Nanocrystal Purification

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An Efficient and Low-Cost Method for the Purification of Colloidal Nanoparticles**

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Efficient purification is critical to the fundamental and practical exploitation of nanoparticles in the technological domain. Whether for lighting, bio-imaging, coatings, photovoltaics, or displays, a routine, low-cost purification method that is directly applicable post-synthesis and in reuse/recycling would be of tremendous benefit to the commercialization of nanoparticle-based devices. Moreover, purification is essential to understanding the functional properties of nanoparticles, which are strongly dependent on purification history.[1]

In nonaqueous media, the most common technique for nanoparticle purification is the precipitation–dissolution method.[2] This technique requires significant time and materials, including expensive centrifuges that do not scale well in an industrial setting. Meanwhile, the efficiency of this technique varies with the morphology and the nature of the nanoparticles, in particular giving lower yields with certain smaller and shaped nanoparticles. Other techniques, such as dialysis,[3] ultra-filtration,[4] and diafiltration,[5] remain problematic as they rely on controlled-pore-size materials that are expensive and suffer from fouling. Additionally, these techniques, along with size-exclusion and high-performance liquid chromatography,[6] have high solvent burdens and suffer from slow dynamics. Other interesting techniques involving microemulsions or particular ternary solvent systems may be difficult to generalize.[7]

Collectively, the purification techniques developed to date for nanoparticles in nonaqueous media have issues with cost, scale-up, applicability, and/or the lack of green processing. These issues are tremendous obstacles for efficient manufacturing and, by consequence, to the widespread development and implementation of nanoparticle-based technologies. Herein, we report an effective nanoparticle purification method based on reversible electrophoretic deposition, defined here as electropurification, which overcomes most the disadvantages of traditional techniques.

Electrophoretic deposition is the deposition of colloidal particles through the application of an electric field, a widely-adopted industrial process used, for example, in automobile coatings.[8] Electrophoretic deposition has also been applied in several embodiments to deposit nanoparticles such as CdSe to form permanent fixed coatings.[9] Herein, however, we describe a method to reversibly deposit nanoparticles onto an electrode surface. We can use the reversible nature of this process, achieved through the addition of particular non-solvents to the electrodeposition solution, to selectively collect and separate nanoparticles from unwanted impurities in solution. The collected nanoparticles are then redispersed into clean solvent.

Figure 1 shows how a simple lab-scale setup can be used to separate and collect nearly 100% of oleic acid (OA)-capped CdTe nanoparticles from solution within a matter of minutes. The setup comprises two electrodes, an aluminum bar and a stainless steel mesh, placed in a glass beaker and connected by a glovebox feed-through to a DC power supply. The initial solution is the unpurified reaction media[10] diluted with about 1.5 volume equivalents of acetone, a non-solvent. This reaction media contains the primary solvent (octadecene) and contaminants, such as excess OA, tributylphosphine (TBP), leftover precursors (cadmium oleate and Te-TBP), and reaction byproducts. Within minutes, an applied DC potential of 500 V causes the nanoparticles to collect on the aluminum anode, leaving a nearly colorless residual solution. The adsorbed nanoparticles are further washed with acetone while still on the electrode. Thus purified, the nanoparticles may be collected either as a solid or redispersed in a good nonpolar solvent, such as chloroform, hexane, or toluene. A real-time video demonstration, showing both the collection and redissolution of CdTe nanoparticles in less than two minutes, is available in the Supporting Information.

