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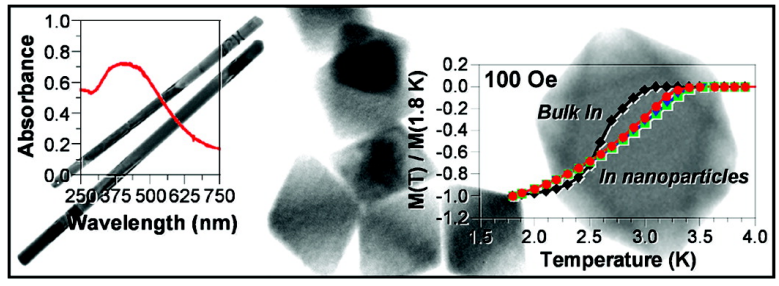

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Room-Temperature Chemical Synthesis of Shape-Controlled Indium Nanoparticles

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The synthesis of shape-controlled metal nanocrystals is motivated by their wide range of properties that are useful for applications that include optics, electronics, magnetism, and catalysis.[1] As a target for shape-controlled nanocrystal synthesis, indium metal is attractive because it is superconducting,[2] is active for surface plasmon resonance (SPR),[3] and is used as a component in low-melting solders[4] and solid-state lubricants.[5] Nanocrystalline In with predominantly spherical shapes has been synthesized using a variety of physical and chemical methods. Representative physical methods include laser ablation,[6] evaporation,[2] ultrasonication,[5] and dispersing molten In into paraffin oil.[7] Chemical methods have typically required the use of strong reducing agents such as sodium metal,[3] zinc powder,[8] and alkalides and electrides.[9] Decomposition of low-valent organometallic complexes has also been used to synthesize In nanoparticles[10] and nanowires.[11]

While In^{3+} should be reducible to In^0 by BH_4^- based on standard reduction potentials ($E^o_{In3+/In} = -0.338$ eV vs SHE, $E^o_{B(OH)3/BH4-} = -0.481$ eV vs SHE), there have been no reports describing the synthesis of In nanocrystals using borohydride reduction, polyol reactions, or related mild solution methods that are among the most common strategies for generating shape-controlled nanocrystals.[12] Here we describe a simple kinetically controlled borohydride reduction process for synthesizing shape-controlled In nanocrystals at room temperature.

In nanoparticles were synthesized by the dropwise addition of a solution of $NaBH_4$ in tetraethylene glycol (TEG) to a solution of $InCl_3$ and poly(vinyl pyrrolidone) (PVP, MW = 630000) in isopropyl alcohol (IPA). In a typical synthesis, $InCl_3$ (10 mg) and PVP (0.10 g) were dissolved in 10 mL of IPA. After purging with Ar, 15 drops (13 μL/drop, ~0.2 mL total) of a freshly prepared $NaBH_4$/TEG solution (0.07 g of $NaBH_4$ in 5 mL of TEG) were added at ambient temperature. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol. It is important to note that if an IPA solution of $NaBH_4$ is used, In nanocrystals do not form, presumably because of a faster reaction of $NaBH_4$ with the alcohol than with In^{3+}. Using TEG as the solvent for $NaBH_4$ maintains its reactivity long enough to reduce In^{3+} to In^0 after it is added to IPA.

The rate of dropwise addition of the $NaBH_4$/TEG solution to the $InCl_3$/IPA solution, and therefore the reduction kinetics, influenced the shape of the In nanocrystals. For example, Figure 1a shows transmission electron microscope (TEM) images of In nanowires (50−70 nm diameter, 3−4 μm long, 95% yield) synthesized by initially adding 10 drops of $NaBH_4$/TEG at a rate of 1 drop every 2 s, then waiting 50 s before adding 5 additional drops at the same rate. The selected area electron diffraction (SAED) pattern in Figure 2 confirms that the nanowires are composed of In metal. The powder X-ray diffraction (XRD) pattern for this same sample (Figure 2) shows evidence of preferred orientation, with the 011, 002, and 022 peaks exhibiting relative intensities much higher than predicted for an isotropic sample. Figure 2 also shows the XRD pattern for irregularly shaped In nanocrystals synthesized without controlling the reduction rate (Supporting Information, Figure S1), which shows no preferred orientation.

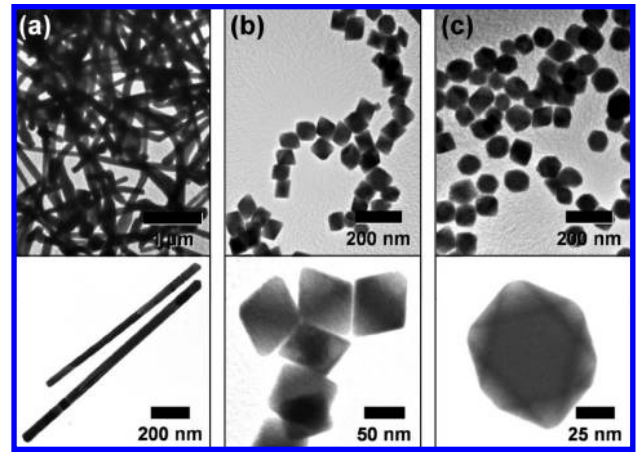

Figure 1. TEM micrographs of indium (a) nanowires, (b) octahedra, and (c) truncated octahedra synthesized by borohydride reduction of In^{3+}.

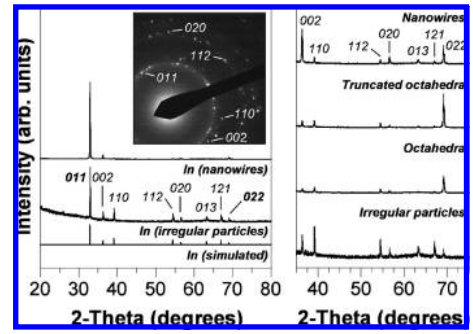

Figure 2. (Left) Powder XRD patterns for In nanoparticles and simulated XRD data for In metal; (right) higher-angle XRD data for all samples; (inset) representative SAED pattern for In nanowires.

