Silica Encapsulation of Hydrophobically Ligated PbSe Nanocrystals

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Spherical PbSe@SiO$_2$ nanoparticles have been successfully synthesized within reverse micelles via metal alkoxide hydrolysis and condensation within a microemulsion system. These core–shell nanoparticles were characterized by transmission electron microscopy (TEM), NIR absorption spectroscopy, energy-dispersive X-ray analysis, and TEM electron diffractions. It shows that the obtained core–shell structures have a spherical shape with narrow size distribution (average size approximately 35 nm) and smooth surfaces. The size of the particles and the thickness of the shells can be controlled by manipulating the relative rates of the hydrolysis and condensation reactions of tetraethoxysilane (TEOS) within the microemulsion.

Introduction

Semiconductor nanocrystals (NCs) have attracted much attention due to their unique size-dependent behavior; their optical properties in particular differ greatly from the corresponding molecular and bulk materials.[1–3] NCs may play a major role in future technologies, such as nanoelectronics, photonics, telecommunication, and biological and environmental sensors.[4–6]

PbSe NCs are promising candidates for a wide variety of potential applications such as IR detectors, photographic plates, selective and photovoltaic absorbers, and others. During the past two decades, PbSe NCs have been intensively studied.[7–8] They have been prepared by various methods such as chemical bath deposition, molecular beam epitaxy, vacuum deposition, electrodeposition, the pulse sonoelectrochemical method, the photochemical method, microwave assisted heating, and the successive ion layer adsorption and reaction technique.[9–11] Murray et al.[12] synthesized discrete spherical PbSe NCs, with narrow size-distribution and tunable band-gap at the near-IR spectral regime (0.5–1.1 eV). Lifshitz et al.[13] reported a synthetic procedure for the preparation of discrete spherical PbSe/PbS core–shell NCs, with average sizes ranging between 2.5 and 7 nm, and with enhanced photoluminescence quantum yield. Syntheses of very small PbSe nanocrystals ($d = 2$–3 nm) as well as larger PbSe quantum wires, rods, and cubes have also been recently reported.[14–15]

Problems such as bent surfaces, dangling bonds, (photo-)oxidation, coalescence, and other instabilities[16–17] become increasingly important with decreasing nanocrystal size. To overcome these drawbacks, nanoparticles can be either coated with a large-band-gap semiconductor material, a polymer, or insulators such as silica, titania, etc.[18–19] The silica coating of colloidal particles has been studied extensively during the past decade. A wide variety of the applications of silica coatings on metal, semiconductor, and inorganic colloidal particles stems from the fact that silica is chemically inert and optically transparent. Additionally, the silica surface can be easily modified with different functional groups by conventional surface chemistry.[20–23]

Various methods for the coating of different colloids with silica can be found in the literature. The classical Stöber synthesis[24] (base-catalyzed hydrolysis of tetraalkoxysilane-precursors with subsequent condensation of these hydrolyzed species and its derivatives) has been used for silica coating of different kinds of colloidal particles. Liz-Marzan, Mulvaney, and co-workers[25–26] have extensively studied metal–silica core–shell particles prepared by a liquid-phase procedure in which the use of a surface primer (a silane coupling agent) was necessary to provide the

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surface with silanol anchor groups. Rogach et al.[27] also introduced a method of adding mercaptopropyltrimethoxysilane (MPS) as a coupling agent to incorporate semiconductor nanocrystals into silica. Major disadvantages of the Stöber-based methods are the high requirements on purity of the reactants, the difficulty and multiplicity of the preparation steps, and the fact that it is not possible to directly coat nanoparticles with nonpolar ligands.

