Effect of shells on photoluminescence of aqueous CdTe quantum dots

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ABSTRACT

CdTe cores with various sizes were fabricated in aqueous solutions. Inorganic shells including CdS, ZnS, and CdS/ZnS were subsequently deposited on the cores through a similar aqueous procedure to investigate the effect of shells on the photoluminescence properties of the cores. In the case of CdTe/CdS/ZnS quantum dots, the outer ZnS shell provides an efficient confinement of electron and hole wavefunctions inside the quantum dots, while the middle CdS shell sandwiched between the CdTe core and ZnS shell can be introduced to obviously reduce the strain on the quantum dots because the lattice parameters of CdS is situated at the intermediate-level between those of CdTe and ZnS. In comparison with CdTe/ZnS core–shell quantum dots, the as-prepared water-soluble CdTe/CdS/ZnS quantum dots in our case can exhibit high photochemical stability and photoluminescence efficiency up to 80% in an aqueous solution, which implies the promising applications in the field of biomedical labeling.

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1. Introduction

In last decades, the high-quality (narrow size distribution, high stability, and high photoluminescence (PL) efficiency) colloidal semiconductor quantum dot (QD) has attracted more attentions compared with organic dyes in many applications, such as light-emitting devices, lasers, and biomedical fluorescent labels [1–5]. Compared with the traditional organic fluorophores, QDs can present many advantages in terms of high PL quantum yield (PL QY), tunable emission wavelength, multiplexing capabilities, and high photoresistance. The current emphasis has been focused on the investigation of biological imaging, ranging from single-molecule tracking to in vivo imaging and immunological labeling [6–9].

The key parameters that determine the practical feasibility of luminescent QDs mainly contain three different aspects: (i) the high PL QY, (ii) the stability of PL properties under actual operating condition, and (iii) the solubility of QDs in a desired solvent, all of which are closely related to the passivation effect of dangling bonds present on the QDs surface. Although attaching organic ligands to the nanocrystal surface can provide increased solubility and high PL QY, the PL QY is strongly dependent on the QDs surroundings and usually shows a tendency to drop in time because the dynamic equilibrium between the unstable organic ligands and the surrounding medium always lead to the oxidation of particle surface [10,11].

It has been illustrated that the epitaxial growth of a wider band-gap inorganic shell on the surface of luminescent QDs is an ideal approach to improve the PL properties of QDs by eliminating both the anionic and cationic dangling bonds, which gives birth to an enhancement of PL QY and stability [12]. Such core–shell particles display efficient luminescence along with stability superior to single phase nanopaticles and organic dyes, and are of great interest to researchers in the field of biological imaging and light-emitting devices [13,14].

Several wide band-gap semiconductors including ZnS [15,16], CdS [11,12,17,18], and ZnSe [19,20] have been employed as the shell material. It is well-known that ZnS is a nontoxic and chemically stable wide band-gap (3.8 eV for the bulk material) semiconductor, so that the corresponding ZnS shell should provide the perfect passivation of CdTe core. However, it has been confirmed that the large mismatch between CdTe and ZnS lattice parameters can induce the strain at the interface between the core and shell, and consequentially form the misfit dislocations to relax the strain in nanocrystal structure when the thickness of ZnS shell exceeds 2 monolayers. The defects of the ZnS thick shell are expected to have negative influence on both PL efficiency and stability of CdSe/ZnS QDs. It is worth mentioning that the particle size distribution becomes broader substantially with the increase of the thickness of ZnS shel.

Due to the bandgaps of CdS and CdTe nanocrystals, 2.42 and 1.45 eV respectively, the lattice mismatch between the core and shell materials is relatively small in the case of CdTe/CdS QDs [21]. Wang and co-workers reported that the PL QY of 1-thioglycerol

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capped CdTe/CdS QDs synthesized by the ultrasonic irradiation method can reach up to 20% [22]. Peng's group achieved the thioglycolic acid (TGA) capped CdTe/CdS QDs with enhanced photostability [23]. Nowadays, over coating CdS layer outside of the CdTe core has been the primary way to enhance the PL QY and photostability of QDs. Various core–shell materials such as CdSe/ZnSe, CdSe/CdS, and CdSe/ZnS [15,24] QDs have been studied in recent years. Additionally, Gao's group introduced the preparation of green-emitting CdTe QDs with CdS-like shell by illuminating the nitrogen (N_2) saturated sample solutions with low-pressure mercury-rare-gas discharge lamps [25]. In fact, the band gap of CdS is not wide enough to produce the necessary potential barrier to block both the electron and hole inside CdTe core. The CdS shell can be excited by UV light, which is broadly used in biological tagging applications. However, highly luminescent CdTe QDs with multiple shells such as CdS and ZnS is still desired for bioapplications.

The direct excitation of the QDs shell usually brings in the rapid photooxidation that makes CdTe/CdS QDs unsuitable for many biolabeling applications. In order to improve the PL QY and stability of luminescent QDs, the simple approach based on modifying the energy band-gap and lattice spacing inside a heterogeneous QD is proposed in the present work. CdS and ZnS double shell (or core/shell/shell) structure allows a stepwise change of lattice spacing from the emitting CdTe core to the protecting ZnS shell and a considerable reduction of the strain on the QDs. CdS can be employed as the middle shell material because the band gap and the lattice spacing of CdS lie at an intermediate-level between those of CdTe and ZnS. CdTe/CdS and CdTe/ZnS core/shell QDs were also prepared to investigate the effect of shells on the PL properties of CdTe cores.

