

Synthesis of water-soluble PbSe quantum dots

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Water-soluble PbSe semiconductor quantum dots (QDs) with near-infrared absorption of 1100–2520 nm (corresponding to a diameter of 3–13 nm) were synthesized using 2-aminoethanethiol (AET). The oleic acid-stabilizing ligands used in the traditional synthesis of PbSe were exchanged with the 2-AET ligands, which promoted the solubilization of the QDs in an aqueous medium. This occurred due to the attraction of the surrounding water molecules to the exposed amino group, thus allowing the particles to reside in the water environment. The water-soluble PbSe QDs have very narrow size distribution ($\sigma \approx 4.5\text{--}5.5\%$). Transmission electron microscopy, spectrophotometric measurements, and Fourier transform infrared spectroscopy indicate that the morphology, size, size distribution, and chemical composition of the PbSe QDs remained unchanged during the transfer to an aqueous medium. In conclusion, the ability to synthesize water-soluble PbSe QDs with stable properties and uniform size distribution will allow them to have substantial advantages for biological applications such as biosensors and drug delivery.

I. INTRODUCTION

The synthesis and use of nanoparticles constitute a major research area that has attracted both academic and industrial interest.^{1,2} Due to quantum confinement effects, semiconductor nanocrystals [i.e., quantum dots (QDs)] exhibit special physical and chemical properties that are greatly different from those of their corresponding bulk materials.^{3–6} Over the past two decades, great efforts have been put into the synthesis of highly fluorescent II–VI semiconductor nanocrystals.^{7–12} One of the multitude of synthesis methods, the TOP (trioctylphosphine)/trioctylphosphine oxide (TOPO) synthetic approach, has become one of the most successful and mature methods for preparing highly fluorescent II–VI QDs to date.^{7,8,10}

However, the direct product of the TOP/TOPO synthetic approach is insoluble in water, which to some ex-

tent limits the application of TOP-stabilized QDs as bio-labeling materials.^{13,14} Many applications require these particles to be water dispersible and to remain suspended in water with no loss of physical or chemical properties over extended periods of time.² Unfortunately, water-based syntheses of nanoparticles are fraught with problems as a result of ionic interactions, which are typically overcome by using low reactant concentrations (about 5×10^{-4} M),¹⁵ or because the synthesis is carried out in the presence of stabilizers that are subsequently difficult to remove.¹⁶ In contrast, particles synthesized in organic solvents can be made at relatively high concentrations (up to 1 M of reactant)¹⁷ with predefined size and shape,^{18,19} and with improved monodispersity compared to those prepared in aqueous solutions. Such particles are, however, water immiscible, which limits their range of applicability.²

Hence, to overcome this difficulty, the main strategy used in this study was to first synthesize the QDs by traditional methods in the organic phase, and subsequently to replace the surface-binding TOP with bifunctional molecules that are capable of both strongly binding to the surface of the QDs (e.g., the thiol group) and also exposing a strong polar group (e.g., COOH or NH₂ groups) to the aqueous medium.²⁰ Here, we report on the

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preparation of water-soluble PbSe nanocrystals stabilized by 2-aminoethanethiol (AET). These QDs turned out to be very stable in aqueous solutions after a long time period. Moreover, they exhibited a narrow size distribution, with their average size essentially unchanged upon their transfer to an aqueous solution, and identical spectroscopic and crystalline structures.

II. EXPERIMENTAL SECTION

A. Materials

2-AET ligands (AET 98%, 97%+ purity), methanol (CH_3OH , $d = 0.79 \text{ g/cm}^3$, boiling point (b.p.) 65°C), and chloroform (CHCl_3 , spectroanalytical grade 99%, $d = 1.48 \text{ g/cm}^3$, b.p. 62°C) are commercially available products and were purchased from Aldrich (Milwaukee, WI).

Lead acetate trihydrate (Pb-Ac, $\text{Pb}[\text{CH}_3\text{COO}]_2 \cdot 3\text{H}_2\text{O}$, GR) was purchased from Merck (New York, NY), along with PhEt ($\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$, 99%), oleic acid [OA; $\text{CH}_3(\text{CH}_2)_7\text{CHCH}(\text{CH}_2)_7\text{COOH}$, 99.8%], TOP ($\text{C}_8\text{H}_{17}\text{P}$), and selenium (Se, 99.995% purity).

