Synthesis and Characterization of Quantum Dots: A Case Study Using PbS

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S Supporting Information



ABSTRACT: A research project for senior undergraduates of chemistry has been developed to introduce syntheses of a series of monodispersed semiconductor PbS quantum dots (QDs) and their characterization methodologies. In this paper, we report the preparation of monodispersed semiconductor PbS QDs with sizes smaller than the exciton Bohr radius using a simple, one-step process, and the characterization of the QDs using a range of instruments, including Fourier-transform infrared spectroscopy, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray spectroscopy. Our synthesis approach involves dissolving powdered sulfur (as the S precursor) in 1-tetradecene and adding PbCl₂ as the Pb precursor to the suspension as well as oleylamine as a capping ligand. The PbS QD project represents, we believe, an almost ideal opportunity to provide exposure of undergraduate students to nanotechnology research via syntheses and characterization of semiconductor nanoparticles.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Testing/Assessment, Crystals/Crystallography, IR Spectroscopy, Materials Science, Colloids, Nanotechnology, Synthesis, Semiconductors

dvances in nanotechnology in the past 20 years have resulted in enormous interest in introducing nanomaterials and associated technologies into the undergraduate curriculum, especially in chemistry.¹⁻⁶ As examples, Pavel et al.² have reported experiments involving a scattering species, rhodamine 6G (R6G), adsorbed onto silver nanoparticles (AgNPs), with the purpose of quantitatively measuring the surface-enhanced Raman scattering (SERS) phenomenon for the system; this study also incorporated absorbance and emission measurements. Reid et al.³ developed a laboratory experiment involving semiconductor ZnO quantum dots (QDs) focusing on band gap³ and absorbance characterization. Also, Lisensky et al.⁶ discussed a laboratory experiment involving absorbance and emission characterization of semiconductor CdSe QDs. However, most of the reported studies involve theoretical issues that are somewhat sophisticated for undergraduate chemical education purposes. In this article, we present our recently developed research project of semiconductor QD synthesis and characterization to help to promote and improve college-level education focusing on undergraduate research. We also demonstrate that an undergraduate research project can be conveniently utilized as a laboratory experiment for curriculum development purposes.

The main reason we selected lead sulfide QDs to introduce nanoscience research to our undergraduates is that lead sulfide QDs can be conveniently synthesized under mild temperature in a simple, one-step noninjection process. Our approach significantly reduce burn risks to undergraduates that may occur when high-temperature syntheses are undertaken. In addition, undergraduates can gain some basic knowledge related to semiconductor QDs and their applications.

Semiconductor lead chalcogenide (PbS, PbSe, PbTe) QD materials show strong quantum confinement effects due to their relative large exciton Bohr radii and dielectric constants.^{7,8} The quantum confinement phenomenon³ associated with lead chalcogenide QDs can be easily observed.^{9–11} More specifically, PbS is a direct narrow band semiconductor with a bulk band gap of 0.41 eV and an exciton Bohr radius of 18 nm,^{8,10} and its band gap can be tuned by changing its size.¹²

PbS QDs have been widely investigated as nanocrystal QDbased solar cell materials and as sensor materials. Semiconductor PbS QD-based photovoltaics (PVs) have the advantage of processability and tunability, the latter facilitating the maximizing of overlap of incident optical excitation with the absorption spectrum for so-called third generation PV devices.^{13–15} Moreover, semiconductor PbS QDs are also promising candidates in the development of optical sensors and probes¹⁶ as well as for infrared detectors because of the sensitive influence on optical properties resulting from chemical changes occurring at the surface. With their intrinsic utility in mind, we have chosen to use PbS QDs to expose our students to their first research project involving nanomaterials.

The syntheses of semiconductor PbS QDs usually necessitate high temperatures and inert media.^{12,17} However, as indicated earlier, the present project aims to teach students how to obtain monodispersed semiconductor PbS QDs under simple, mild reaction conditions. Also, we describe a simple, low-temperature, and low-cost method for the solution synthesis of lowcost, large-area, flexible PbS QD-based photovoltaic devices. It is to be noted that students would also have the option of using the semiconductor PbS QDs as substrates for SERS study.

