Nano-brass colloids: synthesis by co-hydrogenolysis of [CpCu(PMe_3)] with [$ZnCp^*_2$] and investigation of the oxidation behaviour of α/β-CuZn nanoparticles†

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A novel, non-aqueous organometallic access to colloidal copper and copper/zinc (brass) nanoparticles is described. Hydrogenolysis of the precursor [CpCu(PMe_3)] (**1**) in mesitylene at 150 °C and 3 bar H_2 quantitatively gives elemental Cu. Analogously, a solution of [$ZnCp^*_2$] (**2**) reacts with H_2 to give elemental Zn in 100% yield. Co-hydrogenolysis of **1** and **2** in exactly equimolar quantities selectively yields the intermetallic phase β-CuZn characterised by powder X-ray diffraction (PXRD). Deep red colloidal solutions of nano-Cu as well as red to violet colloids of nano-brass alloys (α/β-CuZn) are obtained by co-hydrogenolysis of **1** and **2** in the presence of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as surfactant. All samples of the general formula $Cu_{1-x}Zn_x$ ($0.09 \leqslant x \leqslant 0.50$) were characterised by means of elemental analysis, PXRD, transmission electron microscopy (TEM, EDX and SAED) and UV-Vis absorption spectroscopy. The presence and alloying of metallic Cu and Zn in the β-CuZn sample as a representative example of the series was confirmed by extended X-ray absorption fine structure spectroscopy (EXAFS). The oxidation behaviour of the nanoparticles was investigated by EXAFS, PXRD and UV-Vis spectroscopy indicating, that CuO_x@Cu core–shell type particles were formed for pure copper particles, while in the case of brass particles preferential oxidation of the Zn component takes place, which results in core–shell particles of the type $(ZnO)_\delta$@$Cu_{1-x}Zn_{x-\delta}$.