B. Synthesis of organically capped and water-soluble PbSe QDs

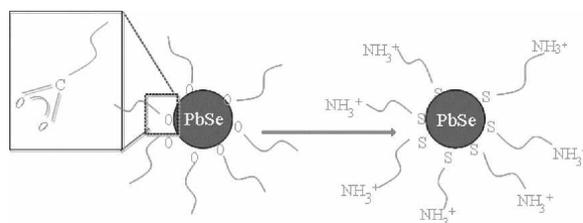
Several synthesis routes generating PbSe QD cores that were stabilized by organic surfactants were previously reported in the literature.^{21–26} In this work, the preparation of PbSe QDs core stabilized by organic surfactants was followed by the TOP-based procedure reported previously,²⁶ which included the following stages: (i) 0.71 g of lead acetate trihydrate (Pb-AC) were dissolved in a solution that was composed of 2 mL of PhEt, 1.5 mL of OA, and 8 mL of TOP, under standard inert conditions in the glove box, and were inserted into a three-necked flask (flask I); (ii) 10 mL of PhEt were inserted into a three-necked flask (flask II) under the inert conditions of the glove box; (iii) both flasks were taken out of the glove box, and were placed on a Schlenk line and heated under a vacuum to $100\text{--}120^\circ\text{C}$ for 1 h; (iv) flask I was cooled to 45°C , while flask II was heated to $180\text{--}210^\circ\text{C}$, both under a stream of argon gas; (v) 0.155 g of selenium powder was dissolved in 2.0 mL of TOP, forming a TOP:Se solution, under standard inert conditions of a glove box, then 1.7 mL of this solution was injected into flask I on the Schlenk line; and (vi) the contents of flask I, containing the reaction precursors, was injected rapidly into the PhEt solution in flask II, reducing its temperature to $100\text{--}130^\circ\text{C}$, leading to the formation of PbSe QDs within the first 15 min of the reaction. The procedure described produced QDs with a narrow size distribution, and a tunable average size between 3 and 9 nm, which was controlled by the temperature and the duration of the reaction.

To create water-soluble PbSe QDs with a positively charged capping, 100 μL of an organically capped PbSe QD solution was dissolved in 5 mL of chloroform. Subsequently, 100 μL of a 0.5 M methanol solution of AET was added. The relatively stronger affinity of the thiol group originating from AET [$\text{HS}(\text{CH}_2)_2\text{NH}_3$] ligands to the PbSe surface,^{20–22} with respect to that of the OA carboxyl group, led to a ligand exchange, as shown schematically in Scheme 1. Thus, the exterior surfaces of the PbSe QDs exchanged aliphatic terminating groups (the CH_3 end-groups of the OA) with the amine groups of the AET ligands. This immediately causes flocculation of the PbSe QDs in chloroform. Subsequently, 5 mL of water was added to the suspension, resulting in a separation of the mixture into two phases (water above chloroform). Upon further shaking, the flocculated QDs dissolved into the water phase and formed a clear suspension.

III. RESULTS AND DISCUSSION

Water-soluble, AET-capped PbSe QDs show exciton absorbance at room temperature. Figure 1 presents the absorbance spectra of PbSe QDs, where the main transition ($1S_h\text{--}1S_e$)²³ can be observed. The absorbance spectra of the aqueous solution showed a broad absorption peak around 1525 nm that was slightly red shifted in energy due to the influence of different dielectric constants of the environment,²² indicating that the size of QDs remains essentially unchanged. The QDs after transfer to the aqueous solution were inspected using transmission electron microscopy (TEM).

Figure 2 shows the TEM images of the QDs in an aqueous suspension after phase transfer, while the inset in Fig. 2 shows the PbSe QDs as prepared in a chloroform suspension before phase transfer. No obvious shape or size change was found between the samples before and after the phase transfer. The TEM images confirm that no significant aggregation of the transferred QDs occurred. The diffraction pattern (Fig. 3) indicates a crystalline structure for the QDs after the phase transfer. Table I summarizes the analyzed data from the diffraction pattern and the d spacing of the PbSe QDs in an organic solution. The diffraction analysis proved that the PbSe QD structure remained unchanged upon the transfer to the water solution. These QDs are stable in water under



SCHEME 1. Ligand (capping) exchange of PbSe QDs by AET ligands.