The water-in-oil (W/O) microemulsion system in conjunction with the Stöber synthesis and silane coupling method has been used for the preparation of silica-coated, metallic, magnetic and semiconductor nanocrystals.[28–30] In contrast to a previously published Stöber-based method, the procedure is very robust against slight changes in the reaction parameters and the purity of reactants, and it does not need any surface modification and pretreatment. Furthermore, it can be easily scaled-up, and no purification steps are required during the preparation of silica shell.
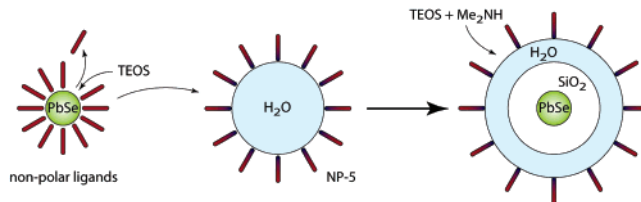
To our knowledge, studies on silica encapsulated PbSe NCs have not been achieved so far. Guided by these considerations mentioned above and regarding that it is desirable in view of industrial applications to coat the nanoparticles by a more convenient method, we demonstrate a simple method by which monodisperse silica coated PbSe can be prepared using a water-in-oil (W/O) microemulsion containing NP-5 (see Chemicals, below), cyclohexan and water system. In this article we report the details of this synthesis approach. The procedure yields nanocrystals encapsulated in a silica shell with a thickness of about 14 nm. To prevent the dissolution of the PbSe cores, dimethylamine was used as catalyst for the hydrolysis and condensation of tetraethoxysilane (TEOS).

Experimental Section

Chemicals. All of the chemicals were used as received from Aldrich without further purification. Poly(ethylene glycol) nonylphenyl ether (Synperonic NP 5) was purchased from Fluka; ammonia aqueous solution (33 wt %), dimethylamine (40 wt %), cyclohexane, acetone, butanol, propanol, and ethanol were from internal sources.

Preparation. The synthesis approach of PbSe NCs is based on a procedure developed by Murray et al.[12,31–33] using a similar device. Typically, 1.081 g of lead acetate [Pb(Ac)₂·3H₂O, 99.999%] was added into 15 mL of phenyl ether (99%) in the presence of 3.6 mL of oleic acid (90%) with constant agitation. The mixture was heated to 150 °C under flowing argon, remained for 30 min, and then cooled to room temperature. Under argon atmosphere, this cooled solution was subsequently mixed with 8 mL of Se-TOP solution (1M for Se) which was pre-prepared by dissolving metallic selenium (99.99%) into trioctylphosphine (TOP, 90%) in a glovebox and rapidly injected into 15 mL of hot phenyl ether which was heated to 180 °C under argon stream on a Schlenk line. The hot mixture was vigorously stirred for 6 min. The resulting PbSe colloids were cooled to room temperature by quickly removing the heating source and then isolated by adding a sufficient amount of ethanol and by separating with centrifugation. The resulting precipitate was re-dispersed in hexane followed by a size-selection treatment. The overall yield was around 65–80 wt %.

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The PbSe@SiO₂ particles were prepared by a modified W/O microemulsion method at room temperature. The microemulsion system was made up of cyclohexane, NP-5, PbSe, and dimethylamine. Typically, 10 mL of cyclohexane, 1.3 mL of NP-5, 400 μL of PbSe stock-solution (8.72 × 10⁻⁷ mol/L), and 50 μL of TEOS (99.999%) were added in a glass container under vigorous stirring. Thirty minutes after the microemulsion system was formed, 100 μL of dimethylamine aqueous solution (40 wt %) was introduced to initiate the polymerization process. Following the reaction, the first evidence for silica-encapsulation is provided by the color of the precipitate containing the composites, which are typical for specific NCs and their sizes and the disappearance of that color from the solution by an increase of light-scattering. The silica growth was completed after 24 h of stirring. The nanoparticles were destabilized from the microemulsion using acetone and precipitated by centrifugation. The resultant precipitate of PbSe@SiO₂ composite particles was washed in sequence with 1-butanol, 1-propanol, ethanol, and water to remove any possible surfactant and unreacted molecules. For each washing step, followed by centrifugation, a sonicator bath was used to completely disperse the precipitate in the corresponding solvent and remove any physically adsorbed molecules from the particle surfaces. Finally, aqueous dispersions of the composite particles were obtained.

Characterization. The products have been characterized by means of transmission electron microscopy (TEM), NIR absorption spectroscopy, energy-dispersive X-ray analysis, and electron diffraction. TEM specimens were prepared by evaporating one to two drops of reaction solution onto carbon-coated copper grids. TEM studies, combined with energy dispersive analyses of X-ray emission (EDAX) and selected area electron diffraction SAED, were carried out on a Zeiss LEO 912 Omega operating at 120 kV. Absorption spectra were recorded using an Omega 20 NIR spectrometer.

