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Nanocrystal Synthesis in an Amphibious Bath: Spontaneous Generation of Hydrophilic and Hydrophobic Surface Coatings**

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Nanocrystalline materials are of intense and widespread interest because of their promising applications in biological labeling, chemical catalysis, micro or nanoelectronics, and energy production.[1] On the nanometer scale, semiconductors show size-dependent photoluminescence,[2] metals exhibit tunable surface plasmon bands,[1a,b] magnetic materials become superparamagnetic,[3] and chemical catalysts become more active.[1c,4] Recent research has led to high-quality and monodispersed colloidal nanocrystals by using a number of synthetic methods including reactions in reverse micelles,[5] arrested precipitation in aqueous solution,[5a,6] and organic-phase high-temperature syntheses using hydrophobic coordinating ligands.[2a,7] The nanocrystals synthesized by using these methods have shown various degrees of crystallinity, monodispersity, size-tunability, stability, and processibility. However, a major limitation is that the resulting nanoparticles are soluble only in the reaction solution or in chemically similar media.[8] For example, nanocrystals synthesized in trioctylphosphine oxide or other organic solvents are only soluble in non-aqueous media, whereas nanocrystals prepared in aqueous solution are not compatible with nonpolar solvents that are often used for fabrication of composite materials, device incorporation, and catalytic reactions.[9]

Herein we report a new strategy that couples the synthesis and encapsulation of high-quality nanocrystals to yield nearly universal solubility. This method is based on the use of an "amphibious bath" that consists of amphiphilic multidentate ligands in a noncoordinating solvent, such as low-molecular-weight polyethylene glycol (PEG). The multidentate polymer ligands—amphipols[10]—contain aliphatic chains and carboxylic acid functional groups, and are found to act as both ligands for metal ion precursors and nanoparticle surface stabilizers. A major finding is that the resulting nanocrystals are instantly soluble in both polar and nonpolar solvents (such as water, acetone, DMF, and chloroform). We demonstrate that this "amphibious bath" method is applicable to a wide variety of technologically important nanocrystals including photoluminescent semiconductors (II–VI and IV–VI quantum dots), catalytic metals (palladium), noble metals (gold and silver), and superparamagnetic materials (iron oxide). This work broadly improves the applicability of nanocrystals in biolabeling, catalysis, and device fabrication.

As depicted in Figure 1, the multidentate polymer serves as a coordinating ligand for metal ion precursors, replacing traditionally used monovalent ligands such as such as oleic acid or stearic acid. At elevated temperatures (150–280 °C), these polymeric carboxylate precursors react in a similar fashion to their monovalent fatty acid analogues.[7,11] Upon nanocrystal nucleation, these multidentate polymers bind strongly to the nanocrystal surface during growth to yield monodisperse and highly stable colloids. The resulting nanocrystals are nonpolar because of directional coordination of the amphiphilic ligand on the crystal surface, which allows solubility in nonpolar solvents. However, metal ions are consumed during nanocrystal growth, releasing free polymer molecules into the reaction solution. When exposed to polar solvents, the multidentate polymer spontaneously encapsulates and solubilises the nanocrystals through the formation of hydrophilic micelles. This strategy is fundamentally different from previous approaches in which nanocrystals with amphibious attributes are coated with amphiphilic polymers such as polyethyleneimine,[12] or poly(2-(dimethylamino)ethyl) meth-

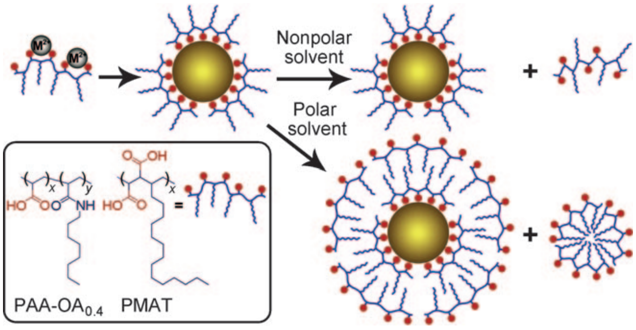

Figure 1. Schematic diagram showing the use of amphiphilic multidentate ligands to prepare nanocrystals that are instantly soluble in both polar and nonpolar solvents. The resulting nanocrystals are coated with the multidentate polymer, and are soluble in organic solvents. Upon exposure to water or other highly polar solvents, these nanocrystals are spontaneously solubilized by a second layer of the excess multidentate polymer, without any additional materials or steps. The inset shows the structures of two multidentate polymer ligands: octylamine-grafted polyacrylic acid (PAA-OA$_{0.4}$, $x = 0.6$, $y = 0.4$) and hydrolyzed poly(maleic anhydride-*alt*-1-tetradecene) (PMAT). M = metal.