Figure 2 shows the absorption and emission of electropurified CdTe nanoparticles as compared to those before purification and those conventionally purified by repeated precipitation–dissolution. The essentially identical first exciton and emission peak positions and spectral broadening indicate that there are no significant variations between the electropurified nanoparticles and those purified by conventional precipitation–dissolution. The H^1 NMR spectrum of these electropurified nanoparticles (Figure 3) reveals a clean product. Broad resonances consistent with bound oleic acid[11] are observed at $\delta = 1.1$, 1.44, and 2.3, and 5.56 ppm. There is a notable absence of resonances attributable to the cadmium

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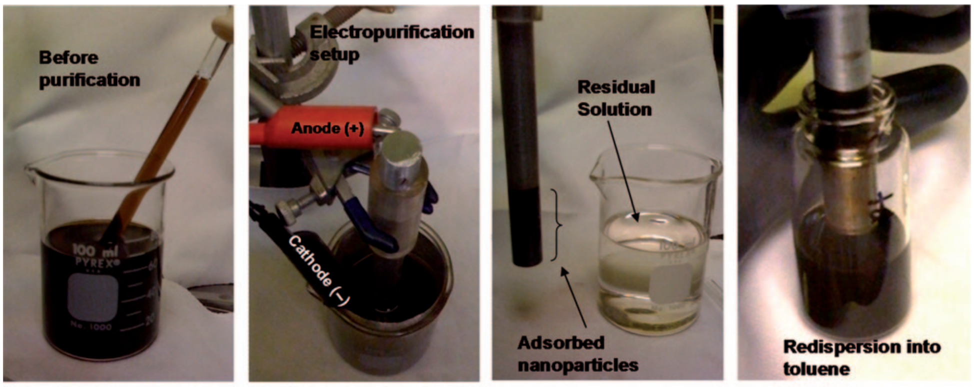

Figure 1. Electropurification process showing, from left to right, an as-synthesized nanoparticle solution (CdTe) before, during, and after reversible deposition on the electrode. The final frame shows the redispersion of the nanoparticles into clean solvent, contrasting the bottom of the electrode, which has been exposed to toluene and is clean, with the top of the electrode, which still contains adsorbed nanoparticles.

oleate precursor, octadecene, or tributylphosphine. The absence of these species was further corroborated by FTIR analysis (Supporting Information), demonstrating the overall effectiveness of electropurification.

Electropurification is a versatile technique applicable to a variety of nanoparticles with different shapes, compositions, and ligands (Table 1 and Figure 4). For example, tetrapod CdTe nanoparticles are easily purified, yielding nanoparticles with spectral signatures that are almost identical both to the unpurified nanoparticle solution and nanoparticles purified by conventional precipitation–dissolution (Supporting Information). Similar results were also obtained for CdSe/CdS nanorods capped with alkyl phosphonic acids and alkyl amine ligands (Supporting Information).

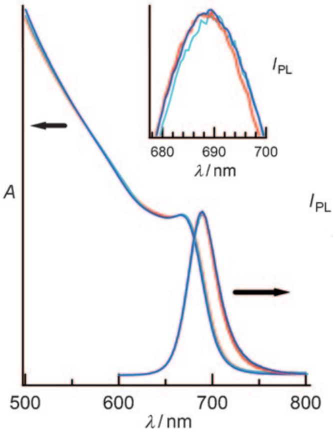

Figure 2. Absorption and emission spectra for CdTe nanoparticles synthesized using oleic acid and tributylphosphine in octadecene. Red: post-synthesis, cyan: conventionally purified by precipitation–dissolution, blue: electropurified.

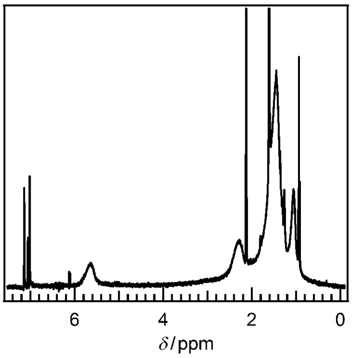

Figure 3. ^{1}H NMR of the electropurified oleic acid capped CdTe nanoparticles. Note the broad signals corresponding to bound ligand centered at 5.65 (olefinic), 2.3 ($-H_2C-COO-$ and $-H_2C-H_2C=$), 1.44 (methylene), and 1.1 (methyl). The sharp peaks are due to [D$_8$]toluene and residual hexane.

Table 1: Nanoparticles purified by reversible electrophoretic deposition.