Results and Discussion

The water-in-oil microemulsion is an important method to prepare nanomaterials of small sizes.[34–37] In this method, reversed micelles are formed, i.e., water nanodroplets in an organic medium, and used as nanoreactors for the formation of nanoparticles. Additionally encapsulation in microemulsions offers a promising versatile technique for the synthesis of a wide variety of coated nanoparticles with the ability to control precisely the thickness and monodispersity of the core–shell particles formed.[38–39]

In the current reverse microemulsion system, cyclohexane served as a continuous phase in which TEOS and the PbSe-nanocrystals were dissolved. The microscopic water droplets were stabilized by NP-5. The formation of silica starts from the hydrolysis of TEOS at the oil/water interface catalyzed by amine

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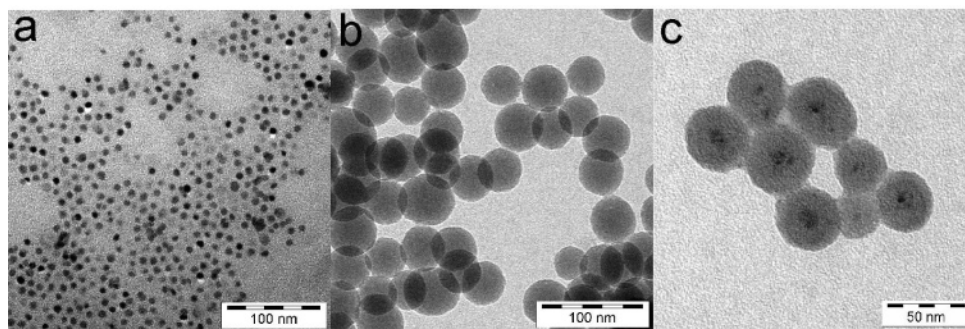(39) Darbandi, M.; Thomann, R.; Nann, T. *Chem. Mater.* **2005**, *17*, 5720.

Figure 1. TEM micrographs of (a) PbSe nanoparticles, (b) PbSe@SiO$_2$ nanoparticles, ammonia as catalyst, and (c) PbSe@SiO$_2$ nanoparticles, dimethylamine as catalyst.

aqueous solution. It is anticipated, that the PbSe@SiO$_2$ core−shell structures are formed on spontaneous exchange of the organic capping ligands of the NCs with TEOS and subsequent transfer to the hydrophilic phase of the microemulsion. On addition of the amine catalyst, the TEOS is polymerized and silica is formed on the surface of NCs (schematic presentation displayed in Scheme 1).

Figure 1 depicts TEM micrographs of the native PbSe nanocrystals and the products of the silica encapsulation in the presence of ammonia and dimethylamine as catalyst for TEOS polymerization. Reaction of the monodisperse PbSe−NCs (cf. Figure 1a) with TEOS using ammonia as catalyst, resulted in core-free silica particles (shown in Figure 1b). This is a confirmation that PbSe nanocrystals are dissolved in the presence of ammonia. Using dimethylamine as catalyst, clearly PbSe-silica core−shell nanoparticles were obtained (Figure 1c). Since the electron density of PbSe is significantly higher than that of silica, darker and lighter parts of particles correspond to PbSe and silica, respectively. If the concentrations of the reagents were not well-adjusted, multiple PbSe cores could occur.

Therefore, the coating of PbSe nanoparticles in a standard microemulsion process poses an additional difficulty that is related to the chemical instability of such particles in the presence of ammonia

$$PbSe + 2NH_3 + 2H_2O \rightarrow Pb(OH)_2 \text{ (s)} + 2NH_4^+ + Se^{2-}$$
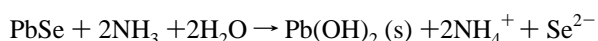
Since the pK_b value of dimethylamine (3.27) is lower than that of ammonia (4.75), the basicity cannot be the primary reason for the dissolution in ammonia. Possible reasons could be that the dimethylamine is sterically hindered to approach the PbSe surface on evolution of a very thin silica shell. Another reason could be the passivation of the PbSe nanocrystals at higher pH values.

