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In^0 Nanoparticle Synthesis Assisted by Phase-Transfer Reaction

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The synthesis of nanoscale elemental metals exhibiting uniform size and shape is motivated by issues of fundamental research as well as technical application.[1] Potential quantum size effects, superconducting properties, and the use of reactive metals as a general platform to prepare metal compounds (i.e., InN, InP, InAs, In_2O_3, In_2S_3) are points of interest.[2−5] Heterogeneous catalysis (e.g., in organic synthesis), III−V semiconductors (e.g., for light emitting diodes), and optical materials (e.g., In_2O_3:Sn as transparent conductive oxide) belong to those aspects of technological relevance.[2−7] Right now, nanoscaled indium has been gained by gas-phase methods such as laser ablation,[8] evaporation techniques,[9] or thermal decomposition of organometallic compounds.[10] Liquid-based synthesis has been performed applying polyol-type methods,[11] ionic liquids,[12] parafin,[13] or alkali metals[14] and alkalides/electrides[15] as strong reducing agents. Recently, octahedrally shaped and rod-like indium has been realized by $NaBH_4$-initiated reduction in isopropanol.[16] Here, In^0 with 80−100 nm as the lowest size has been realized in the presence of polymer stabilizers such as polyvinylpyrrolidone. Altogether, advanced and expensive indium precursors as well as advanced synthesis techniques are quite often required to perform the reduction and to exclude moisture and air. Aiming at In^0 particles sized below 20 nm, the reactivity and moisture sensitivity will further increase.

In this study, the synthesis of uniform In^0 nanoparticles 10−15 nm in diameter is assisted by a phase-transfer reaction. This two-step approach, including reduction in alcohol and phase transfer to alkanes, allows a straightforward separation of In^0 nanoparticles from excess precursors as well as remaining salts and guarantees a sufficient colloidal and chemical stabilization.

The two-step synthesis of In^0 nanoparticles was performed in detail as follows: at first, the indium precursor was dissolved in diethylene glycol (DEG) as the polar phase. This allows a usage of standard and low-cost indium salts (i.e., $InCl_3 \cdot 4H_2O$, $In_2(SO_4)_3 \cdot xH_2O$). Reduction of In^{3+} was per-

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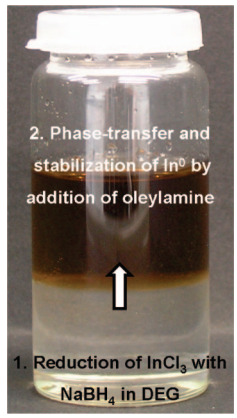

Figure 1. Scheme and photograph of phase-transfer synthesis with In^0 nanoparticles located in the upper dodecane phase.

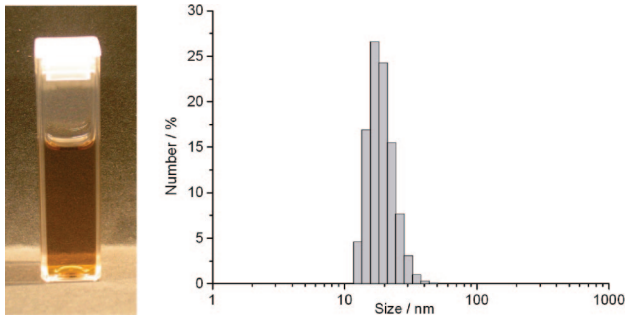

Figure 2. Photograph and dynamic light scattering displaying the In^0 in dodecane after phase-transfer as well as the relevant particle size distribution.

formed thereafter by addition of $NaBH_4$. As a second step, as-prepared indium nanoparticles were separated from excess precursor and remaining salts by oleylamine-driven phase-transfer to nonpolar dodecane or pentane. Reduction and phase transfer can be easily followed visually by the occurrence and location of dark brown indium (Figure 1). Although so-called polyols (e.g., DEG, glycerol) are well-known for nanomaterials stabilization,[17−20] as-prepared In^0 in DEG is with limited stability regarding agglomeration and reoxidation. In fact, sedimentation and decolorization was observed within a day.

Subsequent to phase-transfer reaction, In^0 suspensions in dodecane exhibit a brownish but transparent appearance and turn out to be stable within months (Figure 2). According to dynamic light scattering (DLS), the mean hydrodynamic diameter of In^0 particles in dodecane amounts to 18 nm (Figure 2). Thus, nanoscale particles with a narrow size distribution are formed. Size and absence of agglomerates are in accordance with the transparency and excellent stability of suspensions. Such suspensions can also be stored at ambient temperature in air. Neither a sedimentation of particles nor a decolorization due to formation of colorless $In(OH)_3$ or In_2O_3 was observed. Considering the reactivity of a nanoscaled, less-noble metal ($E_0(In) = -0.34$ V),[21] the overall stability is quite high. Thus, beside colloidal stabilization the phase-transfer reaction also allows an efficient protection of In^0 against air- and moisture-driven oxidation. In fact, phase transfer driven by long-chained amines has been described previously, for instance, in the case of CdSe-type quantum dots and Au nanoparticles.[22] The two-step sequence of metal reduction and particle nucleation in a polar phase followed by phase-transfer for separation and stabilization of less-noble metals, however, has not yet been reported.

