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Silica encapsulation of thiol-stabilized lead selenide (PbSe) quantum dots in aqueous solution

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Abstract

Silica encapsulation of lead selenide quantum dots (PbSe QDs) in aqueous solution is reported. Thioglycolic acid (TGA) stabilized PbSe QDs were modified with 3-mercaptopropyl trimethoxysilane (MPS) through vigorous stirring in water for 18–24 h in alkaline solution (pH 10.4–10.6). Silica shell was developed by controlled deposition and precipitation of silicates from sodium silicate solution onto MPS modified QDs surfaces. TEM images showed multiple PbSe QDs encapsulated in silica shell. The size of PbSe-SiO₂ core-shell nanocrystals was estimated to be 25–30 nm by TEM. Elemental compositions (Pb, Se and Si) were investigated by EDX analysis. The purified colloids of PbSe-SiO₂ QDs were stable for months when kept at 4 °C.

Keywords

Lead selenide; Quantum dot; Silica encapsulation; Colloidal stability

1. Introduction

Semiconductor quantum dots (QDs) of lead selenide (PbSe) exhibit strong absorption in infrared (IR) to near-IR range, and thus are attractive materials for photovoltaic applications and solar energy conversion [1–3]. They also possess narrow band-gap, fast response time and large nonlinearity for optoelectronic and communications applications within the IR region [4, 5]. To date, the synthesis of PbSe QDs has been studied with organometallic routes and precursors [6–12]. These QDs are photochemically sensitive as other QDs and consequently develop colloidal instability unless protected from light due to the oxidation of surface stabilizers [8, 9]. Formation of Pb-ligand complex between loose surface Pb atoms and ligand has been also reported to degrade colloidal stability [9, 13].

Silica (SiO₂) as a chemically inert material has been utilized for encapsulating various QDs to improve colloidal stability in aqueous solution over a wide range of ionic strength and temperature conditions [14–18]. It is also biologically nontoxic enhancing the biocompatibility of hazardous nanocrystals. Silica coating of hydrophilically ligated QDs is often performed via catalyzed hydrolysis of tetraalkoxysilane precursors (i.e., Stöber synthesis) [15–18]. This approach is not suitable for direct passivation of PbSe QDs that are prepared in organic solvents with hydrophobic ligands. Prior to coating with silica, QDs must be brought in water by surface modification that often yields less stable colloids or changes physical and optical properties of the QDs. Several studies have reported silica coating of hydrophobically ligated PbSe QDs with water-in-oil microemulsion of

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nonylphenyl ether, cyclohexane and water [14], and using silica xerogel matrix yielding mostly spheroidal nanocrystals without a definite shape [19]. Recently, oleic-capped PbSe QDs were coated with silica in Igepal reverse micro-emulsion yielding 28 nm PbSe-SiO₂ QDs [20].

Direct synthesis of silica encapsulated PbSe QDs in aqueous solution has been a difficult task since the water-soluble suspensions are highly unstable due to relatively high stabilization energies of Pb-thiolate complexes and susceptibility of QD surfaces to pH, temperature, and light exposure [13]. In this study, we report direct synthesis of silica encapsulated PbSe QDs from thiol-stabilized PbSe QDs in aqueous solution. Effects of different thiol ligands and experimental conditions were investigated on stability of surfaces and coating with silica. The formation of PbSe-SiO₂ core-shell nanocrystals was verified by transmission electron microscopy and (TEM) and energy dispersive X-ray spectroscopy (EDX).

