Photoluminescence of CdTe quantum dots ligated with caprylic acid synthesized at low temperature

Ming-Qiang Zhu*, Li Peng and Ming-Feng Zhu

Wuhan National Laboratory for Optoelectronics, College of Optoelectronic Science & Technology, Huazhong University of Science & Technology, Wuhan, 430074, China

(Received 23 September 2010; final version received 24 January 2011)

Photoluminescent semiconductor nanocrystals or quantum dots (QDs) are usually produced using expensive ligands and solvents at high temperature above 280°C to ensure high-quality optical properties, particularly the photoluminescence of QDs. The reproducibility of highly stable photoluminescence in QD preparation, in most cases, varies depending on many effects, such as the ligand used and temperature. Here a facile preparation of photoluminescent semiconductor CdTe nanocrystals or quantum dots (QDs) is conducted in the presence of caprylic acid at moderate temperatures between 80–140°C, which are much lower than the high temperatures used in conventional organic-phase preparation of CdTe QDs. The results show that the optical properties of CdTe QDs depend considerably on the reaction time, temperature and ligand used.

Keywords: photoluminescence; cadmium telluride; quantum dot; caprylic acid; ligand

1. Introduction

Photoluminescent semiconductor nanocrystals or quantum dots (QDs) are of great fundamental and industrial interest owing to their size-dependent photoluminescent properties [1–3]. QDs are usually produced using expensive ligands and solvents at small scales and the reproducibility of QD preparation, in most cases, varies depending on the ligand used. Therefore, facile large-scale preparation of low-cost and high-quality QDs is of critical importance for many purposes, especially commercial applications [4]. Compared with CdSe QDs, CdTe QDs possess greater luminescent stability with strong resistance to thiols. Thus, there is no special necessity for them to be capped with an additional semiconductor shell [5–8]. In fact, CdTe nanocrystals are potentially better candidates since they have additional near-IR activities in comparison to CdSe nanocrystals for definite applications, such as solar cells [9] and in vivo biodetections [10,11]. Traditionally, CdTe nanocrystals with relatively narrow size distributions can also be synthesized using well-established organometallic approaches [12,13] and aqueous solution approaches [14,15]. The classical methods to prepare CdTe QDs in organic solvents rely on high temperature (above 280–300°C) reactions and expensive raw materials as well as solvents, such as organic phosphines, octadecene (ODE) and aliphatic amines [16–18]. If the production cost of QDs could be significantly reduced by using suitable ligands and a low reaction temperature, preparation and wide practical application of CdTe QDs would be possible. Here a
facile preparation method of CdTe QDs using caprylic acid (CA) as ligand at 80–140°C is introduced. Using this energy-efficient method, preparation and optimization of CdTe QDs with efficient photoluminescent properties has been demonstrated at relatively low temperature.

In order to reduce the product cost and environmental size-effects of QD preparation, an inexpensive commercial diesel was selected as reaction solvent with aliphatic acid serving as the only ligand for CdTe QDs. In comparison to conventional reaction solvents, diesel seems a more promising candidate as a reaction medium. As solvent and fuel, commercial diesel is more environmentally benign, cost-effective and more stable in the atmosphere than the solvents or ligands reported previously, such as trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), or ODE. Secondly, the lower boiling range of light diesel facilitates ligand exchange and diffusion in the reaction mixture. Most importantly, it was demonstrated that commercial diesel had no influence on the photoluminescent properties of as-prepared QDs even in the open air. In addition, considering that the growth dynamics of QDs is a function of both reaction temperature and boiling point of solvent or ligand, CA was chosen as ligand for CdTe QDs. The boiling point of CA is much lower than advanced aliphatic acids, such as oleic acid and dodecanoic acid. A reaction temperature close to the boiling point of CA will facilitate molecular diffusion and ligand exchange on the surface of CdTe QDs [19].

2. Experimental section

2.1. Materials

CdO (99%), Te powder (analytical grade), caprylic acid (CA, analytical grade), oleic acid (analytical grade) and hexanoic acid (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China, and used as obtained. Triocetylphosphine (90%) was obtained from Aldrich Co. Diesel (0#) was purchased from a commercial gas station and purified against an alumina column. Rhodamine 6G (with a photoluminescence quantum yield of 95% in ethanol) was obtained from Sigma Co.

