Characterization of the interface between Pt nanoparticles and ZrO_2 substrates by aberration-corrected HRTEM and EELS

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Owing to their enhanced surface-to-volume ratio the physical properties of metallic nanoparticles may be significantly altered upon deposition onto a substrate. Hence, for an optimum choice of the substrate material which is intended to foster the desired particle properties, a thorough understanding of the particle-substrate interaction is mandatory. This in turn requires a thorough characterization of the nature of the chemical bond between the particle and the substrate. For the showcase of Pt nanoparticles deposited onto ZrO_2 particles (referred to as "substrates" in the following) it is shown how this information can be obtained from aberration-corrected high resolution (scanning) transmission electron microscopy (HRTEM / STEM) in combination with electron energy loss spectroscopy (EELS).

Pt nanoparticles were prepared by inert gas condensation (IGC) and deposited onto holey carbon-coated Cu grids pre-seeded with commercially available nanopowders of ZrO_2. Due to their preparation via IGC the surfaces of the Pt particles are clean and free of any organic stabilizers usually employed in chemical preparation routes for steric separation. Likewise prepared samples were characterized by HRTEM and STEM utilizing a *FEI Titan^3 80-300* microscope (FEG, 300 kV) equipped with C_S image corrector, monochromator, high angle annular dark field detector (HAADF) and a *Gatan Tridiem 865* EEL spectrometer.

Fig. 1a shows in an overview image how the Pt particles are attached to the ZrO_2 "substrate" particles supported by the holey amorphous carbon film (α-C). From the HRTEM micrograph in Fig. 1b it can be seen that the interface between Pt and ZrO_2 is characterized by the frequent occurrence of vacancies and a non-uniform relative arrangement of atom columns across the interface. For a closer inspection, the reader is referred to the yellow circles which mark a few prominent examples for these structural details. Together with the fact that there is no significant lattice strain present in the vicinity of the interface this indicates a merely loose (van-der-Waals type) of chemical binding between the Pt particles and their ZrO_2 substrates.

An indication for a strong chemical bond between the Pt particles and the ZrO_2 would be the oxidation of the interfacial Pt atoms. In addition to the HRTEM investigations, the interface regions between Pt and ZrO_2 were investigated by means of STEM in combination with EELS. Fig. 2a shows a typical HAADF micrograph as obtained by STEM of a region of the sample where the ZrO_2 substrates extend into a hole of the supporting α-C film. The smaller (and heavier) Pt atoms can be easily recognized from the higher Z contrast in the image (bright spots). EEL spectra were then recorded after positioning the electron probe right at the Pt-ZrO_2 interface. Fig. 2b shows exemplarily such an EEL spectrum as obtained for shot exposure times. After appropriate subtraction of the background signal the oxidation-sensitive Pt-$N_{6,7}$ edges [1] become clearly visible. From the fact that there is no shift of these

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absorption edges towards lower energies as compared to the peak positions of elemental Pt it can be deduced that there is no oxidation of the Pt atoms at this interface. This finding confirms the results of the structural characterization. The effect of (carbon) contaminations on the observability of the Pt-$N_{6,7}$ edges will be discussed.