Material	Ligand(s)[a]	Shape/size [nm]	Yield[b]
CdTe	OA, TBP	mixed: spherical, ellipsoidal and rod-like	94–98%
CdTe	OA, TOP	tetrapods	
CdSe/CdS	alkyl phosphonic acids	5–10×10–50 nm rods	
PbSe	OA, TOP, DPP	spherical	90–95%

[a] OA: oleic acid, TBP: tributylphosphine, TOP: trioctylphosphine, DPP: diphenylphosphine. [b] Based on the absorbance at the first exciton peak for CdTe and at 650 nm for PbSe to minimize solvent interference.

A comparison of electropurified nanoparticles and nanoparticles purified conventionally by two precipitation–dissolution cycles was also performed for PbSe nanoparticles. UV/Vis/NIR absorption measurements (Figure 5) show that the positions of the first exciton peaks are nearly identical: (1631 ± 2) nm for the conventionally purified nanoparticles and (1628 ± 4) nm for the electropurified nanoparticles. The nanoparticle yields, quantified on the basis of absorption measurements, were also nearly identical to within ± 4%.

Electropurification is comprised of three processes, electrophoretic migration of the nanoparticles to the electrode surface, nanoparticle aggregation at the electrode surface and, redispersion of the nanoparticles in fresh solvent. Electrophoretic migration arises from charges on the nanoparticle surface that are compensated by opposing charges outside the slip boundary. Electrophoretic mobility in nanoparticle systems, including CdSe and PbSe in nonpolar solvents, is well documented.[1a,12] The magnitude and direction of the electrophoretic mobility varies with the ligands[12] and solvent,[8] and thus can be tuned through additives and co-solvents.

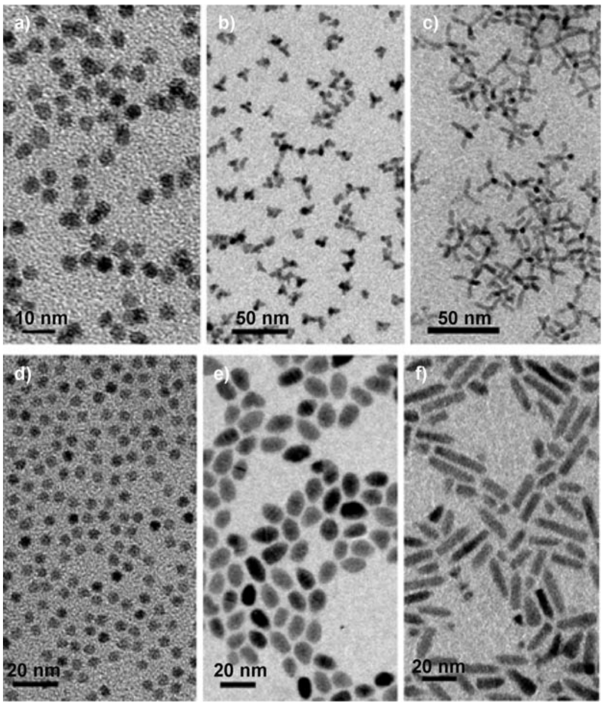

Figure 4. TEM images of a) spherical, b) mixed-shape, and c) tetrapod CdTe nanoparticles, d) spherical PbSe and e) rice-shaped CdSe/CdS nanoparticles, and f) CdSe/CdS nanorods that were successfully purified by electropurification.

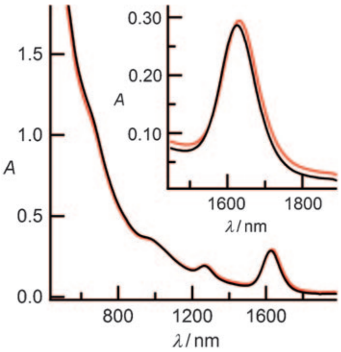

Figure 5. Absorption spectra showing PbSe nanoparticles conventionally purified (red) and purified by reversible electrophoretic deposition (black). Inset: an expansion of the first exciton peak region.

