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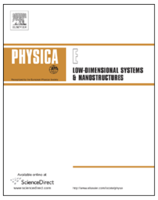

# Aqueous synthesis of thiol-capped CdTe quantum dots and its photoluminescence enhancement via room temperature treatment with alkyl chain diamines

Xiangming Liu, Jintao Tian*, Jinhui Dai, Xin Wang

*Institute of Materials Science and Engineering, Ocean University of China, Songling Road 238, Qingdao 266100, PR China*

## HIGHLIGHTS

- The CdTe QDs are synthesized with three types of thiol-contained ligands.
- The growth kinetics and the PL efficiency vary a lot with the ligands.
- PL enhancement is achieved for the TGA and MPA capped QDs from diamines.
- The PL enhancement on the LCys capped QDs is practically meaningless.

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## ABSTRACT

In this study the CdTe quantum dots (QDs) are synthesized in aqueous solution with three thiol-contained capping ligands of thioglycollic acid (TGA), 3-mercaptopropionic acid (MPA), and L-cysteine (LCys). The photoluminescence (PL) enhancement of the as-prepared QDs is also conducted via room temperature treatment with alkyl chain diamines. Our measurements on the ultraviolet–visible (UV–vis) absorption and fluorescence emission reveal that both the growth kinetics and the PL efficiency of the QDs vary a lot with the molecular structures of the three involved ligands. In comparison with TGA and LCys, MPA endows the QDs with a wide color tuning range from cyan to deep red and strong PL emission while its full width at half maximum (FWHM) is regretfully large. Notable enhancement on PL emission is achieved for the TGA and MPA capped QDs via room temperature treatment with diamines solutions while in the case of the QDs capped by LCys the enhancement is practically meaningless.

## 1. Introduction

During the last decade, thiol-capped CdTe quantum dots (QDs) have attracted a wave of research interest worldwide, resulting in at least hundreds of publications per year which not only addressed different aspects related to this specific kind of material but also introduced a broad palette of related developments in different research fields [1]. Especially, with outstanding size-dependent and tunable photoluminescence (PL) in the whole visible region, CdTe QDs undoubtedly attract great attention in the domains of the optoelectronic and biological applications, such as photovoltaics (PVs) [2], light emitting diodes (LED) [3], bio-imaging and bio-coding [4], etc. Concerning the synthesis of CdTe QDs, lots of methods have been developed, such as thermal decomposition [5], solvothermal route [6], microwave irradiation route [7], and the sonochemical method [8]. The aqueous synthetic approach, as a green alternative, can be carried out at a much lower temperature in which the solvent of water, is nontoxic, inexpensive and abundant compared to organic solvents, thus facilitating the manipulation and scaling up of the synthetic process [9]. Sufficient progress has been made in the preparation of water-soluble CdTe QDs [10]. The most effective way is the colloidal QDs directly synthesized in aqueous solution with thiol-containing capping ligand [11]. So far the most frequently used ligands of mercapto acid compounds for CdTe QDs, thioglycolic acid (TGA) and 3-mercaptopropionic acid (MPA) can transfer negative surface charge to nanoparticles, allowing to obtain strongly emitting colloids which are stable for several months and even years in terms of both their colloidal stability against coagulation and their constantly high emission quantum yield [12]. The use of amino acids (L-cysteine) is promising for better biocompatibility of nanoparticles. To the best of our knowledge, there are few reports on low temperature synthesis of CdTe QDs using TGA, MPA, and L-cysteine as ligands in the aqueous phase [13]. Temperature such as 100 °C for the synthesis of CdTe in aqueous phase is a typical

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* Corresponding author. Tel.: +86 532 66781690; fax: +86 532 66781320.
*E-mail address:* jttian@ouc.edu.cn (J. Tian).

