



Comparative photoluminescence properties of type-I and type-II CdTe/CdS core/shell quantum dots



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ABSTRACT

High quality type-I and type-II CdTe/CdS quantum dots (QDs) were designed and synthesized in water at 90 °C using the same 3.0-nm CdTe core QDs with different CdS shell thicknesses. Time-resolved and temperature-dependent photoluminescence techniques were used to study comparatively their optical properties, showing strong luminescence peaking at 550 nm with the short decay time of 20 ns for type-I CdTe/CdS QDs; and strong luminescence in the near-infrared region of 700–830 nm with very long decay time of 190 ns for the type-II ones. In addition, exciton–acoustic phonon interaction is much stronger in type-I QDs compared to that in type-II ones that is rationally due to the stronger confinement effect.

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1. Introduction

Semiconductor QDs have attracted remarkable attention since the last two decades because they are very interesting objects both from the fundamental and applied research points of view [1–6]. Particularly, the optical properties and potentially related applications, which stem from the quantum confinement effect at nanometer sizes, have been studied for different semiconductor QDs. One could mention the achievements in the syntheses of high quality CdSe, CdTe, InP, CuInS₂ QDs and their core/shell structures in which the shell is usually a material having larger bandgap energy like CdS, ZnSe or ZnS [2–9]. Depending on the band offset, the core/shell structure can be type-I or type-II and their possible applications would be various accordingly. Type-I core/shell QDs could strongly emit luminescence because the excited electrons and holes are confined in the same material, therefore they are very good candidates for applications in fluorescence biolabeling/biosensor and in light emitting diodes [4–6,9,10]. Meanwhile, type-II core/shell QDs give more chance for separating the photo-generated electrons and holes because of the band offset, they are more promising for photovoltaic and photocatalytic applications. Because the total energy of the electron and the hole in a

QD depends not only on the nature of material but also on the charge confinement in such QD, one can manipulate the confinement to have the band-edge alignment of the core and the shell to have the type-I or type-II quantum structure. In a previous paper we demonstrated the success of bandgap engineering by adjusting the CdS shell thickness (to change the quantum confinement energy) on the same CdTe core QDs to have the transition from type-I to type-II CdTe/CdS core/shell QDs, which emit strong luminescence peaking in the spectral range of 550–800 nm [11]. For biolabeling applications, there are arguments on the toxicity of Cd-based materials, consequently other nanomaterials such as CuInS₂ QDs or rare-earth ion-doped InP QDs have been synthesized and studied as alternatives [12–14]. Practically, CdSe and CdTe QDs with shelling by ZnS or CdS/ZnS or ZnSe/ZnS could be used as the reasonable fluorescence biolabels because the amount used is usually very small, and in many cases biosensing is just *ex vivo* that all make the elimination of direct toxicity.

There have been much less publications on CdTe/CdS core/shell QDs compared to those on other core/shell systems like CdSe/ZnS, CdSe/ZnSe/ZnS; that is possibly due to the less luminescence quantum yield (LQY) of CdTe/CdS QDs. Recently, because of promising applications in photovoltaic devices and as the near-infrared (NIR) emitters, type-II CdTe/CdS and CdTe/CdSe core/shell QDs have become to be more considered [15,16]. Bulk CdTe/CdS shows to be type-II structure with the offsets of 0.02 eV and 0.99 eV for the conduction and valence bands, respectively [15]. Therefore, in the quantum structures of CdTe/CdS, depending on the contribution

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of the confinement energy to the total energy of conduction electrons, CdTe/CdS core/shell QDs can exhibit to be type-I or type-II. This has been the basis for our design to have the transition from type-I to type-II quantum structure by gradually thickening the CdS shell (to reduce the confinement energy) on the same sized-CdTe core QDs [11]. CdTe QDs could be effectively synthesized in water with 3-mercaptopropionic acid (MPA) or mercaptosuccinic acid (MSA) as surfactants or in oil medium with balancing the coordinating capacity and the selected surfactants [11,17]. Then, shelling with CdS and/or CdS/ZnS or CdS/ZnO would make CdTe/CdS core/shell or CdTe/CdS/ZnS or CdTe/CdS/ZnO core/shell/shell QDs highly luminescent (LQY of 50–90%) [11,17–19].

In this paper we present the success in aqueous synthesis of high quality CdTe seed QDs at room temperature, and further development at 90 °C to obtain type-I and type-II CdTe/CdS core/shell quantum structures from the same 3.0-nm CdTe core QDs with different CdS shell thicknesses. The optical properties of the obtained type-I and type-II QDs were comparatively studied by using time-resolved and temperature-dependent photoluminescence (PL) techniques, showing strong luminescence peaking at 550 nm with rather short decay time of 20 ns for type-I CdTe/CdS QDs, and strong luminescence in the near-infrared (NIR) region of 700–830 nm with very long decay-time of 190 ns for type-II ones. Moreover, with increasing temperature, the much more bandgap narrowing and much stronger exciton–acoustic phonon interaction in type-I CdTe/CdS QDs compared to those in type-II ones were observed. These are reasonably attributed to the stronger confinement of excitons in type-I QDs. Type-II CdTe/CdS QDs gained both the high LQY at the near-infrared (NIR) region and the long decay time in hundreds of ns which are very suitable for biolabeling, besides their potential applications for photovoltaic cell and photocatalysis.