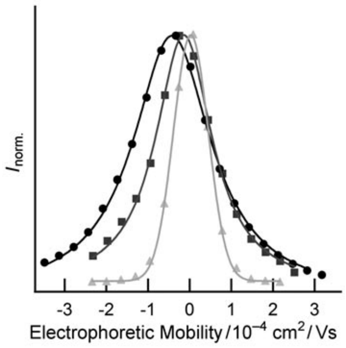

Figure 6. Electrophoretic mobility measured at a field strength of 25 V cm^{-1} for CdTe nanoparticles in the as-synthesized reaction mixture (▲) and diluted 1:3 (■) and 5:3 v/v with acetone (●). Solid lines are fits to the data (Lorentzian for the two series strongly broadened by Brownian diffusion; Gaussian for the narrower series).

We investigated nanoparticle mobility during electropurification, and specifically the effect of adding acetone, using laser doppler electrophoresis. The average mobility of as-synthesized CdTe nanoparticles (OA, TBP) is slightly positive at $(0.02\pm0.01)\,\mu\text{m}\,\text{cm}\,\text{V}^{-1}\text{s}^{-1}$. Dilution with acetone (1:3 v/v acetone/reaction mixture) changes the sign of the average mobility and greatly increases its absolute magnitude to $(-0.17\pm0.02)\,\mu\text{m}\,\text{cm}\,\text{V}^{-1}\text{s}^{-1}$. At a 5:3 acetone/ reaction mixture ratio, conditions suitable for electropurification, there is an additional increase in magnitude to $(-0.47\pm0.03)\,\mu\text{m}\,\text{cm}\,\text{V}^{-1}\text{s}^{-1}$. Under the deposition potentials used for electropurification (200–1000 V cm^{-1}), this mobility would predict nanoparticle movement over typical distances of 1–2 cm to occur on the order of 10^2 s, in line with timescales seen for purification. Figure 6 shows the mobility distribution of the nanoparticles as a function of acetone addition. In the presence of high acetone concentrations, mobility data is collected at low field strengths (for example, 25 V cm^{-1} in Figure 6) to avoid nanoparticle deposition on the electrodes. At low field strengths, the mobility distributions are quite broad owing to Brownian diffusion. Nonetheless, the average mobility remains constant, being independent of field strength at low applied potential. Migration to the positive anode is consistent with the negative mobility values observed upon the addition of acetone. We speculate that acetone is able to complex positively charged metal complexes, along with providing a high dielectric environment that facilitates charge separation. Alternatively, trace materials, including water, may also be a factor, though other solvents, including anhydrous alcohols, can also be effective.

Aggregation is determined by the balance of van der Waals and electrostatic forces and steric interactions owing to the presence of the ligands. We speculate that aggregation and redispersion are controlled mainly by these steric interactions,[13] which lead to stable dispersions in good solvents and aggregation in poor solvents. The addition of acetone or other non solvents reduces the solvent quality and pushes the system closer to its critical dissolution/aggregation transition. The electrophoretic force then facilitates the transition to a weakly aggregated state at the electrode. Temperature-, pressure-, and volume-controlled critical aggregation points are already known in colloidal systems.[13a] Removal of the potential, which does not cause redispersion, shows that the aggregated state at the electrode is in a reasonably deep potential well. Redispersion is achieved when the system is exposed to a good solvent system that is sufficient to overcome the ligand–ligand interactions of aggregated particles. Beyond this, additional factors that may contribute to the balance of forces responsible for colloidal stability during electrodeposition include concentration-driven changes in the permittivity and nanoparticle–ligand interface as the environment between nanoparticles become dominated by that of the (waxy) ligand shell, double layer distortion owing to flow, and charge transfer to the electrode. We do not have sufficient evidence at this time to clarify the underlying physics.