Particle size and size distribution of as-prepared In^0 were further evaluated by scanning electron microscopy (SEM). Figure 3A shows as-prepared In^0 immediately after formation in DEG with uniform particles and very few agglomerates. In^0 nanoparticles are further displayed after oleylamine-driven phase transfer to dodecane (Figure 3B). In both cases the particle diameter amounts to 10−15 nm. In contrast to samples from DEG, those made from dodecane show a significant tendency to form agglomerates. This finding is in contradiction to DLS results as well as to the transparent appearance of suspensions. However, strong van der Waals interaction of the long-chained amine shell is to be expected and in accordance with the formation of particle clusters when drying the samples for electron microscopic characterization.[23]

Characteristic TEM images exhibit spherical, nonagglomerated indium particles with a very uniform size and morphology (Figure 3C). Distinct distances between individual particles again confirm the surface stabilization due to oleylamine. Obviously, the particles are nonagglomerated and with particle diameters of 10−12 nm. Lattice fringes with *d*-values of 2.73(5) Å (Figure 3D) are observed with a comparably weak contrast and confirm the presence of elemental indium (literature data: (100) with 2.72 Å).[24] In fact, the nanocrystals turn out to become noncrystalline under HRTEM conditions on a minutes time scale. Considering current densities up to 100 A/cm^2 at high magnification, such a finding is not surprising and has been reported previously.[10] In addition to electron microscopy, crystallinity and composition of as-prepared In^0 are further confirmed by X-ray powder diffraction patterns (Figure 4). On the basis of Scherrer's equation the crystallite size can be deduced to 15−20 nm.

Altogether, the phase-transfer reaction results in a straightforward synthesis of uniform indium nanoparticles. Besides size and uniformity of these In^0 particles, the usage of standard, and low-cost indium salts, the facile separation from excess precursors and remaining salts and the sufficient colloidal and chemical stabilization can be denoted as special advantages of the synthetic approach. The two-step sequence of synthesis will be transferred to the formation of other metal nanoparticles next. Moreover, the resulting less-noble metals might be useful to establish less-noble metals as a general

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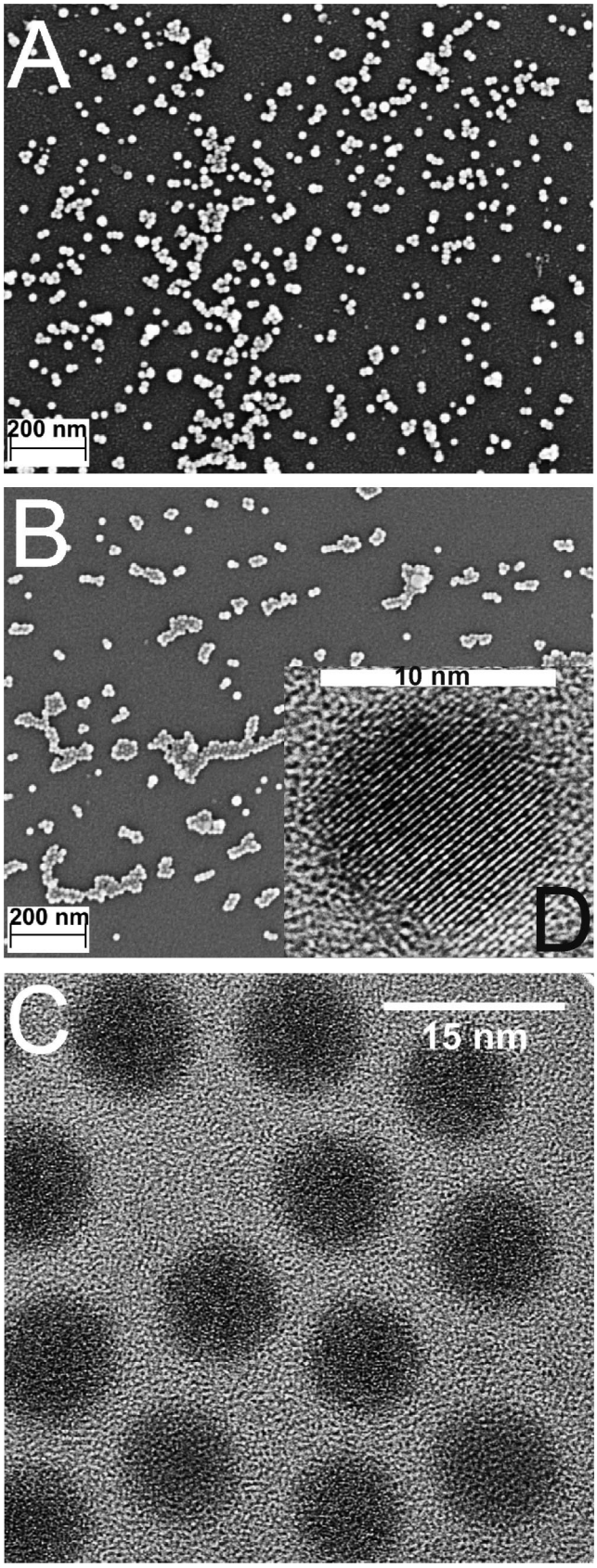

