J Mater Sci (2007) 42:4265–4269
DOI 10.1007/s10853-006-0679-2

Luminescent stability of water-soluble PbS nanoparticles

**Xu-Sheng Zhao · She-Yang Xu · Li-Yan Liang ·
Tao Li · Sam Cauchi**

Received: 10 February 2006 / Accepted: 17 July 2006 / Published online: 28 February 2007

Abstract Thiol-capped PbS semiconductor nanoparticles (NPs) stabilized with a mixture of 1-thioglycerol/dithioglycerol (TGL/DTG) were colloidally prepared at room temperature. UV–vis spectroscopy and photoluminescence (PL) spectra showed an obvious redshift in both the absorption shoulder and PL peak with the increase of DTG/Pb molar ratio. Room temperature photoluminescence quantum efficiency (PLQE) of freshly prepared PbS NPs (7–11%) remained higher than 5% upon aging for 3 weeks when the NPs were stored in an ice-bath in the dark, and higher than 5% for at least 5 weeks when additional DTG ligand was introduced into the nanoparticle solution every 2 weeks. The combination of reasonable room temperature quantum efficiency and strong, stable luminescence covering the 1.3 μm telecommunication window make these NPs promising materials in optical devices and telecommunications.

Introduction

Semiconductor nanoparticles (NPs) have been received intense attention during the last decade due to their unique size-dependent physical and chemical properties (the quantum confinement effect) [1–6]. Precise control over nanoparticle size, shape, size distribution and surface properties leads to an understanding of the special properties of such materials evolved from molecular to bulk solids. So far, however, the preparation of semiconductor quantum dots has been hindered by the technological problems of instability, irreproducibility and/or harsh synthetic condition. Nanoparticles are usually surrounded by dielectrics (such as air, polymers, organic solvents) which have much lower refractive index (RI) than semiconductor NPs themselves. This RI boundary established between nanoparticles and the surrounding medium can have manifest impact on the photophysical and optical properties of semiconductor nanocrystals (NCs), hence on the ultimate application of the resulting nanoparticles. Experimentally, various methods have been developed to cap the surfaces of semiconductor NPs. Wet chemical synthetic approach has been well developed for II–VI or/and III–V NCs in non-aqueous solutions using high boiling point non-coordinating solvents TOP/TOPO (trioctylphosphine/trioctylphosphine oxide) as stabilizers and in aqueous solutions using various thiols as capping agents [7, 8].

PbS quantum dots are expected to have exceptional third-order non-linear optical properties, and may find applications in optical devices, such as optical signal processors and switches, and biolabeling. Though there has been much work about the preparation and optical characterization of PbS semiconductor NCs obtained by organometallic methods [9–11] or by the use of micellar, polymeric, glasses and crystalline hosts [12–16], little work was reported in aqueous synthesis of PbS NCs. Recent progress in the use of PbS NCs includes their

---

X.-S. Zhao (✉) · S.-Y. Xu ·
L.-Y. Liang · T. Li
Guangzhou Institute of Chemistry, Chinese Academy of Sciences, P.O. Box 1122, Guangzhou 510650, P.R. China
e-mail: zhao7503@yahoo.com

S. Cauchi
Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Rd, Toronto, ON, Canada, M5S 3G4

electroluminescence in a polymer matrix [9], room temperature optical gain in a glass matrix [17], and room temperature optical gain in solution-processed PbS NC films [18]. Recently, our group reported a facile route to the synthesis of water-soluble PbS NCs with stable efficient luminescence in the near-IR spectral range (1,000–1,400 nm) [19, 20]. These quantum dots were stabilized with a delicate balance between two capping agents, 1-thioglycerol (TGL) and dithioglycerol (DTG). Herein we report luminescent stability of PbS quantum dots with the emphasis on photoluminescence (PL) and room temperature photoluminescence quantum efficiency (PLQE) with storage time, and the effect of extra ligands on PLQE of PbS NCs.

Experimental

Lead (II) acetate trihydrate (99.99%), sodium sulfide nonahydrate (99.99%), 1-thioglycerol (TGL, 95%), dithioglycerol (DTG, 95%) and triethylamine were purchased from Sigma-Aldrich and used as received. The water used in all experiments was deionized to a resistivity of 18.2 MΩcm.