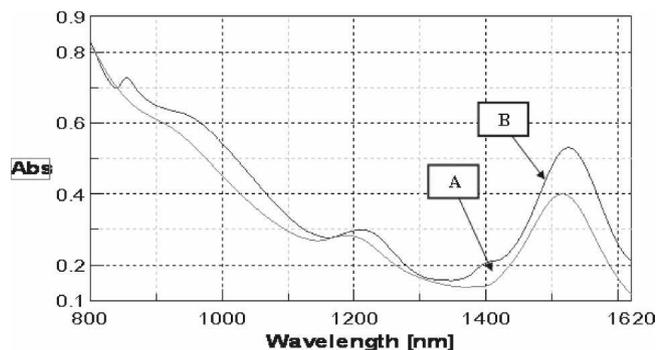


FIG. 1. Absorbance spectra of PbSe QDs (A) before and (B) after the capping exchange.

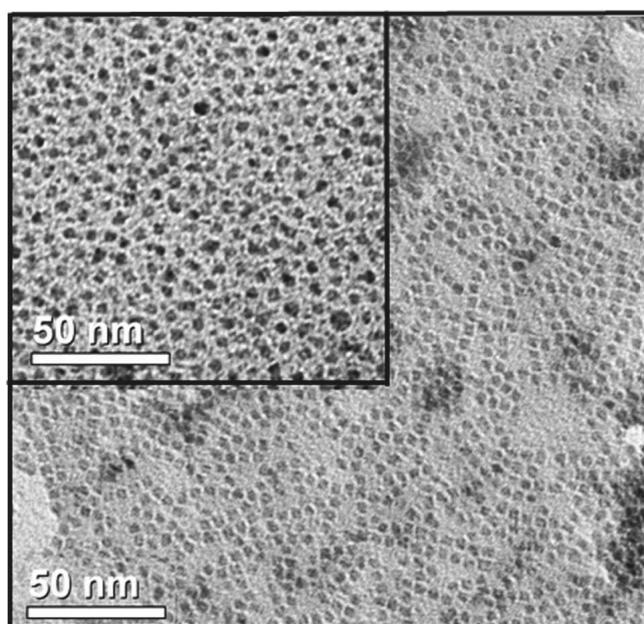


FIG. 2. TEM images of PbSe QDs in a water solution capped by AET. Inset: The PbSe QDs in chloroform (organic phase prior to ligand exchange).

nitrogen for months, without any indication of aggregation or photodegradation. However, the samples can photodegrade within a day in air.

Figure 4 illustrates the size distribution of the QDs in the aqueous phase and in the organic phase. Clearly, the size-distribution graphs indicate a narrow size distribution of the particles before and after the exchange of the capping ligands. The strong affinity of the thiol group (from AET) to the PbSe surface ensures that the AET will bind preferentially through its thiol end and prevent the further growth of the particles.^{20,21} The average size before and after the phase transfer is similar (3.9 ± 0.47 to 4.01 ± 0.54 nm). This indicates that the size of the QDs remains essentially unchanged during their transfer to the aqueous medium.

Figure 5 shows the Fourier transform infrared (FTIR) spectrum of the PbSe QDs after the phase transfer

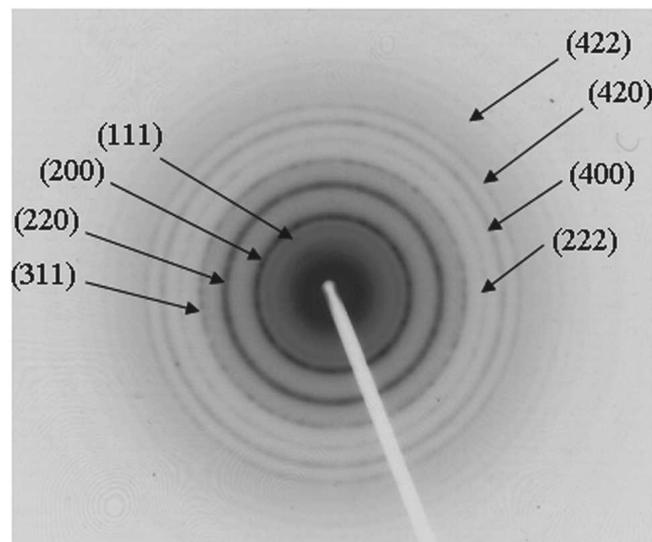


FIG. 3. Electron diffraction of the water-soluble PbSe quantum dots. The rings fit the rock-salt structure of bulk PbSe (summarized in Table I).