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condition [14]. Our research suggests that CdTe QDs could be obtained within a large temperature range. In order to easily control the reaction system in a water bath, 90 °C is a better selection for synthesis of CdTe QDs. Most of the colloidal syntheses of semiconductor nanocrystals are based on the Ostwald ripening phenomenon [15]. Theoretical understanding of the mechanism and modeling of nucleation and growth of thiol-capped QDs as well as factors influencing their emission properties has been addressed by several research groups in recent years [16]. The formation of nanocrystals in solution is a dynamic process. After nucleation, further particle growth occurs via dissolution of small clusters in favor of the growth of larger particles [17]. Energy should be provided to favor the growth of QDs, such as refluxing in aqueous solution [18]. By prolonged refluxing, we could obtain QDs with different grain size. Post treatment is a modified method of passivation on the surface of CdTe QDs, especially organic amine reagents [19]. Diamines, such as ethylenediamine (EDA) and hexamethylenediamine (HDM), have better surface modified advantages to QDs. Also they are very common reagents in organic synthesis process [20]. According to the previous report, post treatment on the synthesized CdTe QDs with EDA can increase the PL intensity and PLQY [21]. We introduce HDM as another diamine to explore the effect on thiol-contained CdTe QDs. To sum up, our research provides a better understanding of the effects of reaction temperature, ligand nature, and prolonged refluxing on aqueous growth of CdTe nanocrystals. Besides, diamine addition offers a method to obtain CdTe QDs with high qualities.

## 2. Experimental procedure

Several chemicals of cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), thioglycollic acid ($HSCH_2COOH$, TGA), 3-mercaptopropionic acid ($HSCH_2CH_2COOH$, MPA), L-cysteine ($HSCH_2CH(NH_2)COOH$, LCys), sodium hydroxide (NaOH), tellurium powder (Te), sodium borohydride ($NaBH_4$), ethylenediamine (EDA), and hexamethylenediamine (HDM) are used in this study as raw materials. All of them are of analytical grade and used as received without any further purification. All aqueous solutions are prepared using deionized water.

The CdTe QDs are synthesized in this study in aqueous solution by directly mixing of a Cd source solution containing $Cd^{2+}$ and a Te source solution containing sodium hydrogen tellurium (NaHTe) that is from a reaction occurring between $NaBH_4$ and Te powder [22]. In a typical synthesis, 0.1233 g $CdCl_2 \cdot 2.5H_2O$ and 0.064 mL TGA (or 0.08 mL MPA or 0.112 g LCys) are dissolved in 150 mL deionized water to form a Cd source solution. The solution is adjusted to be a pH value of 11.2 by adding a 1.0 M NaOH solution. The Cd source solution is then deoxygenated in a three-neck flask by bubbling nitrogen for at least 30 min. Meanwhile, 0.0115 g Te powder and 0.0136 g $NaBH_4$ are added into 10 mL deionized water under nitrogen atmosphere to form a black mixture. The mixture is then continuously stirred under nitrogen until the black color disappears and the Te source solution containing NaHTe is obtained. The freshly prepared NaHTe solution is then injected into the flask with syringe under nitrogen atmosphere at room temperature. The molar ratio of $Cd^{2+}/Te^{2+}$/TGA (or MPA or LCys) in the final solution is 6/1/10.2. The reaction solution is then heated to high temperature through a water bath and maintained at this temperature with stirring for a period of reaction time. After that, 10 mL solution is taken out from the flask with a pipette and conserved as a colloid sample in nitrogen filled bottle for optical measurements. In order to enhance its photoluminescence emission, the as-prepared CdTe QDs are treated with alkyl chain diamine solution at room temperature. 6 mL QDs solution is incorporated into 4 mL EDA (or HDM) solution and kept for 8 h. The concentrations of EDA (or HDM) solution are intended to be 0, 1, 2, 3, 4, 6, 8, and 10 mM.