To initiate this project, we created a laboratory experiment for an intensive summer research project involving PbS QDs that utilizes a doctoral student as coordinator and a faculty member as the overall coordinator. The project allowed senior undergraduates to conduct nanomaterial-related research and at the same time update important literature search and laboratory practical skills of particular importance in the nanoscience field. About 15 undergraduates have participated in this project since its inception in 2010. Participating students are from the Department of Chemistry of the City College of New York and other undergraduates from the City University of New York. They were supported by the National Science Foundation (NSF)-funded Center for Exploitation of Nanostructures in Sensors and Energy Systems. During this project, students had about 5 h to synthesize and 5 h for characterization of singlesized PbS QDs. The entire project typically spanned a period of two months. Guidance for students in the laboratory (temporal expectations for procedures) was provided for essentially every aspect of the experiment, but students were required to prepare their own experiment outlines and procedures for each synthesis step. The undergraduates acquired knowledge concerning the morphology, composition, crystal structure, band gap, and ligand dynamics characterizations^{18,19} of the synthesized PbS QD. Aspects of the QD characterization approaches were conducted by students themselves such as Fourier-transform infrared (FT-IR) spectroscopic measurements. However, other characterization procedures, such as transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray spectroscopy (EDS), were performed by graduate students. Furthermore, students prepared the samples and observed the TEM-related measurement at the instrument console and learned how to estimate band gaps of semiconductor QDs from their observed physical sizes. By teaming up with doctoral graduate students, the undergraduates learned practical skills/techniques for synthesis and characterization of monodispersed PbS QDs; they also learned the following valuable nanoscience-related research skills: exposure to the use of cutting-edge instruments in the nanotechnology field; participation in discussion and group meetings as well as preparation of progress reports; poster and oral presentations; and expanded knowledge concerning the syntheses of colloidal QDs.

SYNTHESES OF COLLOIDAL NANOCRYSTALS

A mechanism for the synthesis of colloidal nanocrystals dates back to the classic work of LaMer and Dinegar from 19401950. These authors suggested a three-stage colloidal formation model (Figure 1): 20 (I) monomer accumulation, (II) homogeneous nucleation, and (III) diffusion-controlled growth (i.e., Ostwald ripening). The three stages are depicted in Figure 1.



Figure 1. Three-stage colloidal formation model (LaMer's model): (I) monomer accumulation; (II) homogeneous nucleation; and (III) diffusion-controlled growth (i.e., Ostwald ripening).

Two methods are normally used for nanocrystal synthesis: hot-injection and noninjection approaches.^{21–23} The hot-injection method was first reported by the Bawendi group in 1993 for the synthesis of monodispersed cadmium chalcoge-nide QDs.²⁴ This method is a special case of LaMer's three-stage crystal formation model since it excludes step I. The noninjection approach was initially introduced by the Cao group in 2004,²⁵ which includes all three steps of LaMer's model.

Intrinsically, the noninjection approach is the simplest and most convenient one for undergraduates due to the less demanding experimental processes. However, the typical noninjection method necessitates a high reaction temperature and long reaction time due to the fact that the nonmetal precursors, generally used, are solids and need to be dissolved at an elevated temperature to initiate the burst nucleation.²⁶ The approach that we are advancing is to synthesize PbS QDs via a noninjection method, which allows us to conduct the synthesis at a relatively low temperature and with a short reaction duration so that it can be used for classroom demonstration and as a suitable lab experiment for introducing undergraduates to an area of nanotechnology. While there are few reports dealing with the synthesis of PbS using noninjection methods even at high temperature, PbS QDs have been synthesized with a hot-injection method using PbCl₂ as a metal precursor.¹⁰ In this latter study, S was dissolved in oleylamine (SOLA) and used as the nonmetal precursor, and the solvent, that is, oleylamine (OLA), also acted as a capping ligand to limit particle size.

Noninjection Synthesis of PbS QDs

In our initial efforts, we attempted to use all chemicals in a hotinjection approach. Specifically, we utilized the metal precursor $PbCl_2$ and the nonmetal precursor SOLA, including the capping ligand OLA,¹⁰ and simply heated the mixture. The chemical reaction occurred, but PbS particles obtained were not monodispersed. We found that two factors led to the sizedispersed distribution of PbS particles. One was that the SOLA was too active to release activated sulfide during the monomer



Noninjection Synthesis

Figure 2. Noninjection synthesis of PbS QD.

accumulation stage; the other was that there was no solvent effect (OLA acted as both the capping ligand and solvent) in the reaction mixture—the monomers could not accumulate to reach a higher critical supersaturation concentration.