2. Experimental

2.1. Chemical substances

The following chemical agents were used for the synthesis of CdTe and CdTe/CdS core/shell QDs: cadmium bromide (CdBr₂, 99%), 3-mercaptopropionic acid (MPA, 99%), sodium borohydride (NaBH₄, 99%) and TeO₂. They were purchased from Merck and Aldrich, were used without further purification.

2.2. Synthesis of CdTe and CdTe/CdS QDs

CdTe and CdTe/CdS QDs were synthesized in aqueous solution following the procedure described elsewhere [11]. Briefly, a stock NaHTe solution was quickly injected into CdBr₂ solution at room temperature in the presence of MPA as a stabilizing agent to create the CdTe nanocrystals (hereinafter called CdTe seed QDs). The molar ratio of Cd:Te:MPA was fixed at 1:0.1:1.5 and the pH of this solution were adjusted to be of 7–8 by adding the 1.0 M NaOH stock solution. The same 2.5-nm CdTe seed QDs were used directly for shelling at 90 °C, pH ~ 12 for 3 h. After undergoing the same heat treatment at 90 °C for 3 h, the CdTe core QDs became as big as 3.0 nm in size as estimated from the high-resolution transmission electron microscope (HR-TEM) image and from the first absorption peak position [16]. The CdS shelling was performed by adding the stock solution made of 86 mg of CdBr₂ and 37 μl of MPA in 10 ml of distilled water; the S precursor was provided from MPA, which would be dissolved at the shelling temperature, with the corresponding amounts calculated to form 1, 2, 3, 5, and 7 monolayer (ML) of CdS into the very Cd²⁺-rich solution containing CdTe seed QDs. We varied the CdS shell thickness by shelling with the corresponding amounts of S precursors rather than by

changing reaction time. This is because even for the 7-ML CdS shell, the thickness of CdS is less than 2.5 nm (1 ML of CdS is around 0.35 nm), which is too small to be controlled by reaction time. In other words, it takes very short time for reacting all the S precursor available to fill the 2.5-nm of CdS. We kept shelling for 3 h is just to make CdTe/CdS nanocrystals good quality. The obtained CdTe/CdS core/shell QDs could be precipitated by adding drops of ethanol or acetone into QDs colloidal solution, then centrifugated. In the final QDs all the excessive Cd²⁺ ions and by-pass products from the as-synthesized QDs colloidal solution could be washed. The precipitated QDs were redispersed in distilled water and kept at the normal room condition for uses afterward.

2.3. Morphology, structural and optical characterizations

Morphology and structural characterizations of CdTe core and the CdTe/CdS core/shell QDs were performed by using a TEM model JEM-2100 and X-ray diffraction (XRD, Siemens D5000). For temperature-dependent optical measurements, QDs were mounted on the cold finger of a closed-cycle helium cryostat (APD Cryogenics HC-2) to vary temperature in the range 15–300 K. In the steady-state PL measurement, a 405 nm laser diode was used as the excitation source. For the time-resolved PL (TRPL) measurement, the 532-nm pulsed light from a frequency-doubled Nd:YVO₄ laser (700-ps pulse duration, 7-kHz repetition rate) was used as the excitation source to excite directly to the CdTe core (to avoid interference excitation to the CdS shell). The PL signals were dispersed by using a 0.55-m grating monochromator (Horiba iHR550) and then detected by a thermoelectrically cooled Si-CCD camera (Synapse) for the steady-state PL measurement or by a fast photomultiplier (Hamamatsu model H733, with the rise time of 700 ps) for the TRPL measurement. Averaging multi-pulses at each spectral point using a 1.5-GHz digital oscilloscope (LeCroy 9362) strongly improved the signal-to-noise ratio. To determine the LQY, we used an absolute method developed in our lab in that the quantum yield is calculated by comparing the integrated emission from the sample to the integrated absorption of the excitation light [20] and relative method which just compares the PLs of a dye (RhG in this case with the known LQY of 95%) and colloidal QDs with the same absorbance.

3. Results and discussion

Fig. 1 shows the HR-TEM images of type-I and type-II CdTe/CdS QDs developed from the same 3.0-nm CdTe core QDs, at the same synthesis batch in the same autoclave at 90 °C for 3 h with the 1-ML, 3-ML and 5-ML CdS shells, and their corresponding energy diagrams. The HR-TEM images also show the atomic facets of an example dot. After shelling 1-ML CdS at 90 °C for 3 h, the 3.0-nm CdTe core QDs became CdTe/CdS core/shell QDs with the size of 3.7 nm (an approximately 0.7 nm increase in size per monolayer of CdS because one ML of CdS is around 0.35 nm). The sizes of CdTe/CdS core/shell QDs were increased with increasing the number of MLs of the CdS shell; having 5-ML-CdS shell, the CdTe/CdS core/shell QDs are as big as 7 nm. We have designed type-I and type-II quantum structured CdTe/CdS QDs based on the suitable band-offsets which are controllable by gradually thickening the CdS shell on the certain-sized CdTe core QDs. Quantitative calculation of the bandgap and band edge alignment of type-I and type-II CdTe/CdS QDs developed from the same 3.0-nm CdTe core QDs, with the 1-ML, 3-ML and 5-ML CdS shells was done based on (i) the bandgap energies and band edge alignment, the band offsets of bulk CdTe and CdS [21–23]; (ii) the electronic transition energy in the 3.0-nm CdTe core QDs and those in the CdS shells with contribution of the confinement energies for electrons and holes; and

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