In-depth characterization of ultrasmall nanoparticles by combined X-ray techniques

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Ultrasmall nanoparticles (usNPs) of noble metals are of high interest in materials science, e.g. in catalysis, photonics and biomedicine, due to their high specific surface area. The synthesis of very small sized particles (1-2 nm) and especially their structural characterization is very challenging and requires complex diffraction, spectroscopic and microscopic techniques using X-ray beam. In this work usNPs of coin (Ag, Au) and platinum (Ru, Rh, Pd, Os, Ir, Pt) metals were wet-chemically prepared by reduction with NaBH₄ and colloidal stabilized with glutathione (GSH). Their monodispersity (possible agglomeration), chemical composition (potential oxidation) and crystallinity (twinning) had to be studied, because their further surface functionalization and applicability in different scientific fields would be strongly affected by this. Thus, after colloid-chemical characterization with disc centrifugal sedimentation (DCS), usNPs were investigated by high-resolution transmission electron microscopy (HRTEM), X-ray powder (PXRD) and electron (ED) diffraction, small-angle X-ray scattering (SAXS), X-ray photoelectron spectroscopy (XPS). It turned out that all prepared usNPs were spherical and monodisperse with an average diameter up to 2.0 nm and possessed a good crystallinity, typically twinned in structure. Despite the extremely broad diffraction peaks caused by the ultrasmall particle size, a challenging quantitative analysis by Rietveld refinement provided important information about the partial oxidation state and the unit cell contraction in usNPs. These results significantly differed from a comparable study of nanoparticles of the same metals, which were larger in size (>5 nm). Additionally to the chemical composition of usNPs as elucidated by PXRD, the oxidation state of the nanoparticles was studied by XPS and supported by ED and HRTEM (Fig. 1). Due to the strong scattering contrast of usNPs (compared to the organic shell), SAXS data mainly provided information about the size and dispersion state of the nanoparticles, including the identification of small aggregates.

Figure 1. Representative HRTEM and ED images (left), PXRD with Rietveld refinement (center), and XPS (right) analysis of partially oxidized platinum usNP.