For the synthesis of PbS semiconductor nanoparticles stabilized with a mixture of TGL and DTG, 15 mL of aqueous solution containing 0.25 mmol of lead (II) acetate trihydrate and 1.5 mmol of TGL were adjusted to pH = 11.2 by the addition of triethylamine, followed by the dropwise addition of DTG (in amount from 0.11 to 0.96 mmol). Then a 0.1 M solution of sodium sulfide was quickly (<1 s) introduced into the system, accompanied by vigorous stirring (1,000–1,300 rpm). The color of the solution instantly or within 10 h (depending on DTG/Pb molar ratio) changed to dark-brown. All samples were produced at room temperature and all data were obtained after the preparation of NPs was finished except that for the determination of PL and PLQE as a function of time. In the latter two cases, the NPs were stored in an ice-bath in the dark.

VIS-near-IR absorption spectra of PbS NPs were recorded at room temperature using a Cary 500 UV/Vis/NIR spectrophotometer. Fluorescence spectra were measured with a PTI spectrometer with liquid nitrogen-cooled Ge detector. Absolute measurements of photoluminescence were carried out in an integrating sphere with excitation provided using an 831 nm semiconductor laser. TEM image was obtained on a JEOL-2010-FEG microscope operated at 200 kV. The samples were prepared by placing a droplet of diluted nanoparticle solution onto a thin carbon-coated copper grid, waiting for ca. 1 min, then gently wicking away the excess liquid.

Photoluminescence quantum efficiency (PLQE) was determined using a spectralon-coated integrating sphere with a 10-cm inner diameter and two equatorial ports. A liquid waveguide led from the exit port of the sphere to a grating spectrometer coupled with a liquid-nitrogen-cooled Ge detector. A two-position sample holder allowed direct or indirect illumination of the sample. The 831 nm excitation laser beam was directed into the sphere through a 2 mm entrance port at near-normal incidence with respect to the cuvette containing the sample. The sample was positioned such that when directly illuminated, any surface reflections were directed onto the sphere wall. The detection system was calibrated by observing the spectral response from a pre-calibrated Tungsten–Halogen lamp.

Results and discussion

Previous work indicated that 1-thioglycerol (TGL) and dithioglycerol (DTG) play an important role in the synthesis of PbS nanoparticles (NPs). A very delicate balance of TGL and DTG is the key to high quality semiconductor nanocrystals (NCs) [19]. When TGL was used as a sole stabilizer, the resulting PbS NPs rapidly increased in size, and ultimately aggregated within several hours, leading to unstable photoluminescence (PL). When DTG was used as a sole stabilizer, NCs were formed which were stable to aggregation and precipitation for 2–5 weeks when sealed properly after preparation. When a mixture of TGL and DTG were used as the stabilizer, higher quality NPs were produced with better optical properties.

We fixed the amount of both TGL and S^{2-} in all experiments (molar ratio TGL/Pb/S = 6/1/0.5) and changed that of DTG in solution, PbS NPs with various sizes (3–5 nm) and stability (stable for 2–3 months at room temperature and in the dark) were prepared systematically. The proper molar ratio of DTG/Pb was from 1.28/1 to 3.40/1 (the corresponding PbS nanocrystal concentrations are ca. 1.5–4.2 mg/mL), though the most stable NPs were obtained at the same ratio from 1.70/1 to 2.55/1 from kinetics study. [20]. With DTG/Pb lower than 1/1, PbS NPs were produced with inferior optical properties such as bad absorption or low luminescent emission, rapid PbS growth and aggregation could not be suppressed. Whereas when the above-mentioned ratio was more than 3.40/1, the formation of NPs took up to several hours (or no NPs formed due to the saturation of Pb^{2+} with ligands). Figure 1 shows absorption spectra of PbS NCs capped with a mixture of TGL/DTG. The absorption shoulder

(860–1,020 nm) greatly blue-shifted compared with bulk PbS (3,020 nm), indicative of the strong influence of quantum confinement. The increment in DTG/Pb mole ratio from 1.28/1 to 3.40/1 resulted in a small red-shift in absorption spectra of NPs, which indicated that their size slightly increased.