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acrylate.[13] These approaches involved surface modification of presynthesized nanocrystals and required removal of the reaction solvent prior to redispersion in a new solvent.

Figure 2 shows the optical properties of CdTe nanocrystals in the size range from 2.5 to 7 nm synthesized in an amphibious bath, as well as their solubility features in a broad range of solvents. We stress that these nanocrystals do not contain a mixture of hydrophilic and hydrophobic surface groups, and are not inherently amphiphilic. The broad solubility arises from the amphibious nature of the reaction mixture towards both polar and nonpolar solvents. The nanocrystals purified in nonpolar solvents are no longer soluble in polar solvents unless excess amphipols are again added to the solution. Similarly, once the nanocrystals are solubilized in a polar solvent, they lose their solubility in nonpolar solvents, even if the polar solvent is removed and excess amphipol is added. This indicates that the hydrophilic coating generated in polar solvents is very stable and is essentially irreversible. As a result, the nanocrystals do not aggregate and remain monodispersed, as shown by light scattering and electron microscopy measurements (see below), and by the narrow surface plasmon absorption peaks of noble-metal nanocrystals (see Figure SF1 and SF2 in the Supporting Information).

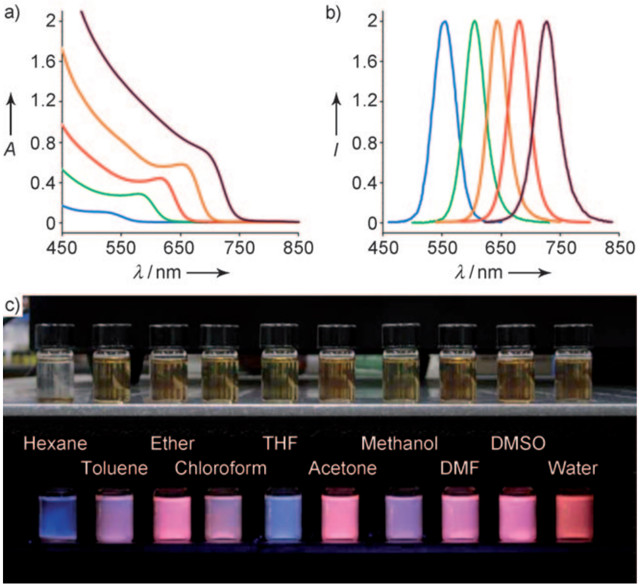

Figure 2. a) Optical absorption and b) fluorescence emission spectra of CdTe nanocrystals in the size range of 2.5–7 nm (diameter) synthesized in an amphibious bath (a mixture of amphipol and PEG). c) Fluorescence photograph of red nanocrystals that instantly dissolved in a broad range of polar and nonpolar solvents. When the nanocrystal fluorescence is quenched, the amphibious mixture shows a blue hue (see samples in hexane and THF).