The hydrolysis of alkoxysilanes occurs by a nucleophilic mechanism. Under basic conditions, water dissociates to produce nucleophilic hydroxyl anions (OH$^-$) in a rapid first step, and then the hydroxyl anion attacks the silicon atom. When an alkoxide group (OR) is replaced by a hydroxyl group, the electron density of silicon is reduced, accelerating the hydrolysis rate of other alkoxide groups (inductive factors). Once an alkoxide group is hydrolyzed, the others will be hydrolyzed rapidly, followed by the condensation of Si(OH)$_4$, resulting in the formation of monodisperse silica shells.[40−42] Therefore, the chemical reactions describing the hydrolysis and condensation of alkoxysilanes, invoking the formation of monodisperse silica shells,

Figure 2. Size distribution histograms of (a) PbSe core particle and (b) PbSe@SiO$_2$ core/shell particle.

can be briefly written as follows:

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$$

$$nSi(OH)_4 \rightarrow nSiO_2 + 2nH_2O$$

The mean diameters of PbSe and PbSe@SiO$_2$ are calculated from the transmission electron micrograph by averaging over a few hundred nanoparticles. The average diameter is 7.19 and 35.15 nm for core and core−shell particles, respectively (histograms depicted in Figure 2). It is possible to control the thickness of the silica shell by the structure and the concentration of the components.[43−44] Therefore, the size of the shell can be controlled and tuned by changing the water-to-surfactant molar ratio (in general, the higher the ratio, the larger the shell size).

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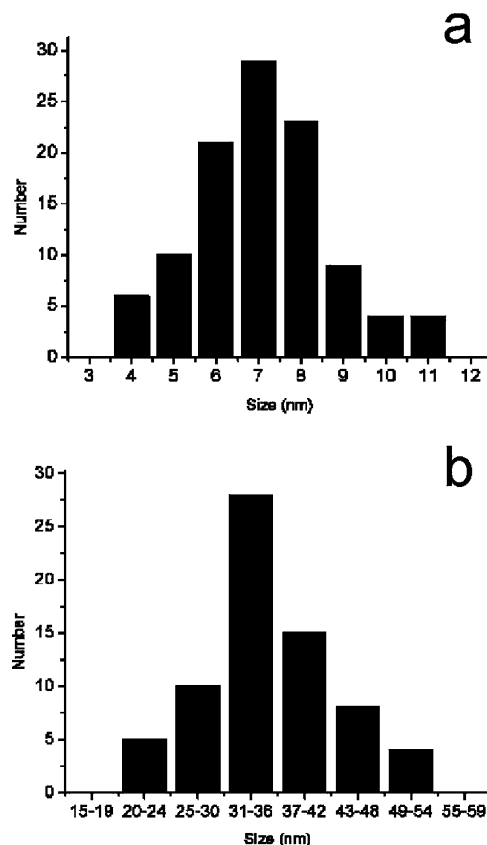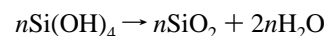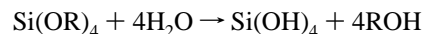(42) Pontoni, D.; Narayanan, T.; Rennie, A. R. *Langmuir* **2002**, *18*, 56.