2. Experimental

2.1. Synthesis and purification of thiol-stabilized PbSe QDs

The synthesis of thiol-stabilized PbSe QDs was performed in aqueos solution using lead acetate trihydrate, Pb(Ac)₂•3H₂O (99.0–103%) and selenium power (99+%) according to the protocols described elsewhere [13]. Selenium stock (0.5 M) was prepared by dissolving Se powder in sufficient volume of HNO₃ and stabilized in 10% HCl. Three thiol ligands, thioglycolic acid (TGA, 98%+), 3-mercaptopropionic acid (MPA, 99%+) and 2mercaptoethyamine hydrochloride (MEA, 98%+), were used for synthesis of PbSe QDs. For synthesis, 0.190 g of lead acetate was dissolved in 250 mL of deionized water in a threeneck flask. Then, 1.0 mL of TGA, MPA solutions or 0.150 g of MEA were added under stirring. The pH of the solution was adjusted to pH 10.0 for TGA and MPA, and to pH 5.5 for MEA with 1.0 M NaOH. Selenium(IV) solution (2.5 mL of 0.5 M) was placed to a second three-neck flask, the flasks were connected through a teflon tubing (4 mm i.d.) and the solutions were deaerated by purging N2 for 30 min. Then, 10 mL of 10% NaBH4 stabilized in 0.1% NaOH solution was slowly added into Se(IV) solution. The H₂Se gas produced was swept into the Pb-thiolate solution under N₂ flow yielding dark PbSe nanocrystals rapidly. Nitrogen was purged for an additional 20 min. Stirring was kept at room temperature for an hour to ensure the formation of stable nanocrystals.

The TGA and MPA-stabilized QDs were purified by precipitating with dimethylsulfoxide (DMSO) in 1:1 (v/v) QD:DMSO medium. The MEA-stabilized QDs were purified by precipitating in 1:3 (v/v) QD:acetone. Precipitations were performed in ice bath by adding DMSO or acetone slowly to QD solution. The purified QDs were redispersed in water in an excess of the ligands.

2.2. Silica encapsulation of PbSe QDs and characterization

Schematic representation of the silica encapsulation of the thiol-stabilized PbSe QDs is illustrated in Fig. 1. The procedure started with displacement of the thiol ligands of TGA-, MPA- and MEA-stabilized PbSe QDs with 3-mercaptopropyl trimethoxysilane (MPS, 95%) in aqueous solution. In a typical experiment, 25 mL of PbSe QDs, 75 mL of deionized water and 5 mL of 1×10^{-3} M aqueous MPS solution were added and the contents were vigorously stirred for 18–24 h at room temperature. Next, 12 mL of 0.6% sodium silicate solution (40% SiO₂) at pH 10.2–10.6 was added. The flasks were wrapped with aluminum foil and the suspensions were stirred in dark for five days for silica to adhere and slowly polymerize on the MPS-modified surfaces. At the end, the thickness of silica layer (e.g., silica shell) was increased by precipitating the QDs in anhydrous ethanol (C₂H₅OH, HPLC grade).

Shape and sizes of the QDs were characterized by using a JEOL JEM-2200FS transmission electron microscope (TEM). TEM samples were prepared by spotting a drop of a 1:10 diluted QD solutions on a CF300-Cu grid (Electron Microscopy Sciences). Compositional analysis of the QDs was made by energy-dispersive X-ray spectroscopy (EDX) with an Oxford Instruments 50 mm² area SiLi drift detector.

3. Results and discussion

MPS has been utilized as silane coupling agent for deposition of silica in preparation of silica coated CdSe and CdTe QDs [15,16]. The trimethoxysilane groups act as a primer rendering the surfaces of the QDs vitreophilic for adhesion of silicate ions allowing deposition of a thin silica layer as depicted in Fig. 1. In case of PbSe QDs, successful surface modification with MPS relied on the stability of Pb(II)-thiolate complexes, which were estimated to be -22.27, -21.51 and -22.53 eV for Pb(II)-TGA, -MPA and -MEA, respectively [13]. The purified suspensions of MEA-stabilized PbSe QDs were the most stable in neutral pH (e.g., pH 7.2), but the colloids were very unstable aggregating in alkaline pHs (e.g., pH 10-2-10.6) required for silica coating. Likewise, attempts with MPA-PbSe QDs were not successful due to the poor stability of their suspensions as supported by higher stabilization energy. In most attempts, the suspensions aggregated during the treatment with MPS.