2. Experimental

2.1. Chemicals

All the starting chemicals mentioned in the current investigation were used directly without additional purification. TGA (99%), Tellurium powder (Te) (99%), $CdCl_2 \cdot 2.5H_2O$ (98%), $Zn(OAc)_2$ (analytical grade) and $NaBH_4$ (96%) were purchased from Shanghai Chemical Reagent Company. Sodium sulfide ($Na_2S \cdot 9H_2O$) and rhodamine 6G were supplied by Tianjin Damao Chemical Reagent Institute and Aldrich, respectively. The pure water was obtained from a Milli-Q synthesis system (resistivity of 18.2 MΩ cm).

2.2. Synthesis of TGA-capped CdTe QDs

Water-soluble TGA-capped CdTe QDs were prepared according to the procedure reported in literature [26]. Briefly, upon a molar ratio of 5:1 for $NaHB_4$:Te, $NaBH_4$ was first mixed with Te in water to obtain a sodium hydrogen telluride (NaHTe) solution at 60 °C. For the preparation of TGA-capped CdTe cores, $CdCl_2 \cdot 2.5H_2O$ (0.4 mmol) and TGA (0.6 mmol) were dissolved in 25 mL of water to get a precursor solution followed by adjusting the pH value to 11 with a NaOH solution of 1 M. After degassing by N_2 for 30 min, the fresh deoxygenated NaHTe solution was added to the above precursor solution under continuous stirring. The typical molar ratio of Cd:Te:TGA was 1:0.5:1.5. The mixture was subsequently refluxed for different reaction times under 100 °C to synthesize the size-controlled TGA-capped CdTe QDs.

2.3. Synthesis of TGA-stabilized CdTe/CdS QDs

A typical synthesis of CdTe/CdS core/shell QDs can be described as follows. 8 mL as-prepared CdTe colloidal solution was precipitated by 8 mL of 2-propanol mixed with ethanol and then redispersed in 20 mL of H_2O mixed with 0.4 mmol of $CdCl_2 \cdot 2.5H_2O$ and 0.6 mmol of TGA to obtain solution A (pH = 11). 0.4 mmol of $Na_2S \cdot 9H_2O$ was dissolved in 67 mL of H_2O to obtain solution B (0.006 M). Both solutions A and B were degased by N_2 for 1 h. After solution A heating up to 100 °C, an injection rate of 1 mL/min was adopted to add certain amount of solution B into A under continuous stirring. The mixture was subsequently refluxed for 30 min under 100 °C to synthesize TGA-capped CdTe/CdS QDs.

2.4. Synthesis of TGA-stabilized CdTe/CdS/ZnS QDs

A ZnS shell was deposited on CdTe/CdS core/shell QDs by the following process. 8 mL as-prepared CdTe/CdS colloidal solution was precipitated by 8 mL of 2-propanol mixed with ethanol and then redispersed in 15 mL of H_2O mixed with 0.4 mmol of $Zn(OAc)_2$ and 0.6 mmol of TGA to get solution C (pH ~ 11). Both solutions C and B were degassed by N_2 for 1 h. Solution C having been heat-treated to 80 °C, an injection rate of 1 mL/min was adopted to add certain amount of solution B into C under continuous stirring to control the thickness of ZnS shell. The mixture was subsequently refluxed for 30 min under 80 °C to synthesize TGA-capped CdTe/CdS/ZnS QDs.

2.5. Synthesis of TGA-stabilized CdTe/ZnS QDs

The synthesis of CdTe/ZnS core/shell QDs is similar with CdTe/CdS core–shell QDs. 8 mL as-prepared CdTe colloidal solution was precipitated by 8 mL of 2-propanol mixed with ethanol and then redispersed in 20 mL of H_2O mixed with 0.4 mmol of $Zn(OAc)_2$ and 0.6 mmol of TGA to obtain solution D (pH = 11). Both solutions D and B were degassed by N_2 for 1 h. After solution D was heat-treated to 80 °C, an injection rate of 1 mL/min was also utilized to add certain amount of solution B into D under stirring to control the thickness of ZnS shell. The mixture was subsequently refluxed for 30 min under 80 °C to synthesize TGA-capped CdTe/ZnS QDs.

2.6. Characterization

UV–vis absorption and PL spectra were measured at room temperature with Hitachi U-4100 and F-4600 spectrophotometers, respectively. The PL QY of samples was estimated in

Table 1
PL properties of TGA-capped CdTe, CdTe/CdS, CdTe/ZnS, CdTe/CdS/ZnS QDs.

Sample	QD kinds	PL peak wavelength (nm)	First excitonic absorption peak (nm)	FWHM (nm)	PLQY (%)
Core 1	CdTe	537	498	37.3	37.8
1	CdTe/CdS	540	500	41.4	63.6
2	CdTe/CdS/ZnS	556	521	42.8	63.6
Core 2	CdTe	563	526	44.8	56.7
3	CdTe/CdS	567	533	45.6	71.1
4	CdTe/CdS/ZnS	579	548	43.2	79.8
Core 3	CdTe	569	533	48.1	62.6
5	CdTe/CdS	581	548	46.2	72.3
6	CdTe/CdS/ZnS	596	566	44.1	75.6
Core 4	CdTe	547	506	39.9	57.1
7	CdTe/ZnS	550	512	41.4	37.3
8	CdTe/ZnS	560	523	46.7	36.6
Core 5	CdTe	571	534	44.4	62.4
9	CdTe/ZnS	572	535	44.6	47.1
10	CdTe/ZnS	579	543	47.4	41.6
Core 6	CdTe	581	546	50.2	77.6
11	CdTe/ZnS	604	568	48.2	41.6
12	CdTe/ZnS	623	573	50.1	21.2