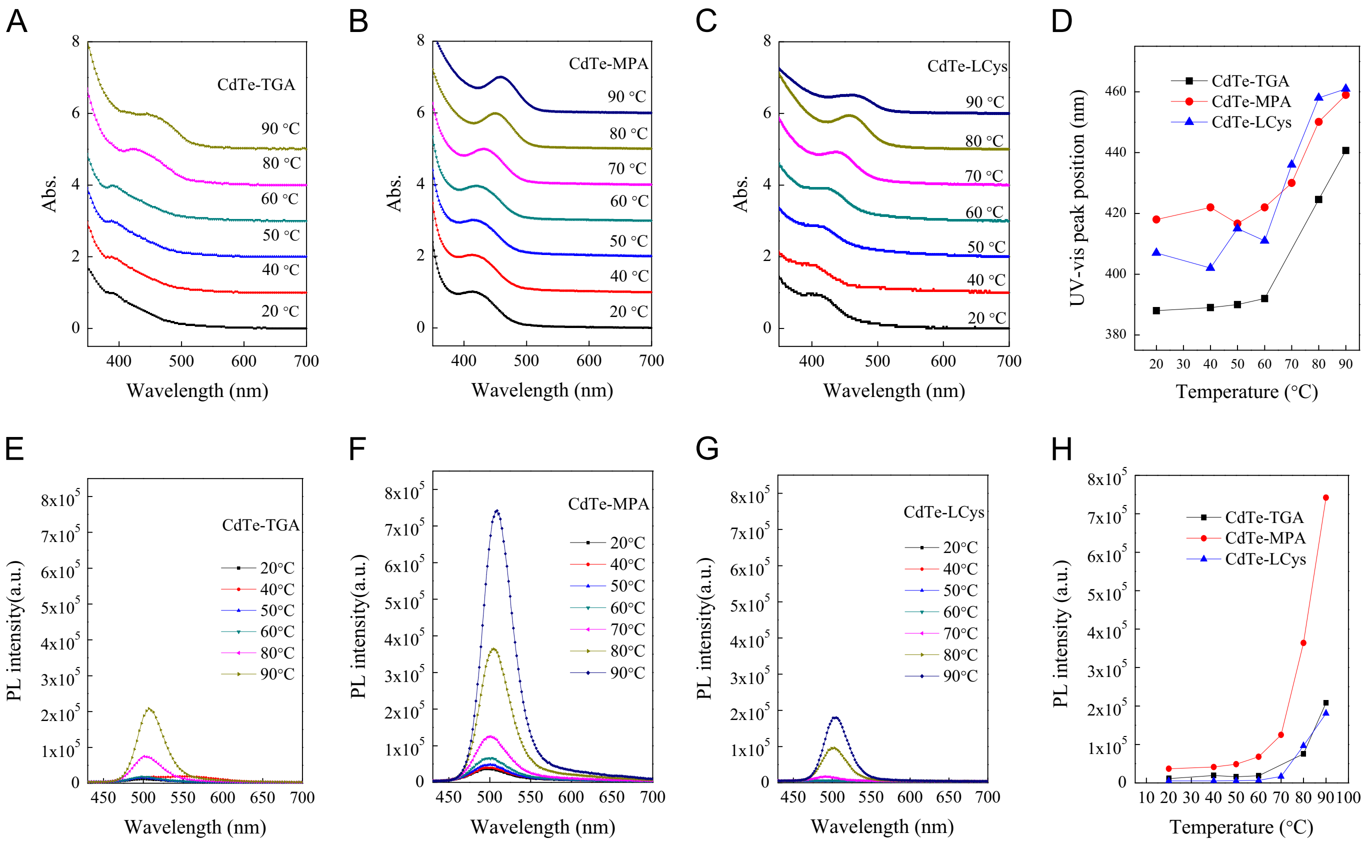

**Fig. 1.** Temperature-dependent optical behaviors of the CdTe QDs capped by the thiol-contained ligands of TGA, MPA, and LCys. (A–C) UV–vis absorption; (E–G) PL emission; and (D and H) derived UV–vis peak position and PL intensity against reaction temperature.