The control of the photoluminescence (PL) properties of semiconductor NPs has been a major objective for developing synthetic chemistry for colloidal semiconductor NCs. Figure 2A illustrates the PL spectra of freshly prepared PbS NPs stabilized with TGL/DTG ligands. An enhanced PL intensity was monitored with the increase of DTG/Pb molar ratio. But when the same ratio approached a certain value (i.e., 2.55/1 in the figure), PL intensity decreased progressively. When the ratio was lower than 1/1, the resulting NPs had poor luminescent properties. For example, we found that when the above molar ratio was 0.43/1, much lower PL intensity (not shown in the figure) of NPs was detected compared with other series of PbS NPs. Whereas when the above ratio was 0.85/1, no PL signal detected, NPs aggregated within half an hour. Figure 2B displays normalized photoluminescence intensity of PbS NPs. The position of the emission maximum also shifts into the infrared region with DTG/Pb molar ratio increased from 1.28/1 to 3.40/1, which coincides with the red-shift of the absorption shoulder, in agreement with the slight increase in particle size speculated from absorption spectra.

We further investigated luminescent emission properties of PbS NPs with variation in storage time. The NPs were stored in an ice-bath after each measurement. We chose three series of NPs synthesized with DTG/Pb molar ratios 1.28/1 (curves a, d and g in Fig. 3), 1.70/1 (curves b, e and h) and 2.12/1 (curves c, f and i), respectively. Over time, photoluminescence peaks of PbS NPs red-shifted (a → d → g, b → e → h, c → f → i) and two luminescence peaks appeared (which is evident from curves d, e and f) during the nanocrystal growth and they evolved differently in time. The shorter-wavelength maximum shrunk and gradually disappeared while the longer-wavelength maximum evolved. This phenomenon has been associated with different fractions of NPs rather than the first and second quantum states of the same NCs [19]. From Fig. 3 we can also speculate that further shift of PL maximum can be achieved to locate over 1.3 μm "telecommunication window", which is of great interest in the fabrication of novel semiconductor NPs as potential amplifiers operating at 1.3–1.55 μm wavelengths for telecommunication devices.

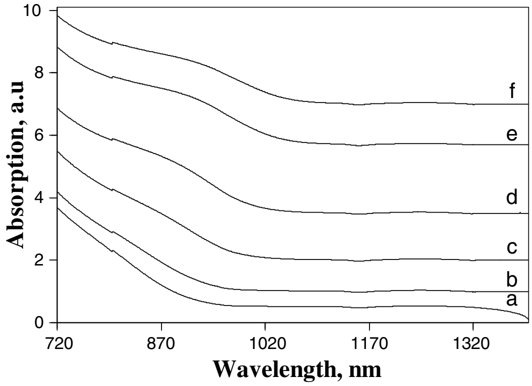

Fig. 1 Room temperature absorption of freshly prepared PbS nanoparticles capped with TGL and DTG. TGL/DTG/Pb molar ratio: a—6/1.28/1, b—6/1.70/1, c—6/2.12/1, d—6/2.55/1, e—6/2.98/1 and f—6/3.40/1

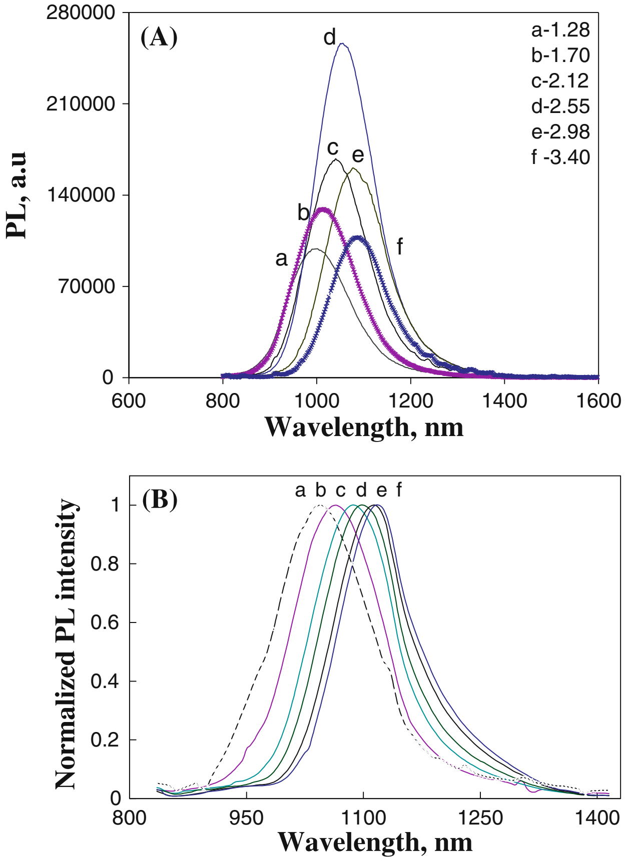

Fig. 2 Photoluminescence spectra (**A**) and normalized photoluminescence intensity (**B**) of as-prepared PbS nanocrystals capped with TGL and DTG. Curves a–f represent different molar ratios of DTG/Pb as indicated in the figure