From our initial efforts, we deduced that for the noninjection method to proceed smoothly to the generation of the desired monodispersed PbS QDs, all reactants needed to be placed in one flask and heated at a rate that allows the controlled release of sulfide, which enables the attainment of a critical supersaturation concentration of monomers during the accumulation stage.

Our efforts led to the approach depicted in Figure 2, where one of the two S atom precursors that we have used is shown as a reagent: either sulfur dissolved in 1-tetradecene (STDE) or sulfur dissolved in 1-octadecene—ODE (SODE) can be used as S precursor in the noninjection synthesis of PbS QDs. However, STDE has been found to be the better S precursor due to its wide concentration tolerance (up to 3 M) and its stability as a homogeneous solution for at least 6 months at room temperature.

RESULTS AND DISCUSSION

All data presented below were acquired from student-prepared samples of QDs. Table 1 shows the synthesis conditions and

Table 1. Synthesis Conditions and Results of the Noninjection Syntheses of PbS QDs^a

Sample No.	Heating Rate (°C/min)	Growth Temperature (°C)	Sample Size (Diameter) (nm)	σ	Band Gap (eV)
QD-1	3.0	45	2.1	8.6%	1.83
QD-2	14.2	90	4.0	6.9%	1.06
QD-3	13.5	130	7.0	6.9%	0.72
QD-4	16.5	160	8.2	7.1%	0.66
QD-5	16.3	185	8.9	6.8%	0.63
QD-6	18.5	200	14.8	7.3%	0.51
QD-7	19.3	220	16.5	7.0%	0.50
^{<i>a</i>} Pb-to-S feed mole ratio is 1:2, and OLA-to-Pb mole ratio is 26:1.					

products of the noninjection syntheses of PbS QDs. The optimal reaction conditions, for example, the Pb to S-feed mole ratio of 1:2 and OLA to Pb mole ratio of 26:1, etc., were determined by a process similar to that used in the syntheses of PbTe QDs and PbSe QDs.^{27,28} The relative standard deviation (σ) of the diameters of the synthesized PbS QDs is below 9% (see Table 1), allowing them to be characterized as being

monodispersed. The PbS QDs synthesized are smaller than the exciton Bohr radius of 18 nm.

PbS QD size based on growth temperature is shown in Figure 3. All parameters except reaction temperature and



Figure 3. Temperature dependent on measured diameters of PbS QDs synthesized using the noninjection approach. The standard deviations of all measured diameters are smaller than the graphed symbols and hence are not shown.

heating rate are the same for all reactions. We note that at the growth time of 5 min, narrowly distributed PbS QDs are synthesized. Figure 3 is useful for developing optimum synthesis conditions for classroom demonstration and lab measurements for the noninjection synthesis of PbS QDs at mild temperature (below 80 °C; a water bath, widely available in most student laboratories, is practical for these studies). The chart serves only as a reference for students to obtain varied sizes of PbS QDs under different synthesis conditions. The sudden decrease of the size of PbS QDs at growth temperature of 180 °C is likely due to the morphological transformation from spherical particles (8 nm) to cubic particles (10 nm); the activation energies for the spherical and cubic crystal formation are different, and the formation of the cubic shaped PbS QDs requires more energy.

Using the noninjection method, other synthesis oriented research training programs can also be designed by changing parameters, such as the concentration of the S precursor,



Figure 4. (a) TEM image of QD-3, with a size 7.0 \pm 0.5 nm. (b) HRTEM image of QD-3. The lattice spacing of QD-3 measured 3.0 \pm 0.1 Å matching the (200) lattice plane for bulk PbS (JCPDS No. 770244, 2.967 Å).

reaction time, growth temperature, heating rate, Pb-to-S feed mole ratio, OLA-to-Pb mole ratio, and capping ligand, etc., which result in the synthesis of different sizes and shapes of PbS QDs.