In order to further understand the surface coatings of these nanocrystals, we have directly compared them with analogous nanocrystals synthesized using monovalent ligands. We prepared CdTe nanocrystals with a first exciton peak at 550 nm by using both the amphibious reaction bath and a conventional organic-ligand method.[14] Theoretically, the inorganic nanocrystals from these two methods should be essentially identical (3.2 nm diameter) because of their nearly identical optical properties.[15] We first characterized both of these colloids in hexane by using dynamic light scattering (DLS). Figure 3 a shows that the hydrodynamic size of the polymer-coated nanocrystals is slightly larger (6.8 nm) than the nanocrystals coated with monovalent ligands (5.2 nm). This is because of the steric bulkiness of the amphipol ligand and its larger radius of gyration than a small monovalent ligand. In fact, the hydrodynamic thickness value of approximately 1.8 nm is consistent with the theoretical prediction of a "loops-trains-tails" binding conformation for a monolayer of this multidentate polymer on the nanocrystal surface.[16] Next, we characterized the nanocrystals in water. To prepare aqueous dispersions of the conventional CdTe nanocrystals, we encapsulated these nonpolar colloids in micelles composed of the same amphipol that was used for the amphibious nanocrystal synthesis (PAA-OA$_{0.4}$). Previous research has shown that the resulting hydrophilic nanocrystals are surrounded by a stable hydrophobic bilayer.[8a,17] When dissolved in water, both of these nanocrystals are similar in size (12–13 nm), as determined by DLS and size-exclusion chromatography (Figure 3 b). They also have nearly identical electrostatic charges with a zeta potential of about −35 mV at pH 8.5. Therefore, these nanocrystals have similar structures in water. The thickness of the anionic micellar shell is 4–5 nm, which matches previous measurements of hydrophobic bilayers on nanocrystals.[8a,16a,17a,18]

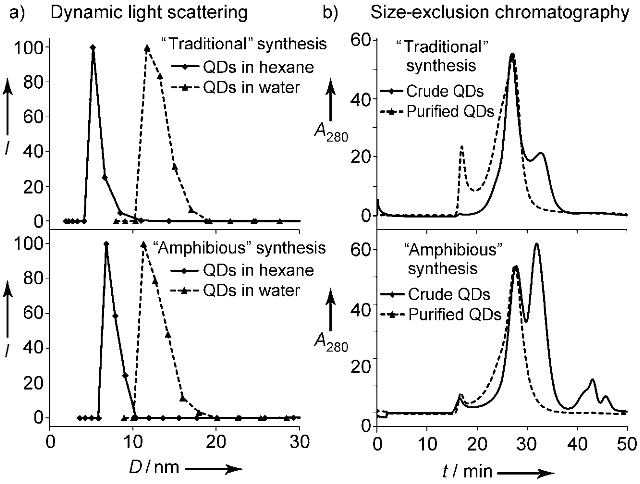

Figure 3. Size characterization of CdTe quantum dots (QDs) in hexane and water. a) Dynamic light scattering measurements of purified CdTe in hexane (solid line) or water (dotted line), prepared by using traditional multistep syntheses (top) or the one-step amphibious synthesis (bottom). b) Size-exclusion chromatograms of aqueous solutions of traditional CdTe QDs encapsulated in a micelle (top) or amphibious nanocrystals (bottom). Chromatograms were obtained from crude reaction mixtures (solid line) and nanocrystals isolated by ultracentrifugation (dotted line). Empty amphipol micelles elute at ca. 32 min and PEG elutes at ca. 42 min. A_{280} = absorbance at 280 nm.

We further examined the self-generated polymeric encapsulation layer by electron microscopy. Transmission electron microscopy (TEM) shows that the CdTe nanocrystals have smaller overall dimensions compared to their hydrodynamic sizes (Figure 4). This is expected because of the inability of electron microscopy to resolve surface-associated solvent molecules and also because of the shell compaction that occurs during the drying process. TEM studies also confirm that the size of the conventional ligand-coated CdTe nanocrystals matches that predicted from their first exciton peak. However, the nanocrystals prepared in the one-step amphibious reaction bath are again observed to be larger in size because of a dense polymeric coating. It is difficult to resolve the interface between the polymeric shell and the nanocrystal surface of such small CdTe nanocrystals, but it is more evident with larger PbSe nanocrystals. For this structural study, we have used PdSe because the multidentate ligands inhibit the growth of large CdTe nanocrystals but not large PbSe nanocrystals. Figure 5 shows images acquired from both Z-contrast scanning TEM (STEM) and scanning electron microscopy (SEM) of 22.5 nm aqueous PbSe nanocrystals. The image contrast from STEM is weighted toward electron-dense regions such as the nanocrystal core, whereas SEM can resolve surface features such as the organic polymer shell. Nearly every individual nanocrystal is found to be coated with a uniform shell with an average dry thickness of 1.6 nm. Some closely packed particles are observed to have organic shells with webbing that connects to adjacent particles, which may indicate interaction between the hydrophobic bilayers upon drying. These structural studies further support the conclusion that a simple single-pot process can be used to synthesize highly ordered micelle-encapsulated nanocrystals that previously could only be prepared using a complex and laborious multistep process consisting of nanocrystal synthesis, purification, and encapsulation.