The stability of the emission is one of the four fundamental parameters (along with the brightness, the emission color and the color purity) of semiconductor NCs. Previous work shows that PbS NCs synthesized at various DTG/Pb ratios had a high room temperature

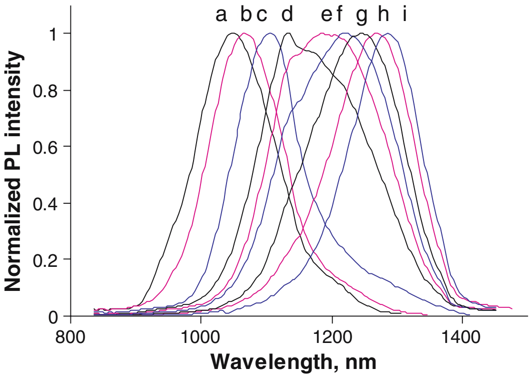

Fig. 3 Normalized photoluminescence intensity of PbS NCs as a function of storage time at room temperature in the dark. a–c—freshly prepared PbS NCs; d–f—7 days of the same NCs; g–i—12 days of the same NCs. TGL/DTG/Pb molar ratio: a, d, g—6/1.28/1; b, e, h—6/1.70/1; c, f, i—6/2.12/1

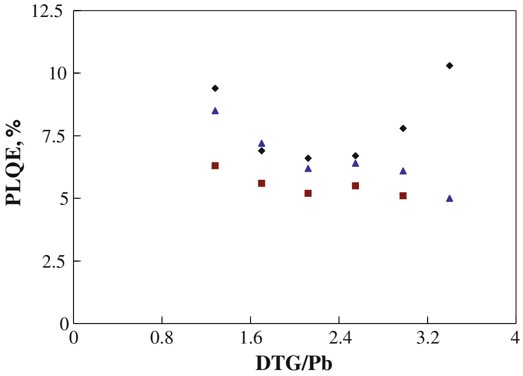

Fig. 4 Room temperature photoluminescence quantum efficiency of PbS NCs as a function of DTG/Pb molar ratio with different storage time. NCs were stored in an ice-bath in the dark. ◆, freshly prepared; ▲, 1 week; ■, 3 weeks

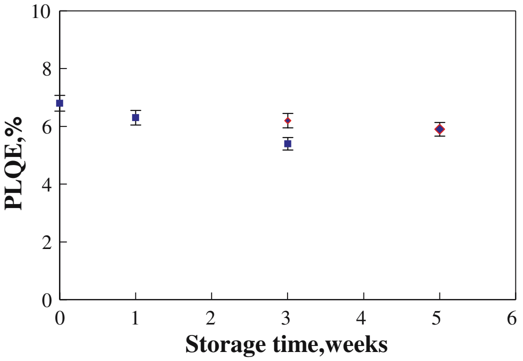

Fig. 5 Effect of extra DTG ligand on room temperature photoluminescence quantum efficiency of PbS NCs upon aging (DTG/Pb = 2.55/1). ■, Without extra DTG ligand; ◆, additional 0.33 mmol of DTG introduced into the nanocrystal solution and stirred for 5 min every 2 weeks

photoluminescence quantum efficiency (PLQE) varying from ca. 7 to 11%, except the series prepared at the smallest DTG/Pb ratio 0.43/1 for which PLQE was ca. 2% [20]. Figure 4 demonstrates the stability of room temperature photoluminescence quantum efficiency of PbS NCs stored in an ice-bath (in the dark) after each measurement.[1] The quantum efficiency of NPs remained higher than 5% upon aging for at least 3 weeks, except the one at DTG/Pb molar ratio 3.40/1 in which PLQE of the NPs decreased to half the amount of the freshly prepared NPs after 1 week of storage under the same condition. In general, a low PLQE is regarded as a result of the surface states located in the band gap of semiconductor NCs, which act as trapping states for the photo-generated charges [21]. The ligands on the surface of PbS NCs may remove some or all of the trapping states and increase the PLQE of semiconductor NCs considerably. It can be reckoned that if additional ligands are added during the storage process of PbS NPs, more stable PLQE could be expected. As confirmation, we produced two parallel PbS nanoparticle samples (molar ratio DTG/Pb = 2.55/1): one was designed for the determination of PLQE per week without extra DTG addition, the other (was sealed and stored properly in an ice-bath in the dark after preparation) with additional 0.33 mmol of DTG introduced into the nanocrystal solution every 2 weeks. We measured PLQE of the above exemplary PbS NPs and found that adventitious DTG ligands do play an important role in maintaining the high quantum efficiency of NPs: PLQE of the latter NCs was 6.2 and 5.9% upon aging for 3 and 5 weeks, respectively (in comparison with the value 5.4% upon aging for 3 weeks without addition of extra ligands), both higher than 5% after 3 and 5 weeks of storage in the same conditions (Fig. 5).[2] The strong and stable room temperature luminescence covering the telecommunication window (1.3–1.55 μm) makes PbS NCs attractive candidates for advanced functional materials in optical device and telecommunications.