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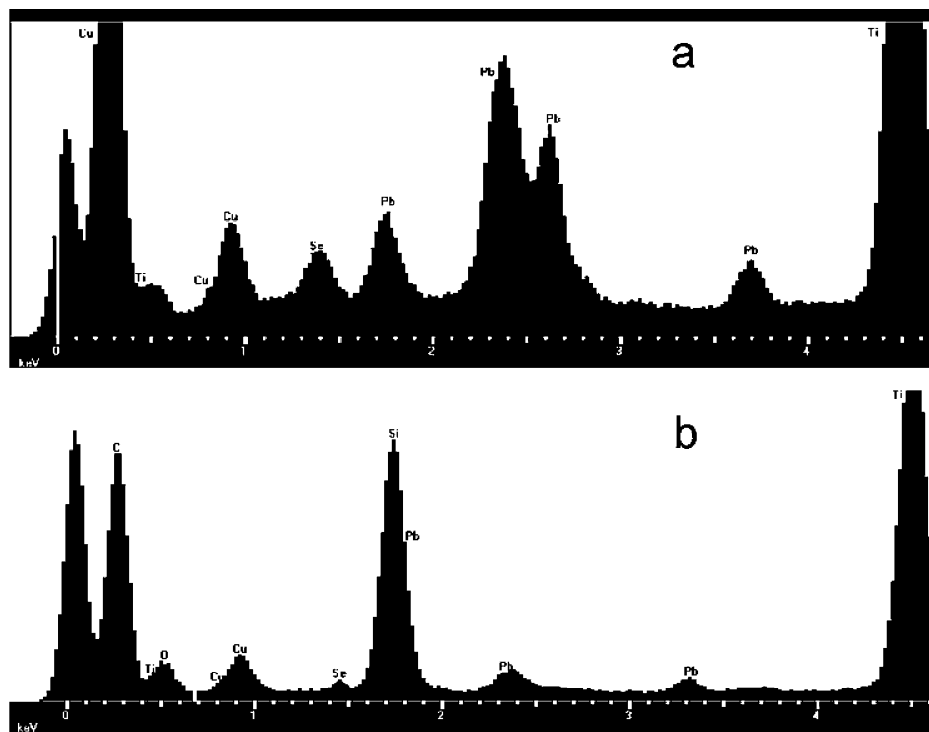(44) Dresco, P. A.; Zaitsev, V. S.; Gambino, R. J.; Chu, B. *Langmuir* **1999**, *15*, 1945.

Figure 3. EDAX spectra of (a) PbSe nanoparticles and (b) PbSe@SiO$_2$ nanoparticles.
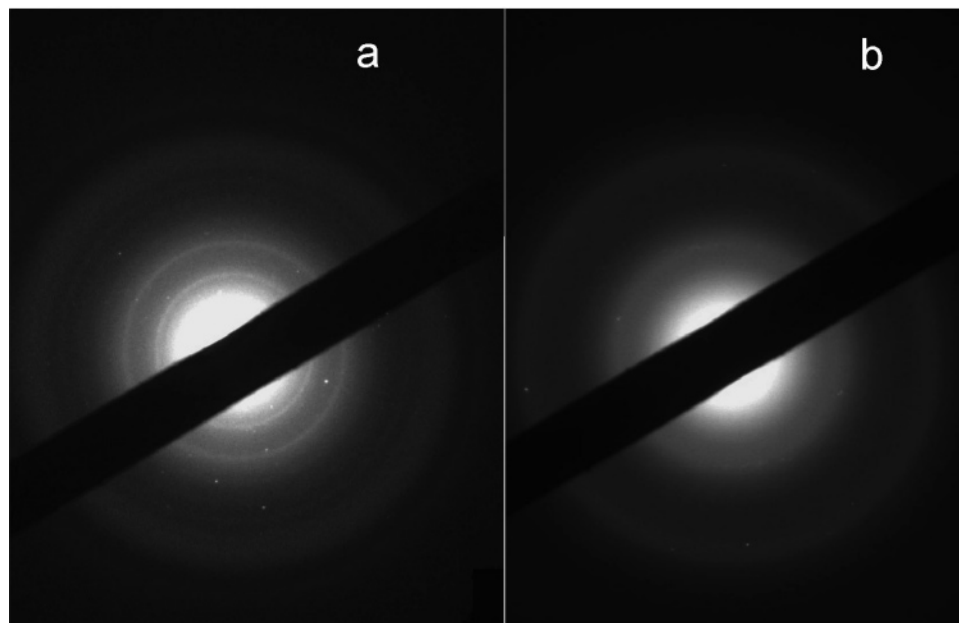

Figure 4. Electron diffraction patterns of (a) PbSe nanoparticles and (b) PbSe@SiO$_2$ nanocomposites.

Figure 3 shows the EDAX analysis of the PbSe NCs as well as PbSe@silica core−shell nanocomposites. EDAX analysis confirms the presence of Pb, Se in the cores (Figure 3a) and core−shell nanoparticles (Figure 3b), and moreover Si and O in core−shell NCs (Cu, C, and Ti are introduced from the TEM grid and sample holder in TEM apparatus).

The crystallinity of the PbSe NCsis proven by selected area electron diffraction (Figure 4a) of the sample, and it is confirmed that the NCs have a rock-salt crystal structure. It is generally believed that, for a spherical single-phase crystal with a size smaller than 10−20 nm, its surface must be a polyhedron containing high-index crystallography planes which possibly result in a higher surface energy.