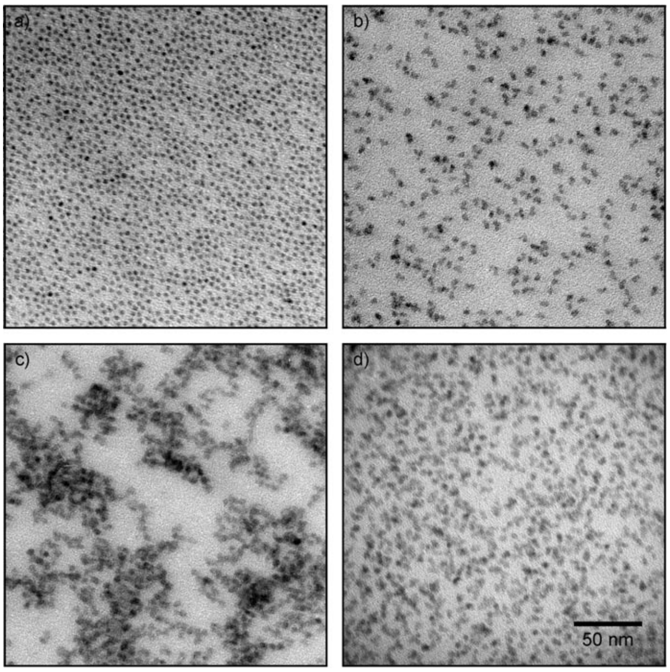

Figure 4. Electron micrographs of purified CdTe nanocrystals cast from a hexane solution, prepared using traditional coordinating ligands (a), or the "amphibious" reaction (b). Also depicted are "amphibious" nanocrystals cast from an aqueous solution before (c) and after purification (d). There was no significant aggregation evident in any of the solvents tested.

This phenomenon of spontaneous encapsulation is related to the nature of the amphiphilic coordinating ligand, as well as the reaction solvent. We have independently evaluated the contributions of both of these reaction components, as summarized in Table 1. The multidentate, amphiphilic structure of the amphipol is crucial for attaining the dual functionality of coordination and encapsulation. Traditional hydrophobic coordinating ligands used in high-temperature nanocrystal reactions, such as oleic acid, can be used to prepare stable, monodisperse colloids in nonpolar solvents. However these ligands are poor surfactants, and cannot stabilize nanocrystals in polar solvents. We have found that the achievement of efficient encapsulation from a coordinating ligand requires a balanced ratio of coordinating groups to hydrophobic groups; that is, too many coordinating groups yield poor encapsulation efficiency, whereas ligands containing too many hydrophobic domains cannot stabilize the nanocrystals during growth. In general, we find that alkylation ratios of 30–60 % work well for aliphatic chain lengths from 8 to 14 carbon atoms. Interestingly, spatial or structural ordering of these domains is not necessary, as amphipols with ordered structures (PMAT, Figure 1) and randomly grafted structures (PAA-$OA_{0.4}$) yield nearly identical particles. On the other hand, the use of a linear, graftlike polymer backbone is crucial for the success of this procedure, as it allows directional orientation of the hydrophilic and hydrophobic domains while preventing cross-linking. Performing this same procedure with a dicarboxy PEG ligand resulted in complete precipitation of the nanocrystals after nucleation because of ligand-induced cross-linking. We also note that multidentate polymeric ligands play an important role in nanocrystal nucleation and growth, more detailed results will be reported in a separate publication.

The self-generation of a micellar surface coating is highly sensitive to the chemical nature of the reaction solvent. Traditional nonpolar solvents, such as dioctylether (DOE) and octadecene (ODE), prevent micellar encapsulation of nanocrystals. The use of PEG as a reaction solvent is important because of its "amphibious" nature (that is, it is miscible with both polar and nonpolar solvents). Hexane, with which PEG is immiscible, is the only solvent in which the nanocrystals are not soluble (Figure 2b). However once PEG is removed from the nanocrystals (see below), they become soluble in aliphatic hydrocarbons. It is thus surprising that the nanocrystals are instantly soluble in diethyl ether, a solvent with which PEG is immiscible. We believe that this feature is a result of the amphiphilicity of the amphipol, which can solubilize a large amount of PEG in ether, even when present in small quantities.