The TGA-stabilized PbSe QDs were the most stable during the surface modification with MPS in alkaline pHs (e.g., pH 10) and hence afforded silanization of surfaces. Yet, successful coating of the QDs was sensitive to MPS and sodium silicate compositions. Because the solubility of MPS in water is low, TGA-PbSe QDs were modified in dilute aqueous solutions of MPS through stirring the suspensions vigorously for 18–24 h according to the settings summarized in Table 1. Typical TEM images of resulting nanocrystals are illustrated in Fig. 1S. The most conducive conditions were obtained in Scheme B (5 mL of 1.0 mM MPS and 12 mL of 0.6% sodium silicate). Silica clusters contained few QDs in the presence of 2 mL of MPS solution (Scheme C) indicating inefficient surface modification. Higher sodium silicate concentration resulted in reduced stability of MPS modified suspensions, such that in the presence of 1.0 M sodium silicate QDs aggregated significantly due to the rapid growth of silica shell on the vulnerable surfaces (Schemes A and D).

At the completion of silica deposition, the QDs were precipitated slowly by adding anhydrous ethanol. This step was also critical to prevent the QDs from aggregating as ethanol content influenced the rate of precipitation and thereby the growth of the silica shell. QD:ethanol (v/v) compositions of 1:2, 1:5 and 1:10 were investigated to find the optimum condition. After mixing with ethanol, samples were centrifuged at 6000 rpm for 15 to 60 min depending on the QD:ethanol ratio. The QDs precipitated in 15 min at QD:ethanol ratios of 1:2 and 1:5, but they were not stable when redispersed in water. TEM images indicated that a significant fraction of the nanocrystals were not encapsulated in silica shells. The QD:ethanol ratio of 1:10 (v/v) was optimum in that encapsulated QDs precipitated slowly in about 1 h and were stable when redispersed in water. TEM images of TGA-PbSe core QDs and the resulting PbSe-SiO₂ QDs are illustrated in Fig. 2. The size of the bare QDs ranged between 5 and 8 nm (Fig. 2a). The PbSe-SiO₂ core-shell QDs were spherical with a size distribution around 25–30 nm that contained multiple nanocrystals (Fig. 2b).

Fig. 3 shows the energy dispersive X-ray (EDX) spectra of TGA-capped PbSe and PbSe-SiO₂ core-shell QDs. The results verified the presence of Pb and Se in the cores (Fig. 3a and 3b). In addition, the EDX spectra show intense peaks of Si and O in the silica encapsulated QDs (Fig. 3b). Both images show an intense peak of Cu associated with Cu material of TEM grids. The EDX results were consistent with those reported in literature [14, 21] demonstrating the formation of PbSe-SiO₂ core-shell QDs in the aqueous solution.

4. Conclusions

We have developed aqueous method for preparation of silica encapsulated PbSe QDs at room temperature. Fig. 2S shows the images of aqueous solutions TGA-PbSe QDs and PbSe-SiO₂ core-shell shell QDs. The purified TGA-PbSe QDs were relatively unstable; approximately five days when kept at 4 °C. The silica encapsulated PbSe QDs were more stable against oxidation and aggregation under same conditions. This procedure was also suitable scaling up the concentration of QDs to obtain concentrated solutions (see Fig. 2S) to conduct toxicological investigations and other applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Table 1

Experimental schemes for silica encapsulation of TGA-PbSe QDs. The concentrations of MPS and sodium silicate are for their stock solutions

Variable	Scheme			
	A	В	С	D
TGA-PbSe QDs (mL)	25	25	25	25
Water (mL)	75	75	75	75
MPS (1.0 mM) (mL)	5	5	2	2
Sodium silicate (mL)	12	12	12	12
Sodium silicate (%)	1	0.6	0.6	1