In summary, we have demonstrated that electropurification, utilizing the reversible electrophoretic deposition of nanoparticles through the application of an electric field, can be successfully employed to quickly and efficiently purify a variety of nanoparticles in nonaqueous media in an environmentally friendly manner. This is true for nanoparticles of varying shape, size, and composition, including a number of the most common ligand systems. Recovery yields approaching 100% of highly purified nanoparticles are feasible in as little as a few minutes. Relatively little solvent is used and essentially no degradation in nanoparticle quality is evident; that is, there are no changes in the spectral peak positions or broadening. Electropurification can be directly performed with nanoparticles from their as-synthesized reaction media without any pre-purification steps. It is also applicable to pre-processed nanoparticles, such as may be found in a recycle stream. Finally, our electropurification process is highly scalable, making it relevant to industry-level purification needs. Continuous and semi-continuous applications based on modified rotating drum, disk, ribbon, or belt electrodes can be envisioned, and lab-scale semi-automated purification, as used for the purification of CdSe/CdS, is easily accessible. Achieving such scalability in purification is one of the key factors in reducing the cost of nanoparticles and enabling their widespread adoption in a variety of technical applications.

Experimental Section

Chemicals and materials were obtained commercially or synthesized according to reported procedures with some modifications.[2c,14] Detailed synthetic procedures are available in the Supporting Information. Room-temperature ^{1}H NMR spectra were obtained on an Avance 400 spectrometer in either [D$_8$]toluene or CDCl$_3$. Transmission FTIR was performed on a Thermo Nicolet Nexus 670 on samples spread onto silicon wafers. The high-voltage source was a Fluke 415B or a Matsusada AU series power supply. Photoluminescent spectra were collected on a Jobin Yvon Fluorolog and UV/Vis/NIR absorbance on a Varian Cary 5000 spectrophotometer. Electrophoretic mobility was measured using a Zetasizer Nano ZS (Malvern) using a palladium electrode dip cell (0.2 cm spacing). Runs were performed in triplicate (each consisting of 100 sub-runs of 10 s duration) using applied potentials from 5 to 40 V. CdTe electropurification was conducted in a glove box ($<$ 1 ppm O$_2$ and H$_2$O) to avoid nanoparticle oxidation.

Conventional precipitation–dissolution purification: In a typical procedure, nanoparticles in post-synthesis solution (5 mL) were precipitated by the addition acetone (20 mL) and isolated by centrifugation (10 min, 7500 rpm). The precipitate was redispersed in anhydrous hexane (5 mL), again precipitated with acetone (20 mL), and isolated by centrifugation (10 min, 7500 rpm).

Electropurification: Oleic acid/tributylphosphine capped cadmium-rich CdTe nanoparticles (CdTe-OA) were purified directly from the raw post-synthesis reaction media in hexane (composition: hexane 39.0% v/v, octadecene 60.3% v/v, tributylphosphine 0.7% v/v, 8.5 mM CdTe-OA determined by the method reported in [4], plus any unreacted precursors). In a typical procedure, a 500 V DC potential was set across two FTO-coated glass electrodes placed about 2.5 cm apart in a 50 mL glass beaker containing the solution (10 mL). Owing to the high voltage, care should be taken to maintain a safe working environment. Acetone (15 mL) was then added over 5 min wherein the nanoparticles were deposited on the anode and the solution became optically clear. After 15 min, the potential was shut off and the electrodes were removed from the solution. The collected nanoparticles were washed with acetone (ca. 5 mL) and redispersed in a good organic solvent, such as hexane, toluene, or chloroform. Other electrode arrangements were used for larger batches of materials (see for example Figure 1). Tetrapod CdTe nanoparticles capped with oleic acid and trioctylphosphine and spherical PbSe nanoparticles capped with oleic acid and trioctylphosphine and diphenylphosphine were purified similarly. Once the ideal ratio of solution to non-solvent is known, the procedure can be carried out much more quickly by first adding all the nonsolvent and then applying the potential. CdSe/CdS nanomaterials were purified directly from the raw post-synthesis solution in a semi-automated process, the details of which are reported in the Supporting Information.

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