Figure 4b demonstrates the coexistence of crystalline phase (PbSe) and amorphous phase (SiO$_2$) in the core−shell particles. Their amorphous nature renders further identification by electron diffraction impossible. It reveals the amorphous phase (SiO$_2$) in the core/shell particles, whereas the crystalline phase of PbSe is still detectable.

Room-temperature absorption spectra for PbSe NCs (solid line) and PbSe@SiO$_2$ nanocomposites (dotted line) are presented in Figure 5a. The absorption edge at about 1700 nm shows a strong quantum confinement of the excitons within the PbSe nanocrystals. When a silica shell is grown onto the PbSe nanoparticles, there is an increase in absorbance intensity and a slight red shift in the position of the absorption maximum
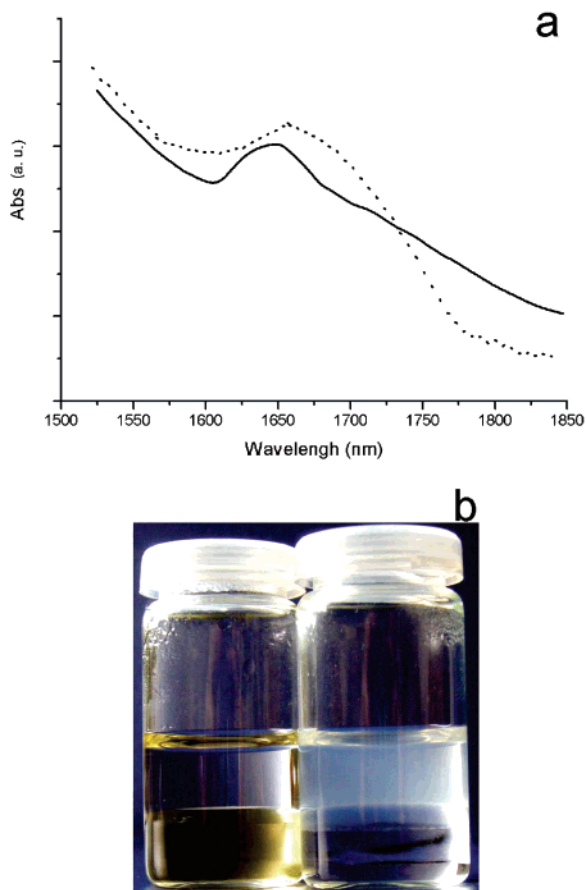
Figure 5. (a) Absorbance spectra of PbSe (solid line) and PbSe@SiO$_2$ nanoparticles (dotted line). (b) Photograph of PbSe NCs before (left) and after (right) silica encapsulation [chloroforme is the lower phase and water is the upper phase].

observed. These effects are due to the increase in the local refractive index around the particles combined with the increased scattering produced by the increase in particle size.

Figure 5b shows the phase-transfer of the black PbSe nanocrystal material from the oil phase to the water phase after silica encapsulation. Initially, the materials are soluble in organic solvents, as shown on the left where the organic phase has a distinctive brown-black color due to the presence of PbSe nanocrystals. The PbSe NCs derivatized for water solubility are shown on the right, where the nanoparticles are now to be found in the aqueous phase. The presence of hydrophilic hydroxyl groups (Si−OH) (existing in the form of negative charges in aqueous solution) on the silica shell renders the nanocrystals water-soluble.

Conclusion

In conclusion, we have developed a straightforward method for preparing monodisperse PbSe@silica nanoparticles. This methodology uses water-in-oil microemulsions in which hydrophobically ligated PbSe nanocrystals are spontaneously transferred to the water phase, and subsequently monodisperse silica shells are formed through a controlled hydrolysis of tetraethyl orthosilicate (TEOS). This method is fast and requires neither the use of silane coupling agents nor of a poorly reproducible precoating step with sodium silicate. The method could be applied to a variety of semiconductor nanocrystals with sphere or rod shape and there is no apparent limit to use the principles developed here for encapsulation of any type of hydrophobic nanocrystals of semiconductors, metals, magnetic materials, or oxides. The thin silica shell increases the mechanical stability, enables transfer into polar solvents and functionalization, and thus has the potential for many new applications.