Another interesting finding is that the PEG terminal groups (methoxy or hydroxy) can influence the colloidal properties of the nanocrystals, even though they do not directly interact with the nanocrystal surface. When the nanocrystals are synthesized in PEG terminated solely by

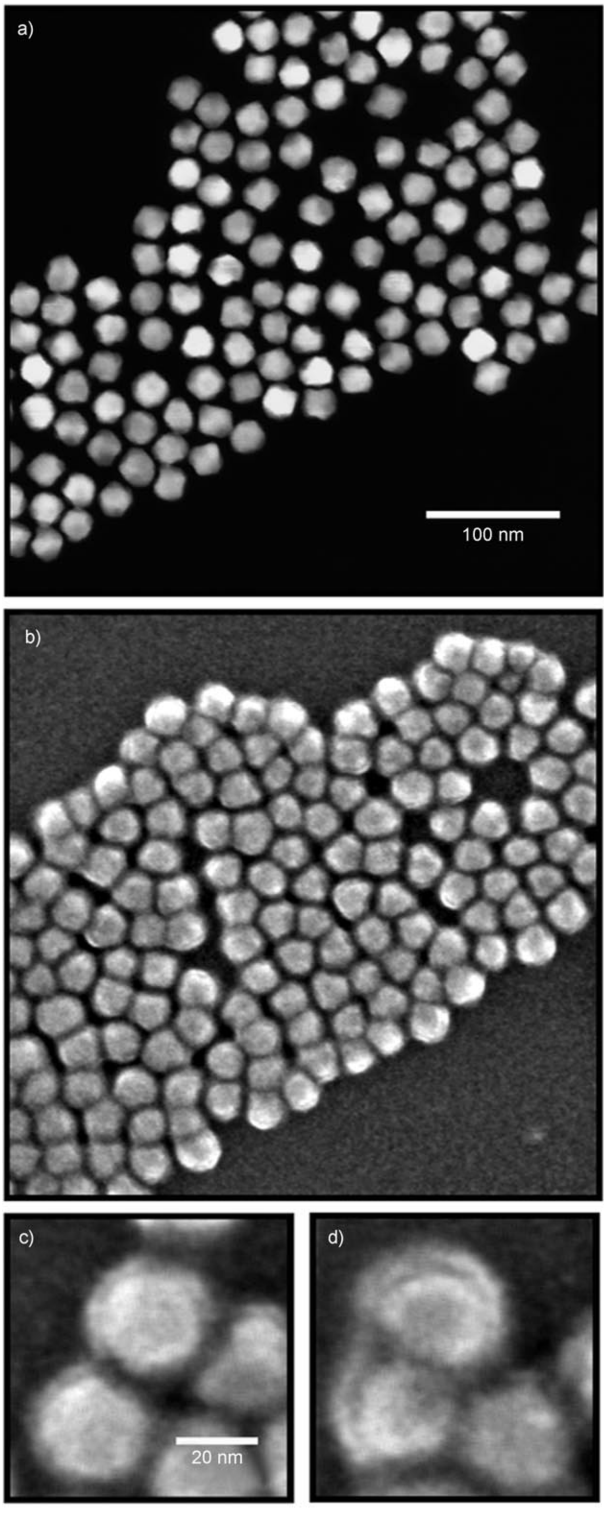

Figure 5. Electron micrographs of PbSe nanocrystals grown in the presence of amphipols, diluted in water, purified, and deposited on a TEM grid. a) Z-contrast STEM revealed that the nanocrystals are quasi-spherical and highly faceted, with an average diameter of (22.5 ± 1.7) nm. b) The same grid was imaged by SEM, showing a size of (25.7 ± 2.5) nm. The scale is identical to that of (a). c) Magnified SEM image showing an electron-dense core and organic shell. d) A rare example of nanocrystals in which the polymer shells are seemingly fused together. The scale is identical to that of (c).