Conclusions

In summary, we produced PbS nanocrystals with stable photoluminescence and high photoluminescence quantum yield via a facile one-stage synthesis at room

---

[1] We note that some 1–8% uncertainty in the measurement of quantum efficiency may apply to the nanocrystals in this figure. It was omitted for clarity.

[2] Additional 0.33 mmol of DTG were introduced into the nanocrystal solution and stirred for 5 min every 2 weeks.

temperature. Room temperature photoluminescence quantum efficiency (7–11%) of PbS NPs was found higher than 5% upon aging for at least 3 weeks when the NPs were stored in an ice-bath, and higher than 5% for 5 weeks when additional DTG ligand was introduced into the solution periodically during the storage process. The combination of high room temperature photoluminescence quantum efficiency and strong, stable luminescence covering the 1.3 μm telecommunication window make this kind of water-soluble semiconductor nanocrystals potential functional materials in optical devices and telecommunications.

Acknowledgements Xusheng Zhao is grateful to the support of K.C. Wong Education Foundation, Hong Kong. This work was partly supported by National Natural Science Foundation of China, Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, Guangdong Natural Science Foundation and Guangzhou municipal government. The authors thank Prof. Eugenia Kumacheva from the Department of Chemistry, University of Toronto, for fruitful discussions.

References

1. Murray CB, Norris DJ, Bawendi MG (1993) J Am Chem Soc 115:8706
2. Alivisatos AP (1996) Science 271:933
3. Li JJ, Wang YA, Guo W, Keay JC, Mishima TD, Johnson MB, Peng X (2003) J Am Chem Soc 125:12567
4. Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP (1998) Science 281:2013
5. Chan WCW, Nie SM (1998) Science 281:2016
6. Peng AZ, Peng X J Am Chem Soc (2001) 123:183
7. Gaponik N, Talapin DV, Rogach AL, Hoppe K, Shevchenko EV, Kornowski A, Eychmuller A, Weller H (2002) J Phys Chem B 106:7177
8. Aldana J, Wang YA, Peng X (2001) J Am Chem Soc 123:8844
9. Bakueva L, Musikhin S, Hines MA, Chang T-WF, Tzolov M, Scholes GD, Sargent EH (2003) Appl Phys Lett. 82:2895
10. Hines MA, Scholes GD (2003) Adv Mater 15:1844
11. Lee S-M, Jun Y-W, Cho S-N, Cheon J (2002) J Am Chem Soc 124:11244
12. Kane RS, Cohen RE, Silbey R (1996) Chem Mater 8:1919
13. Patel AA, Wu F, Zhang JZ, Torres-Martinez CL, Mehra RK, Yang Y, Risbud SH (2000) J Phys Chem B 104:11598
14. Wang S, Yang S (2000) Langmuir 16:389
15. Chen S, Truax LA, Sommers JM (2000) Chem Mater 12:3864
16. Zhou Y, Itoh H, Uemura T, Naka K, Chujo Y (2002) Langmuir 18:5287
17. Wundke K, Auxier J, Schülzgen A, Peyghambarian N, Borelli NF (1999) Appl Phys Lett 75:3060
18. Sukhovatkin V, Musikhin S, Gorelikov I, Cauchi S, Bakueva L, Kumacheva E, Sargent EH (2005) Optics Lett 13:344
19. Bakueva L, Gorelikov I, Musikhin S, Zhao XS, Sargent EH, Kumacheva E (2004) Adv Mater 16:926
20. Zhao XS, Gorelikov I, Musikhin S, Cauchi S, Sukhovatkin V, Sargent EH, Kumacheva E (2005) Langmuir 21:1086
21. Qu L, Peng X (2002) J Am Chem Soc 124:2049