2.2. Characterization

Transmission electron microscopy (TEM) was conducted using a JEM JEOL 2010 transmission electron microscope operating at 100 kV. The sample was prepared by dropping a 3 µl solution onto a carbon-coated Formvar copper grid (300 mesh) followed by solvent evaporation at room temperature. UV–visible (UV-vis) spectra were recorded with a UV2300 spectrophotometer (Techcomp, China). Fluorescence spectra were recorded with F2500 spectrophotometer (Hitachi, Japan) with excitation at 488 nm (slit width 5 mm, spectral width of excitation source 10 nm, 450 W Xe lamp). The fluorescence quantum yield of QDs was measured under the same setting of F2500 spectrophotometer using Rhodamine 6G in ethanol as standard ($QY = 0.95$). The optical density at 488 nm (excitation wavelength) of Rhodamine 6G and QDs was set as a similar value. The first absorption peak of QDs and the absorbance at main absorption peak of Rhodamine 6G were kept under 0.1 to decrease the re-absorption of samples. The fluorescence quantum yields of quantum dots were calculated by comparing the integrated intensity of QDs and Rhodamine 6G.

2.3. The preparation of Cd injection solution

The mixture of 12 mmol of cadmium oxide (1.54 g), 24 mmol of octyl acid (5.0 ml) and 50 ml of 0# diesel was heated to make CdO dissolve completely.
2.4. Synthesis of CdTe QDs

6.0 mmol of Te powder (0.76 g), 1.0 ml of TOP and 50 ml of 0# diesel were loaded into a three-neck flask. The mixture was heated to make Te dissolved at a pre-designed temperature. The Cd injection solution was then added into the solution. The reaction was terminated at a certain time when the thermostat was removed. The solution was diluted into the same concentration for PL measurement. The QDs were precipitated twice through adding the solution into anhydrous acetone, then separated through spinning down at 6000 rpm for 10 min, and dried in vacuum overnight. The amount of CdTe QDs (including caprylic acid coating) obtained was \( \sim 1.2 \) g.

3. Results and discussion

In typical synthesis, Te powder, TOP and diesel were loaded into a three-neck flask and the mixture was heated affording Te stock solution. The Cd-CA solution, which was prepared by heating the mixture of CdO and CA in diesel, was injected into the solution at 140°C. It was observed that the cooler of the reaction mixture changed in seconds, indicating the formation of QDs. The temporal evolution of the size and size distribution of CdTe QDs was monitored by recording UV-vis absorption and fluorescent spectra of the aliquots taken from the reaction system. Figure 1a shows the time-dependent evolution of UV-vis and photoluminescence spectra of CdTe QDs. It is expected that the band gap energy of bulk CdTe is about 860 nm at 300 K. The photoluminescence emission wavelength of QDs showed a gradual red-shift as the reaction proceeded, indicating that QDs grow gradually at a controlled speed (Figure 1a). The stock's shift of CdTe QDs become smaller with the growth of QDs, from 20 nm to 10 nm. The CdTe QDs were near monodisperse, represented by a sharp emission with full width at half-maximum (FWHM) of 25–35 nm when the QD growth was terminated in the ‘focusing of size distribution’ stage. The QDs were well-defined and uniform in size, as demonstrated by the representative TEM image (Figure 1b). A good crystalline structure of the CdTe QDs was confirmed by the HRTEM image of a single CdTe QDs from the same ensemble with existence of lattice planes (Figure 1b, inset).

A representative image of as-prepared CdTe QDs under UV irradiation is shown in Figure 1c (correlated to the sample taken at 30 s), which indicates the strong fluorescence from CdTe QDs. It is known that the crystal structure of CdTe nanocrystals is intensively dependent on the growth temperature. Higher temperature generally leads to a wurtzite structure, whereas a zinc blende structure results at lower temperature. In this instance, the temperature was below 220°C, which is much lower than common reaction temperature for CdTe QD growth, which is usually above 300°C [13,16]. The X-ray diffraction (XRD) pattern also shows that the resulting CdTe QDs possess a zinc blende structure (Figure 1d). The three diffraction peaks located at 24.0, 39.6, and 46.3° correspond to the (111), (220), and (311) planes of zinc blende CdTe.

Further investigation showed that the reaction temperature played a critical role in the growth of CdTe QDs in diesel. Figure 2a illustrates the time-dependent evolution of the photoluminescence emission wavelength of the CdTe QDs after injection of Cd solution at different reaction temperatures. This evolution represents the effect of reaction temperature on the emission wavelength of as-grown CdTe QDs as an identical feed ratio was used for each run. Evidently, CdTe QDs grew much slower with the decrease of reaction temperature, resulting in systematically smaller sizes (Figure 2a). To compare the effect of different temperatures on the fluorescent properties of CdTe QDs, the growth reactions of CdTe
Figure 1. Typical UV-vis and PL spectra and TEM image of CdTe QDs synthesized at 140°C: (a) absorption and PL spectra; (b) representative TEM image, inset: HRTEM image. (c) Digital image of green CdTe QDs. (d) XRD pattern of CdTe QDs.