methoxy groups, they spontaneously precipitate from the reaction mixture when the temperature is cooled below approximately 50 °C. This observation of temperature-controlled precipitation and dispersion could be exploited to bypass the expensive and laborious purification procedures in the large-scale synthesis of various nanocrystals. In contrast to methoxy terminal groups, both monohydroxy- and dihydroxy-terminated PEG solvents result in soluble colloid nanocrystals at room temperature (25 °C). As noted above, PEG does not interact with the nanocrystals because a) the growth kinetics of CdTe nanocrystals are nearly identical when using ODE, DOE, dimethoxy-PEG, monomethoxy-PEG, or dihydroxy-PEG and b) the use of a PEG-based solvent does not increase the hydrophilicity of nanocrystals prepared with monovalent ligands (Table 1). It is thus clear that the strongly binding amphipol ligand is responsible for the amphibious character of the nanocrystals, and PEG is an “adjuvant” that enhances this effect.

The amphibious reaction bath method is broadly applicable to a wide range of nanocrystalline materials (Figure 6). We have synthesized amphibious nanocrystals composed of noble metals (gold and silver, see Figure SF1 and SF2 in the Supporting Information) that have discrete surface plasmon bands in various solvents. We have prepared quantum dots with intense, size-tunable photoluminescence (see Figure SF3 and SF4 in the Supporting Information) that can be used directly in either biological buffers or in devices and composites. In addition, we have prepared catalytic palladium and superparamagnetic iron oxide nanocrystals (Figure SF5 in the Supporting Information). Preliminary studies have shown that the palladium nanocrystals have high catalytic activity in cross-coupling reactions between arylboronic acids and aryl halides in both polar and nonpolar solvents. All of these nanocrystals are stable at room temperature for at least three to four months after purification in both polar and nonpolar solvents, with no major changes in light scattering measurements and electron micrographs. We attribute this remarkable stability to the strong binding between the multidentate ligand and the nanocrystal surface, as well as the stable micellar coating of amphipols in polar solvents. Indeed, amphipols have previously been used to stabilize nonpolar nanocrystals[17] and integral membrane proteins[10a] in aqueous solution through hydrophobic interactions. Previous studies have shown that this hydrophobic binding is essentially irreversible.[8a, 19]

In summary we have developed a new synthesis strategy for a large variety of nanocrystals that are instantly soluble and stable in both polar and nonpolar solvents. A new finding is that multidentate polymers (amphipols) can serve as both coordinating ligands for metal atoms and nanocrystals, as well as micellization agents for nanocrystal encapsulation. To the best of our knowledge, such a highly ordered self-assembly process using a single surfactant for both coordination and hydrophobic encapsulation in a single step has not been reported before. The high temperatures used for crystal growth result in exceptional monodispersity and crystallinity, with reaction yields typically greater than 90 %. For applications in nonpolar solvents, these nanocrystals may be spontaneously purified from the reaction solvent; for applications in

Table 1: Solubility data of CdTe nanocrystals synthesized using multidentate ligands (amphipol) or traditional monovalent ligands (oleic acid) in three different solvents (ODE, DOE, or PEG).

Ligand	Solvent	Spontaneous precipitation	Chloroform solubility [%][a]	Acetone solubility [%][a]	Methanol solubility [%][a]	Extraction to polar solvent [%][b]
oleic acid	ODE	no	ca. 100	0	0[d]	0
	DOE	no	ca. 100	0	0	0
	PEG	yes/no[c]	ca. 100	0	0	0
amphipol	ODE	no	ca. 100	24.7	0[d]	0
	DOE	no	ca. 100	72.2	0	0
	PEG	yes/no[c]	ca. 100	98	98	ca.100

[a] Solubility was assessed as the fraction of nanocrystals stable in solution after dilution of the crude reaction mixture in the chosen solvent (1:10), and centrifugation at 7000 *g* for 10 min. [b] Extraction percentage between hexane and methanol, explained further in the Experimental Section. [c] Spontaneous precipitation only occurs for dimethoxy-PEG, a liquid at room temperature (< ca. 500 Da). [d] ODE is immiscible with methanol.