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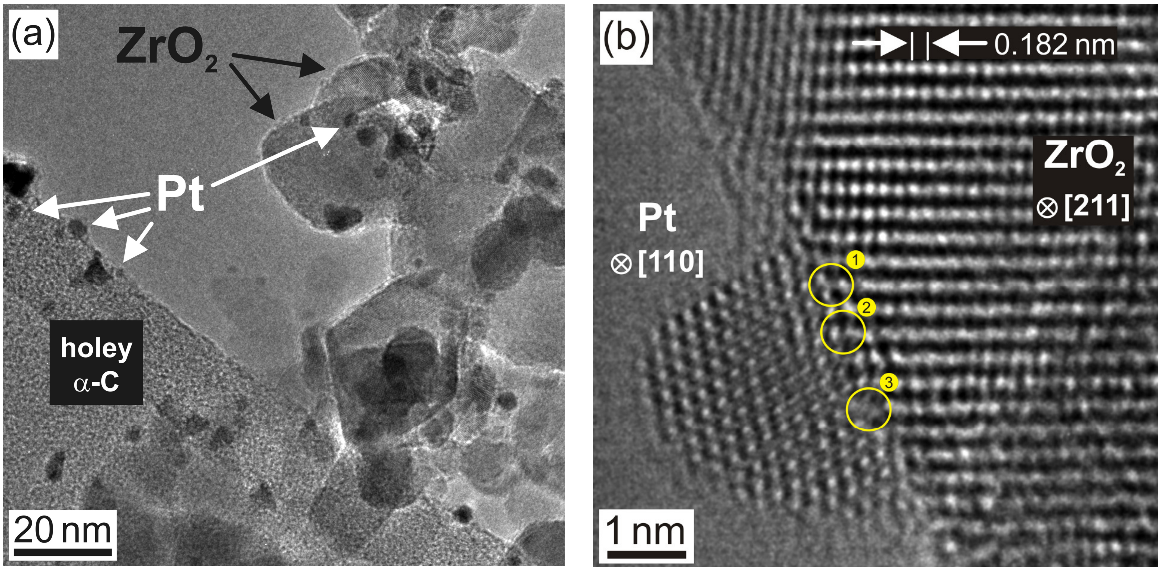

Figure 1. (a) TEM overview image showing Pt particles (small, dark spots) attached to ZrO_2-coated holey carbon grids. (b) HRTEM micrograph highlighting the interfacial region between a Pt particle and its ZrO_2 "substrate" particle. Yellow circles mark areas of the interface with vacancies and different types of mutual arrangements of Pt and ZrO_2 atoms, respectively.

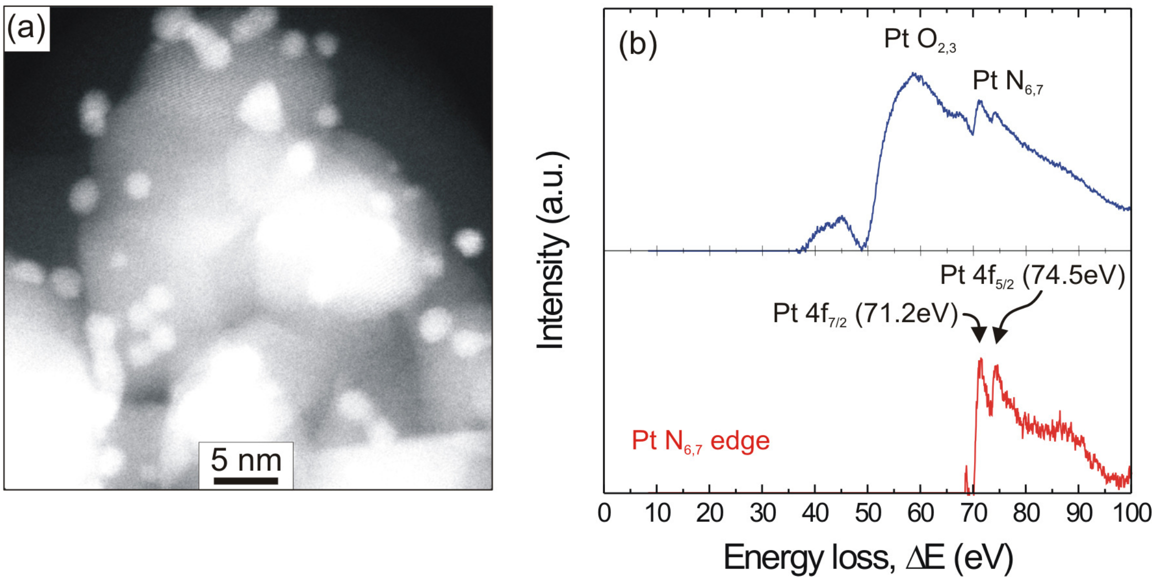

Figure 2. (a) HAADF image of Pt particles attached to ZrO_2 substrate particles. (b) Partial low-loss EEL spectrum as obtained in STEM mode of an interface between a Pt nanoparticle and a ZrO_2 "substrate" particle. The upper and lower plots show the spectrum after different background subtractions and at different intensity zooms.

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