Figure 3. Electron microscopy of In^0 nanoparticles: (A) SEM image of as-prepared In^0 in DEG phase; (B) SEM and (C) TEM image of as-prepared In^0 subsequent to phase-transfer in dodecane; and (D) HRTEM image with lattice fringes.

platform to nanoscale metal compounds such as oxides, sulfides, halogenides, or nitrides.

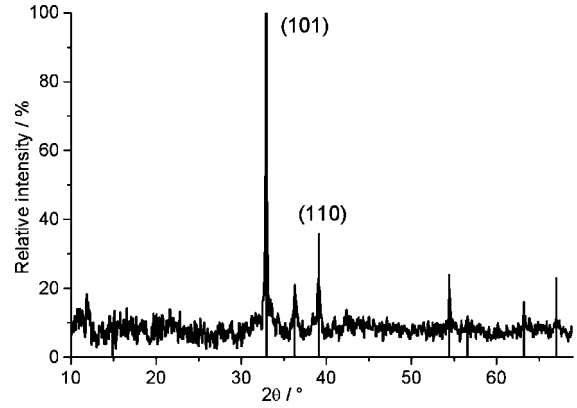

Figure 4. X-ray powder diffraction pattern of as-prepared In^0 nanoparticles (reference: ICCD-No. 5-642).

All experimental work was performed in vacuum or under nitrogen utilizing Schlenk techniques or gloveboxes. All chemicals were applied as received.

Nanoscale indium metal nanoparticles were prepared via a phase-transfer reaction applying diethylene glycol (DEG, Merck, 99%) as a polar phase and dodecane or pentane as a nonpolar phase. First, a colorless solution containing 0.5 mmol (147 mg) of $InCl_3 \cdot 4H_2O$ (Aldrich, 99.9%) in 25 mL of DEG was filled in a three-neck flask and vented with nitrogen. This solution was topped with 25 mL of dodecane (Aldrich, 99.9%). By vigorous stirring the two separate phases were emulsified to initiate an intimate phase contact. Thereafter, the continuously stirred emulsion was heated to 100 °C with a heating mantle. Subsequently, a solution containing 5.0 mmol (189 mg) of $NaBH_4$ (Aldrich, >96%) as reducing agent and 1 mL of oleylamine as a surface stabilizer dissolved in 25 mL of DEG was rapidly added. Within minutes, the emulsion turned dark brown. Complete phase transfer to the dodecane top-phase occurred slowly and takes about 2 h. Thereafter, the polar DEG phase was completely clear and colorless, whereas the nonpolar alkane phase turned dark brown. Finally, the suspension of In^0 particles in dodecane/pentane was obtained by transferring the upper nonpolar phase with a pipet. Powders were obtained by vacuum drying of In^0 particles in pentane. In contrast to In^0 in alkane suspension, which turned out to be very stable even in air, dried powders did show slow oxidation when exposed to air.

Scanning electron microscopy (SEM) was conducted on a Zeiss Supra 40 VP, using an acceleration voltage of 10 kV and a working distance of 3 mm. Samples were prepared by evaporation of dispersions on a silicon wafer.

Transmission electron microscopy (TEM) and electron diffraction were performed on a Philips CM 200 FEG/ST microscope, operating at 200 kV. TEM samples were prepared by ultrasonic nebulization of In^0 suspensions in pentane on a holey carbon-film copper grid.

Dynamic light scattering (DLS) was performed with a Nanosizer ZS from Malvern Instruments (equipped with a He−Ne laser, detection via noninvasive back scattering at an angle of 173°, 256 detector channels). Suspensions in dodecane/pentane were investigated in polystyrene cuvettes at room temperature.

X-ray powder diffraction (XRD) was carried out with a STOE STADI-P diffractometer using Ge-monochromatized Cu $K\alpha_1$ radiation.

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