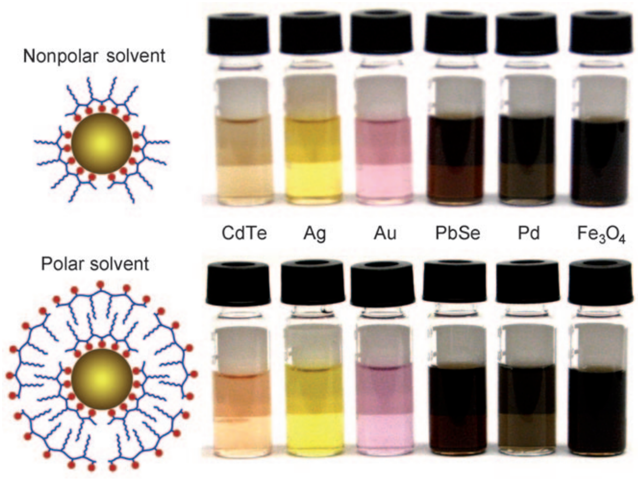

Figure 6. Left: schematic structures of self-generated hydrophobic and hydrophilic coatings on the nanocrystal surface. Right: metal, metal oxide, and semiconductor nanocrystals that are synthesized in an amphibious bath and are instantly soluble in both polar and nonpolar solvents.

aqueous solution, greater than 99 % of these nanocrystals are stable after dilution in water as carboxyl-functionalized colloids. The long-term stability of these nanocrystals is tremendous because of the strong multidentate coordination by the amphipols and the strong hydrophobic interactions of the micelles in polar solutions, both of which are stabilized through multiple anchor points on the surface. The nanocrystals that we have reported herein have great potential for applications in biological environments, homogeneous catalysis, device incorporation, and for the study of the solvent-dependent characteristics of nanocrystalline materials.

Experimental Section

Detailed synthetic procedures are described in the Supporting Information. For a typical synthesis of CdTe nanocrystals, cadmium(II) acetate hydrate (0.1 mmol, Aldrich, 99.99 %), amphipols (0.8 mmol carboxylic acids), and dihydroxy-PEG (4 g, 400 MW, Sigma) were added to a 50 mL flask. The flask was evacuated and charged with argon, and the temperature was raised to 150 °C. The tributylphosphine–telluride precursor, consisting of tellurium (0.05 mmol, Sigma, > 99.999 %), tributylphosphine (0.4 mmol, Aldrich, 97 %), and PEG (2 g), was then added and the reaction temperature was increased to 280 °C. The final nanocrystal size was controlled through the amphipol concentration and reaction time. Samples were obtained from the reaction mixture by removing small aliquots, which were diluted in various solvents while the reaction mixture was still warm. Other nanocrystals were prepared under similar conditions, as described in the Supporting Information.

Dynamic light scattering measurements were performed on a Brookhaven Instruments 90Plus Particle Size Analyzer. Before analysis, nanoparticle samples (1–10 μM) were first centrifuged at 7000 *g* for 10 min and then filtered through a 0.2 μm filter. Photoluminescence spectra were obtained using a Photon Technology International spectrofluorometer with typical slit widths of 4 nm. A xenon lamp was used as the excitation source and a photomultiplier tube used as the detector. Absorption spectra were obtained with a Shimadzu spectrophotometer with slit widths of 1 nm. Electron microscopy and energy dispersive X-ray spectroscopy (EDS) were performed on a Hitachi HD2000. Size-exclusion chromatography was performed on a Superose 6 10/300 GL column, with the absorption at 280 nm monitored on an AKTAprime plus (GE Healthcare) system with a 0.5 mL min^{-1} flow rate. Zeta potential was measured on a Zetasizer Nano-ZS90 (Malvern Instruments). Ultracentrifugal isolation of aqueous solutions of nanocrystals was performed on a Beckman Coulter Optima TLX Ultracentrifuge, typically at 100 000 rpm for 1 h.

The extractions described in Table 1 were performed as follows: An aliquot of a crude reaction mixture containing CdTe nanocrystals (1 mL) was diluted in a mixture of hexane (5 mL) and methanol (8 mL). The solution was mixed vigorously and the percentages of nanocrystals in the top hexane phase and bottom methanolic phase were determined spectrophotometrically.

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