When the reduction rate is increased, other nanocrystal morphologies can be accessed. For example, upon adding 15 drops of $NaBH_4$/TEG solution at a rate of 1 drop/s, 80 ± 7 nm In octahedra are formed in 85% yield (Figure 1b). When 10 drops of $NaBH_4$ solution are added at a rate of 1 drop/s, followed by an 8-s pause and the addition of the remaining 5 drops at a rate of 1 drop/s, 95 ± 5 nm truncated octahedra are formed in 80% yield (Figure 1c).

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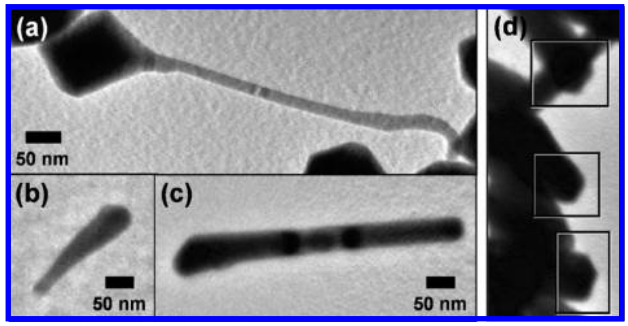

Figure 3. TEM images from intermediate stages of the reaction: (a) In nanowires growing off of octahedral seeds; (b,c) nanowires becoming thicker as the reaction progresses. (d) Enlarged TEM image showing the nanowire tips, which maintain the points defined by the octahedral seeds.

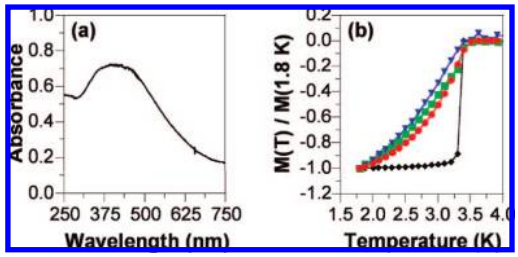

Figure 4. (a) Representative UV−visible absorption spectrum of In nanoparticles (octahedra) and (b) temperature dependent magnetization at a 8.5 Oe applied field (black diamonds, bulk In; red circles, In nanowires; blue triangles, In octahedra; green squares, In truncated octahedra).

Preliminary evidence suggests that other shapes, including triangles and decahedra, can also be accessed.

Shape control in this system appears to be driven by reduction kinetics, rather than by the influence of different types or concentrations of surface stabilizers or additives that are typically used for synthesizing nonspherical nanocrystals.[12] Other shape-controlled metal nanocrystals have been proposed to form by a similar mechanism.[13] The initial slow reduction step generates octahedral In nanoparticles, which act as seeds for the growth of nanowires. Preliminary data are consistent with this hypothesis, showing nanowires growing off of octahedra (Figure 3). This is also consistent with the XRD data showing preferred orientation, which correlates well with the observed morphologies and crystal growth directions (see Supporting Information). For the faster reduction processes, a larger number of seeds are generated initially, limiting growth to zero-dimensional nanocrystals. Slower reduction (after the formation of seeds) leads to the growth of nanowires with tips that maintain the pointed geometry defined by the octahedral seeds (Figure 3d). More detailed mechanistic studies are in progress.

In nanoparticles are known to exhibit an SPR peak at UV−visible wavelengths. The In octahedra show an SPR peak centered around 400 nm (Figure 4a), which is within the range of reported wavelengths for the In SPR band.[3,6,7] Also, bulk In metal is superconducting with $T_c = 3.4$ K,[2] and all of the In nanoparticles are superconducting as well. Temperature dependent magnetization data, $M(T)$, for each sample measured with 8.5 and 100 Oe applied fields are shown in Figures 4b and S2, respectively. The data were normalized to the absolute value of the magnetic moment at $T = 1.8$ K. A sample of bulk In powder is included for comparison. All samples show diamagnetic behavior below 3.4 K, indicating the existence of the superconducting transition, even for the essentially zero-dimensional octahedra. Unlike the sharp transition observed in bulk In at 8.5 Oe (Figure 4b), a gradual drop in magnetization is seen in all of the In nanoparticle samples, similar to that observed for Sn and Pb nanowires.[14] Interestingly, while measurements at 100 Oe significantly decrease T_c in bulk In as expected because of its low critical field, T_c remains almost unchanged for all of the In nanoparticle samples (Figure S2). This suggests that the In nanoparticles have a much higher critical field than bulk In, similar to recently reported results on In nanopowder synthesized via thermal evaporation of bulk In.[2]

In conclusion, shape-controlled In nanoparticles have been synthesized using a room-temperature $NaBH_4$ reduction strategy. In nanowires, octahedra and truncated octahedra can be accessed simply by changing the rate of dropwise addition of $NaBH_4$/TEG into a solution of $InCl_3$/PVP/IPA. These nanoparticles exhibit the expected SPR properties, as well as superconductivity with a higher critical field than bulk In. It is anticipated that the shape-controlled In nanoparticles could also serve as templates for conversion into In-based nanomaterials, including InP and In intermetallics.[10d,15]

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Supporting Information Available: Additional experimental and characterization details, additional TEM images, supporting data for the proposed nanocrystal formation mechanism, and M vs T data for bulk In and In nanoparticles at an applied field of 100 Oe. This material is available free of charge via the Internet at http://pubs.acs.org.

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