Detecting carbon in or on palladium nanoparticles by analyzing the work function

Henrik Grönbeck[1] and Clemens Barth[2]

[1]*Chalmers University of Technology, Department of Physics and Competence Centre for Catalysis, SE-41296 Göteborg, Sweden*
[2]*Aix-Marseille University, CNRS, CINaM, 13288 Marseille, France*
ghj@chalmers.se

Carbon *absorbed in* or *adsorbed on* metal nanoparticles (NPs) plays a major role in various fields of heterogeneous catalysis. Carbon species are, for example, important as intermediates in catalytic reactions and in the growth of carbon nanotubes, carbon shells and graphene. Graphene can be analyzed directly by, e.g., transmission electron microscopy (TEM) whereas X-ray diffraction (XRD) can be used to detect carbon in metal carbide NPs. It is, however, experimentally challenging to detect small amounts of carbon *adsorbed on* NP surfaces, subsurface or *inside* the NPs. A low amount of subsurface or dissolved carbon has been inferred by analyzing chemical reaction properties that change upon presence of subsurface carbon [1,2].

In this contribution, we show that the work function of metal NPs is a good measure of *carbon adsorption* and *absorption*. To accomplish this at the single NP level, Kelvin probe force microscopy (KPFM) is used thanks to its meV and nanometer resolution, which we demonstrate for palladium NPs supported on HOPG (highly oriented pyrolytic graphite). KPFM reveals that a growth of PdNPs at already 150°C leads to an *absorption* of carbon from the HOPG support into the NPs, which strongly reduces the NP's WF. The measurements are corroborated by density functional theory calculations. When growing NPs at higher temperatures, we observe WF changes of up to 1 eV. A WF reduction also appears during post-annealing whereas an extended post-annealing of hours at 650°C leads to carbon precursor structures and graphene *on the top* of the NP's (111) facets [3], as verified by scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) and KPFM. In comparison to UHV annealing experiments, same phenomena of WF changes are observed when decomposing ethylene at PdNPs at temperatures of around 650°C (see Figure).

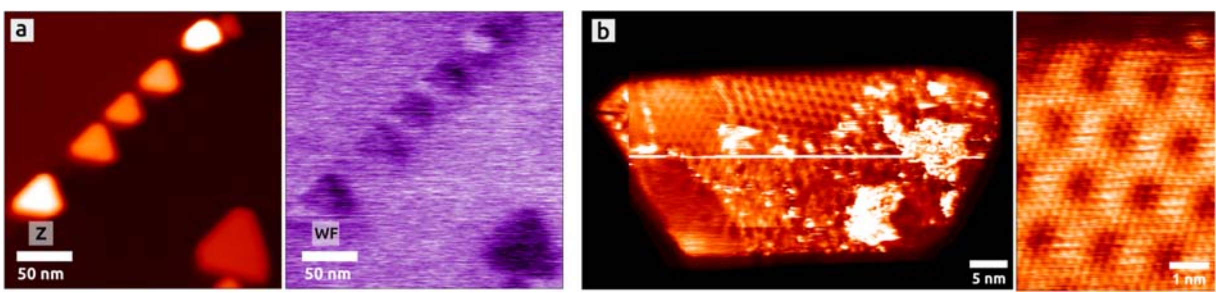

Figure: (a) PdNPs annealed in 247L of C_2H_4 at 650°C. The nc-AFM topography image (left) shows single NPs at the steps of HOPG. The KPFM image (right) shows that the NPs have a very low WF of ~4.2eV (dark), which is even -100 meV below the WF of HOPG (violet). The strong WF reduction is due to graphene covering the NP's facets, which can be observed by STM (b).

References:
[1] B. Brandt, T. Schalow, M. Laurin, S. Schauermann, J. Libuda and H.-J. Freund. J. Phys. Chem. C **111**, 938 (2007).
[2] K. M. Neyman, S. Schauermann. Chem. Int. Ed. **49**, 4743 (2010).
[3] C. Barth, J. Phys. Chem. C **122**, 522 (2018).