TABLE I. The planar spacing of the water-soluble PbSe quantum dots that were calculated according to the diffraction pattern.

Radius of diffraction circle (mm)	Calculated value of d (Å)	d of PbSe phase from Ref. 21	Plane hkl
5.5	3.58	3.5	111
6.5	3.03	3	200
9	2.19	2.1	220
11	1.79	1.8	311
11.7	1.68	1.7	222
13.2	1.49	1.5	400
14.5	1.36	1.4	420
17.1	1.15	1.2	422

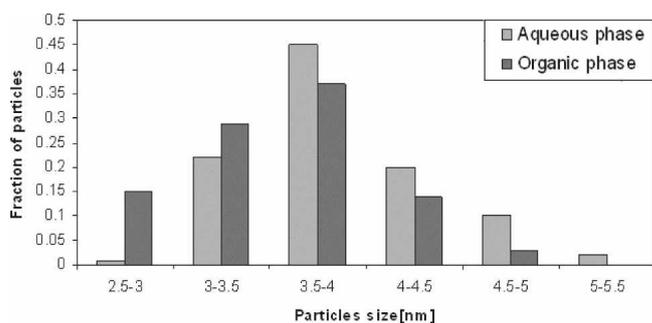


FIG. 4. Size distribution of the PbSe QDs in chloroform and in the aqueous suspension. The average size of the QDs in chloroform is 3.9 ± 0.47 nm, and in the aqueous suspension it is 4.01 ± 0.54 nm.

together with the spectrum of the aqueous medium alone. Two new transmission bands can be observed compared with the spectrum of the aqueous medium, one at 3346.7 cm^{-1} and the other at 3469.3 cm^{-1} . These transmission bands are attributed to the N–H stretching and N–H bending of primary amine groups (R-NH_2)^{27–29} respectively, and are indicative of the presence of the

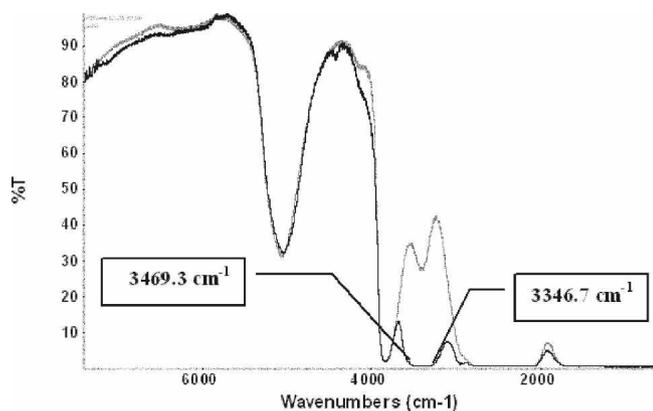


FIG. 5. FTIR spectra of PbSe QDs in an aqueous solution (black line) and in the pure aqueous solution (gray line). Two new transmission bands at 3346.7 and at 3469.3 cm^{-1} can be observed, corresponding to the amine groups of the ligands.²⁷

amine groups on the surface of the PbSe QDs. Because the FTIR spectra of the AET-stabilized solid PbSe QDs have been performed on samples that were thoroughly washed and dried, the likelihood of the presence of free, unbound AET molecules in the sample is very small.

IV. CONCLUSIONS

In this article, we have reported the synthesis of water-soluble PbSe QDs with uniform size and long-term stability in an aqueous solution. Water-soluble PbSe QDs offer advantages in many biological applications such as where QDs can act as biosensors or as part of drug-delivery systems. The method reported here, consisting of the transfer of the PbSe QDs into water by ligand exchange, is also very attractive for its simplicity compared to other methods for producing water-soluble semiconductor QDs. It yields water-soluble PbSe QDs that keep their physical and chemical properties. To our knowledge, this is the first time that water-soluble PbSe QDs have been investigated and their stability tested.

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