Oral presentation

Structure elucidation of ultrasmall Au and Pd nanoparticles by X-ray techniques

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Ultrasmall nanoparticles of noble metals with chemical stability and high specific surface area represent a broad field for their application in heterogeneous catalysis, imaging and biomedicine [1]. With a diameter of 1-2 nm, such ultrasmall nanoparticles can be considered as a mixture of metal clusters containing 100-250 atoms for which the crystal structure might differ from the one of bulk, *e.g* a compression or an expansion of the unit cell. Furthermore, the resulting reactivity on the surface of ultrasmall nanoparticles can be also affected by spontaneous oxidation [2], i.e. a reliable identification of the chemical nature is both of great importance and challenging due to the very small size of NPs.

This work focuses on the structural characterization of ultrasmall gold (Au) and palladium (Pd) nanoparticles synthesized by reduction of metallic precursors with sodium borohydride or amine borane in the presence of either glutathione (GSH) or dodecylamine as stabilizing ligands. The elucidation of the composition and the dispersity of such nanoparticles was only possible by a combination of diffraction and spectroscopic techniques, *e.g.* X-ray powder diffraction (XRD) combined with atomic pair distribution function (PDF) analysis, small- (SAXS) and wide-angle (WAXS) X-ray scattering, high-resolution transmission electron microscopy (HRTEM) combined with electron diffraction (ED), and X-ray photoelectron spectroscopy (XPS).

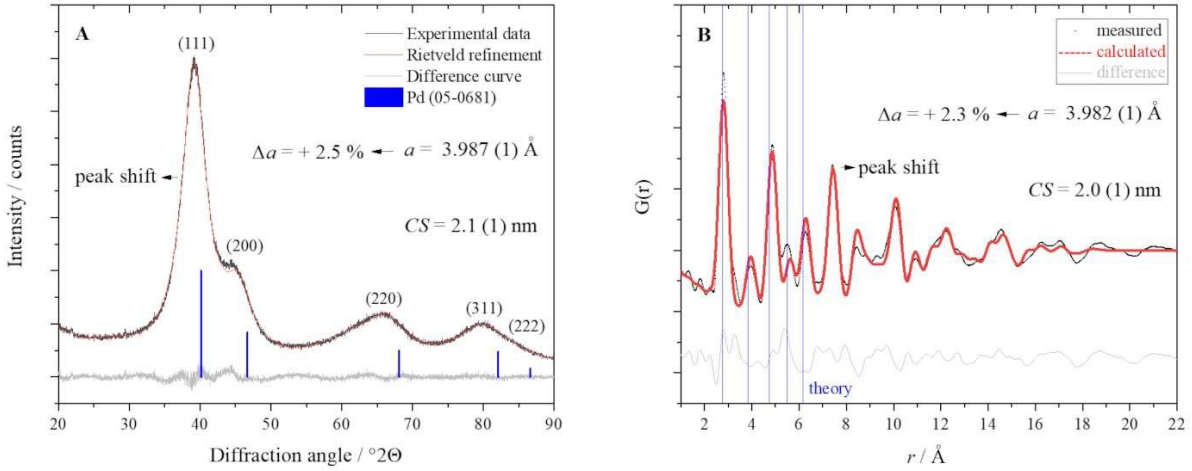

Figure 1. Representative X-ray powder diffraction pattern with Rietveld refinement (**A**) and PDF analysis (**B**) of ultrasmall palladium nanoparticles, functionalized with dodecylamine, as refined with the fcc model using the software TOPAS 7.0.

The prepared nanoparticles had an approximately spherical shape and were monodisperse with a diameter of 1-2 nm as HRTEM and SAXS indicated. The combination of XRD, XPS and ED gave the oxidic character of GSH-loaded nanoparticles, whereas nanoparticles with dodecylamine ligands were not oxidized. Rietveld refinement and PDF analysis (TOPAS 7.0) proved the metallic character for both ultrasmall gold and palladium nanoparticles (Fig. 1), but the calculated lattice parameters differed from that of bulk. Furthermore, comparison of the crystallite size (CS) with the particle size (PS) supported the results from HRTEM with respect to polycrystalline (twinning, CS<PS) and single crystalline (CS≈PS) nanoparticles. Interestingly, after freeze-drying, monodisperse ultrasmall nanoparticles self-assembled into an hcp superstructure that consisted of several nanoparticle layers as quantified from WAXS.

[1] Wetzel, O., Hosseini, S., Loza, K., Heggen, M., Prymak, O., Bayer, P., Beuck, C., Schaller, T., Niemeyer, F., Weidenthaler, C., Epple, M. (2021). *J. Phys. Chem. B* **125**, 5645.

[2] Wetzel, O., Prymak, O., Loza, K., Gumbiowski, N., Heggen, M., Bayer, P., Beuck, C., Weidenthaler, C., Epple, M. (2022). *Inorg. Chem.* **61**, 5133.