The mechanism for PbS QD formation is proposed in chemical eq 1 in the following (see Supporting Information for details). The reaction mechanism can be postulated to involve (i) lead chloride–OLA complexes forming in the reaction mixture through interactions between the Pb^{2+} ion and the lone pair of the amine group of OLA, with the participation of trace amounts of water in the reaction mixture; (ii) polysulfides in the STDE precursor creating a high concentration of hydrogen sulfide in the heated reaction mixture in a very short time period (Stage I monomer accumulation); and (iii) a homogeneous nucleation process occurs: hydrogen sulfide reacts with Pb2+ ion to form PbS cores at the reaction temperature (Stage II homogeneous nucleation); the growth of the PbS core is limited by the amount of OLA molecules surrounding them (Stage III Ostwald ripening); finally, upon quenching the warm reaction mixture with a cold water bath, PbS cores capped with OLA molecules precipitate from the supersaturated reaction suspension to form PbS QDs.

$$(OLA H^{+})_{2}Pb(OH^{-})_{2}Cl^{-}_{2} + H_{2}S$$

$$\xrightarrow{OLA}_{Heat} Pbs QDs + 2H_{2}O + 2(OLA HCl)$$
(1)

Further improvement for the experiment might involve modification and streamlining the synthesis by eliminating (see Supporting Information) the vacuum pump and the temperature controller used.

It is to be noted that we have incorporated the revised synthesis procedure into a physical chemistry lab experiment for senior undergraduate chemistry majors at the City College of New York. A specific experimental study that students undertake is to determine the size of PbS QDs based on the concentration of STDE precursor. Indeed, without any pretreatment and rapid heating of the reaction mixture, students have successfully synthesized various sizes of PbS QDs using different concentrations of the STDE precursor within a warm water bath at 50 $^{\circ}$ C. We plan to discuss the result of a sampling of student finding in a later report.

Characterization of QDs

The morphology, composition, crystal structure, band gap energy, optical properties, and the nature of the surface ligand are fundamentally important to characterize semiconductor QDs. TEM imaging is an important tool that allows for measurement of size, size distribution, and shape of NPs, especially for PbS QDs, since absorbance occurs in the near-IR region,²⁹ and the visual color identification method cannot be used (different compared to the case of CdSe QD, for which QD size differences can be observed by color change.⁶) On the other hand, EDS can provide qualitative analysis of the composition of samples, while HRTEM can indicate the crystal structure of samples. However, FT-IR can help to understand surface changes for the samples. Although near-IR measurements do allow the optical properties of PbS QD to be assessed, we have opted to use a semiempirical equation developed by Moreels²⁹ that can be used to obtain the band gap and optical properties of QD samples. The equation can be used to estimate the band gap of PbS QDs once students determine the sizes from TEM measurements:

$$E_0 = 0.41 + \frac{1}{0.0252d^2 + 0.283d} \tag{2}$$

In eq 2, *d* is the diameter (nm) of the PbS QD, and E_0 (eV) is the band gap of the PbS QD. The estimated band gaps for the semiconductor PbS QDs are listed in Table 1.

The TEM image in Figure 4, panel a indicates that the particle size of sample QD-3 is 7.0 \pm 0.5 nm, and it is of spherical shape. The size distribution is shown in Figure 5. The HRTEM image of sample QD-3 (Figure 4b) demonstrates that the NPs are single crystals. The lattice fringe of sample QD-3 is found to be 3.0 \pm 0.1 Å, which is consistent with the (200) lattice planes for bulk PbS (JCPDS No. 770244, 2.967 Å). In addition, the particles contain only Pb and S elements, as indicated by EDS measurements (see Supporting Information). Further investigation by FT-IR shows a weak band at about 3005 cm⁻¹, which is assignable to the stretching of -CHattached to the -C=C- double bond.²⁷ This reveals the presence of the OLA ligand at the surface of PbS QDs (see Supporting Information). Thus, the characterization results indicate that the samples synthesized are indeed PbS QDs capped with OLA.

SUMMARY

We have presented an undergraduate experimental research project derived from recent research advances in the authors' laboratory that deal with the synthesis of monodispersed PbS QDs. About 15 undergraduates have joined the summer



Figure 5. Histogram of measured diameters of about 213 particles in Figure 4, panel a. The solid curve is a Gaussian distribution fit to the data.

intensive research project since 2010. A one-pot, single-step, noninjection synthesis of semiconductor PbS QDs is provided for inclusion among the experiments used to expose students to important research concepts. It is further to be noted that, in addition, the approach used can offer an avenue to facilitate systematic investigation of the syntheses of nanomaterials and for the use of leading-edge characterization instruments that can enhance college-level students' research activities.

ASSOCIATED CONTENT

Supporting Information

The FT-IR, TEM, and EDS results are presented. The detailed proposed PbS QD formation mechanism, polysulfides formation in TDE solution, and other experimental details are also included. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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