups are introduced into the outermost layers of highly oriented pyrolytic graphite (HOPG) by ion implantation with a beam energy of 100 eV. Palladium nanoparticles (Pd NPs) are then electrochemically deposited onto both pure and nitrogen doped HOPG (N-HOPG). Pd2+ species located at the interface between the NPs and the nitrogen-rich surface were observed in the latter case. The supported Pd NPs on N-HOPG show the same electrocatalytic activity for oxygen reduction reaction (ORR) as compared with those supported on pure HOPG. However, the stability of Pd NPs on N-HOPG towards potential cycling decreases strongly due to the existence of Pd2+ at the interface, which can accelerate the dissolution of Pd atoms. This result is contradictory to results on supported Pt NPs from the literature where the merit of the N-doping was outlined.