QDs were terminated at 2 min. The resulting emission wavelength of CdTe QDs increased monotonously with increasing temperature (Figure 2b). At the same time, photoluminescence intensity of CdTe QDs depended on the reaction temperature. The photoluminescent quantum yield (PL QY) of CdTe QDs shows a gradual increase followed by a decrease with increasing temperature from 80°C to 180°C (Figure 2c). This indicates that an optimal reaction temperature works best for higher PL QY in this system with an optimal temperature at about 140°C. The full-width at half maximum (FWHM) of QDs fell between 25 nm and 37 nm, which indicates that this low temperature method produced high-quality QDs with a narrow size distribution (Figure 2d).
As an alternative to organic phosphine ligands, aliphatic acids from Cd stock solution play a similar protection role for QDs. It is noticeable that a feature of the aliphatic acid, as a poor ligand, is that it allows sustainable QD growth to proceed even in the rather low temperature range of 80–140°C, which is not available in the case of organic phosphines and other stronger ligands. Here, as the only ligand used in synthesis of QDs, CA can function in multiple roles. First, CA is used as organic acid to neutralize CdO into a Cd precursor and make it soluble in nonpolar solvent and, secondly, CA behaves as the ligand to stabilize and control the nucleation and the growth of QDs. In a screen of CA for the nucleation and growth of CdSe QDs, it was observed that the amount of CA influenced the photoluminescent properties of QDs. Figures 3a–3d shows the relationship between optical properties of QDs and the amount of CA added. The time-dependent evolution of fluorescent emission wavelength of CdTe QDs indicated almost the same tendency with different CA content (Figure 3a). The comparison of the resulting CdTe QDs at 2 min indicates an obvious increase in PL QY with the increase of CA content. The more the amount of CA added, the higher PL QY was observed (Figure 3c). However, the CA did not cause much difference in the size and size distribution of QDs, as demonstrated in Figures 3b and 3d.

We compared the effect of aliphatic acids with different carbon chain lengths on the optical properties of CdTe QDs (Figure 4). It was observed that CdTe QDs ligated with hexanoic acid can be synthesized (Figure 4a). However, the PL QY of CdTe QDs ligated with hexanoic acid dropped to 10–20%, which is lower than that achieved using caprylic...
Figure 3. Effect of CA content on the optical properties of CdTe QDs. (a) Curves of emission versus time at different CA content. After 2 min, the emission wavelength (b), PL QY (c) and FWHM (d) of QDs dependent on CA content.

acid. Surprisingly, an attempt to synthesize high-luminescent CdTe QDs ligated with oleic acid failed, the cause of which is under further investigation. The possible explanation is that, in comparison to oleic acid (18 carbons) with high boiling point (~286°C), the molecular diffusion and ligand exchange between QDs and CA molecules with low boiling point (~237°C) are faster and easier, making the synthesis of QDs possible at such a low temperature. Therefore, CdTe QDs can be prepared even at the rather low temperature of about 100°C. At a temperature as low as 100°C, monitoring of reaction kinetics becomes much easier because of the slow growth of QDs compared to those of the high temperature (up to 280–300°C) using the popular methods reported previously [19].

4. Conclusion
In conclusion, the energy-efficient synthesis of semiconductor CdTe quantum dots (QDs) has been achieved at moderate temperatures as low as 80°C by using an aliphatic acid with an appropriate boiling point. This lower-temperature technique for the synthesis of CdTe semiconductor QDs using green ligands has promising prospects in practical application, such as in photovoltaic materials and bioimaging, as a cost-efficient and environmentally friendly alternative to the current mainstream method for producing CdTe QDs.
Figure 4. Effect of reaction temperature on the photoluminescent properties of CdTe QDs ligated with hexanoic acid. (a) Curves of emission versus time at different temperature. After 2 min, the emission wavelength (b), PL QY (c) and FWHM (d) of QDs dependent on reaction temperature.

Acknowledgment
This work was financially supported by the initiating grant of HUST, the NSFC (20874025) and the Fundamental Research Funds for the Central Universities, (HUST-2010MS101).

