Poster

Oxidation state of ultrasmall dodecylamine-coated palladium nanoparticles probed by X-ray techniques

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Palladium shows high activity and selectivity in the heterogeneous catalysis of organic reactions which occur on the surface of this metal. As the raw material price of palladium has increased eightfold in the last 20 years, it is an interesting option to reduce the amount of palladium in these reactions. This could be realised by using ultrasmall nanoparticles with a size of less than 3 nm, as these have a very high specific surface area [1-2].

Typical wet chemical syntheses involve reducing the corresponding metal precursors with suitable agents, followed by colloidal stabilization by a capping ligand. Classical examples are glutathione-stabilized nanoparticles dispersed in water, but they are prone to spontaneous oxidation (**Fig. 1A**). In many published syntheses of ultrasmall nanoparticles, the internal structure and the chemical nature (e.g. the oxidation state) are not well known [1-3]. Here we report a thorough study on the synthesis and subsequent characterization of ultrasmall palladium nanoparticles, prepared in organic solvents and capped with dodecylamine.

Small angle X-ray scattering (SAXS), high resolution transmission electron microscopy (HRTEM) and differential centrifugal sedimentation (DCS) measurements were carried out to determine nanoparticle size, dispersity, and morphology. The crystal structure was derived from powder X-ray diffraction pattern (XRD). Additionally, the oxidation state was determined by X-ray photoelectron spectroscopy (XPS) and indirectly by electron diffraction (ED).

The prepared nanoparticles showed a spherical shape and were monodisperse with a diameter of the metal core1-2 nm, as shown by HRTEM (**Fig. 1B**) and SAXS. The combined results from XRD, XPS and ED analysis confirmed a metallic character of the palladium nanoparticles without signs of oxidation to PdO as in glutathione-coated palladium nanoparticles (**Fig. 1A**).

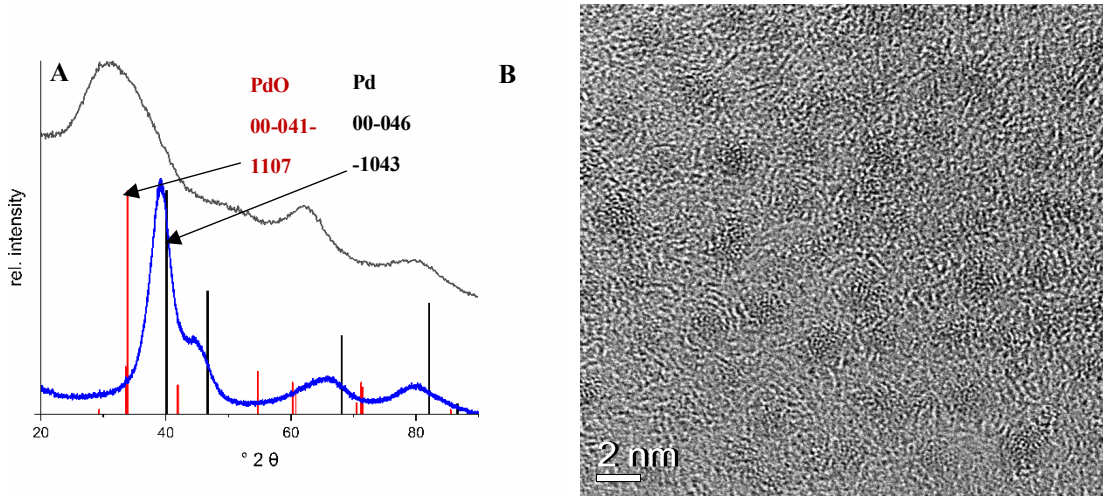

Figure 1. **A**: Representative X-ray powder diffraction pattern of glutathione-coated palladium nanoparticles (**black**) with a diameter of 1.4 nm and dodecylamine-coated palladium nanoparticles (**blue**) with a diameter of 1.9 nm. **B:** HRTEM micrograph of ultrasmall dodecylamine-coated palladium nanoparticles.

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