References
[1] W.C.W. Chan and S.M. Nie, Quantum dot bioconjugates for ultrasensitive nonisotopic detection, Science 281 (1998), pp. 2016–2018.
[2] J. Li, B. Jia, G. Zhou, and M. Gu, Fabrication of three-dimensional woodpile photonic crystals in a PbSe quantum dot composite material, Opt. Express 14 (2006), pp. 10740–10745.
[3] C.B. Murray, D.J. Norris, and M.G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites, J. Am. Chem. Soc. 115 (1993), pp. 8706–8715.
[4] J.J. Li, Y.A. Wang, W. Guo, J.C. Keay, T.D. Mishima, M.B. Johnson, and X. Peng, Large-scale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction, J. Am. Chem. Soc. 125 (2003), pp. 12567–12575.
[5] Z. Tang, Z. Zhang, Y. Wang, S.C. Glotzer, and N.A. Kotov, Self-assembly of CdTe nanocrystals into free-floating sheets, Science 314 (2006), pp. 274–278.
[6] V. Sgobba, C. Schulz-Drost, and D.M. Guldi, Synthesis and characterization of positively capped CdTe quantum wires that exhibit strong luminescence in aqueous media, Chem. Comm. (2007), pp. 565–567.
[7] B.W. Garner, T. Cai, Z. Hu, and A. Neogi, Electric field enhanced photoluminescence of CdTe quantum dots encapsulated in poly (N-isopropylacrylamide) nano-spheres, Opt. Express 16 (2008), pp. 19410–19418.
[8] D.V. Talapin, A.L. Rogach, E.V. Shevchenko, A. Kornowski, M. Haase, and H. Weller, Dynamic distribution of growth rates within the ensembles of colloidal II–VI and III–V semiconductor nanocrystals as a factor governing their photoluminescence efficiency, J. Am. Chem. Soc. 124 (2002), pp. 5782–5790.

[9] X.W. Sun, J. Chen, J.L. Song, D.W. Zhao, W.Q. Deng, and W. Lei, Ligand capping effect for dye solar cells with a CdSe quantum dot sensitized ZnO nanorod photoanode, Opt. Express 18 (2010), pp. 1296–1301.

[10] A.M. Smith, H. Duan, A.M. Mohs, and S. Nie, Bioconjugated quantum dots for in vivo molecular and cellular imaging, Adv. Drug Deliv. Rev. 60 (2008), pp. 1226–1240.

[11] C.-F. Chang, C.-Y. Chen, F.-H. Chang, S.-P. Tai, C.-Y. Chen, C.-H. Yu, Y.-B. Tseng, T.-H. Tsai, I.-S. Liu, W.-F. Su, and C.-K. Sun, Cell tracking and detection of molecular expression in live cells using lipid-enclosed CdSe quantum dots as contrast agents for epi-third harmonic generation microscopy, Opt. Express 16 (2008), pp. 9534–9548.

[12] D.V. Talapin, S. Haubold, A.L. Rogach, A. Kornowski, M. Haase, and H. Weller, A novel organometallic synthesis of highly luminescent CdTe nanocrystals, J. Phys. Chem. B. 105 (2001), pp. 2260–2263.

[13] W.W. Yu, Y.A. Wang, and X. Peng, Formation and stability of size-, shape-, and structure-controlled CdTe nanocrystals: ligand effects on monomers and nanocrystals, Chem. Mater. 15 (2003), pp. 4300–4308.

[14] L. Li, H. Qian, and J. Ren, Rapid synthesis of highly luminescent CdTe nanocrystals in the aqueous phase by microwave irradiation with controllable temperature, Chem. Comm. (2005), pp. 528–530.

[15] A.L. Rogach, T. Franzl, T.A. Klar, J. Feldmann, N. Gaponik, V. Lesnyak, A. Shavel, A. Eychmuller, Y.P. Rakovich, and J.F. Donegan, Aqueous synthesis of thiol-capped CdTe nanocrystals: state-of-the-art, J. Phys. Chem. C 111 (2007), pp. 14628–14637.

[16] Z.A. Peng and X. Peng, Formation of high-quality CdTe, CdSe, and CdS nanocrystals using CdO as precursor, J. Am. Chem. Soc. 123 (2001), pp. 183–184.

[17] S. Kumar and T. Nann, Hexagonal CdTe nanoparticles of various morphologies, Chem. Comm. (2003), pp. 2478–2479.

[18] W.W. Yu and X.G. Peng, Formation of high quality CdS and other II–VI semiconductor nanocrystals in non-coordinating solvent, tunable reactivity of monomers, Angew. Chem. Int. Ed. 41 (2002), pp. 2368–2371.

[19] N. Pradhan, D. Reifsnnyder, R. Xie, J. Aldana, and X. Peng, Surface ligand dynamics in growth of nanocrystals, J. Am. Chem. Soc. 129 (2007), pp. 9500–9509.