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Letter

Synthesis and upconversion luminescent properties of water-soluble CdTe quantum dots

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ABSTRACT

Water-soluble CdTe quantum dots (QDs) with green and yellow emission are prepared in aqueous solution using thioglycolic acid (TGA) as stabilizing agent. The as-obtained CdTe QDs are characterized by absorption and photoluminescence spectra. Strong emission is observed when the CdTe QDs are excited by an 800 nm femtosecond laser. The ln–ln relations between the integral intensity of CdTe QDs and the excitation power are investigated, and the results indicate that the upconversion luminescence is a two-photon assisted process via a virtual energy state.

1. Introduction

Water-soluble semiconductor quantum dots (QDs) with high photoluminescence quantum yield have been extensively explored as biomedical labels or imaging agents [1–7]. When the size of the semiconductor particle is small than its exciton Bohr radius, its energy gap can become larger than that of the bulk material. Due to this size-dependent property, the spectral properties of the semiconductor QDs can be easily tuned by controlling the particle size, shape or surface structure [1]. Among the common semiconductor QDs, II–VI semiconductor QDs (ZnS, ZnO, CdS, CdSe, CdTe, etc.) with excellent optical properties is playing a critical role in this field [6–10]. Among them, CdTe QD has been extensively researched in the past decades [9,11]. Bulk CdTe is a direct band gap semiconductor material with a band gap of 1.5 eV and an exciton Bohr radius of 7.3 nm [9–11]. Relatively larger Bohr exciton radius provides it with stronger quantum confinement effect compared with other II–VI semiconductor QDs, such as CdS and CdSe[12]. On the other hand, fluorescent technology is mostly used in biomedical labeling or imaging agents [1–5,13]. In this process a blue light beam is used to excite the semiconductor QDs in cells [13]. But this needs an external visible illumination sources to fluoresce, which results a strong autofluorescence background [13,14]. Compared with fluorescent technique, background luminescence from cells can be greatly reduced in upconversion luminescence (UCL) process [13,15]. So UCL has potential application in biomedical labeling.

In this paper, we synthesized water-soluble CdTe QDs and investigated the UCL of CdTe QDs under the excitation of an 800 nm femtosecond laser. The UCL process is proved to be a two-photon assisted process. The strong UCL of CdTe QDs shows the potential application in biomedical labeling.

2. Experimental

2.1. Synthesis of water-soluble CdTe QDs

Tellurium power (300 mesh, 99%), $CdCO_3$ (99%), $NaBH_4$ (96%), $HClO_4$ (99%), Thioglycolic acid (TGA) (Fluka, 98%), Dodecanethiol (Alfa, 98%) and acetone (99.5%) are used to synthesize CdTe QDs and they are all commercially available products. $Cd(ClO_4)_2{\cdot}6H_2O$ is prepared in our lab. Ultrapure water used in the experiment is purified with Mill-Q (electric resistivity 18.2 MΩ cm^{-1}) water purification system.

The synthesis of water-soluble CdTe QDs includes multi-step process consisting of (1) synthesis of NaHTe; (2) synthesis of CdTe QDs; (3) purification of CdTe QDs [1–5]. The synthesis of NaHTe is described below. 0.1028 g $NaBH_4$ and 0.1095 g Te powder are transferred to a small flask, then 5 mL ultrapure water(18.2MΩ cm^{-1}) is added. The reacting system is cooled by ice under Ar atmosphere. During the reaction, a small outlet connected to the flask is kept open to discharge the pressure from

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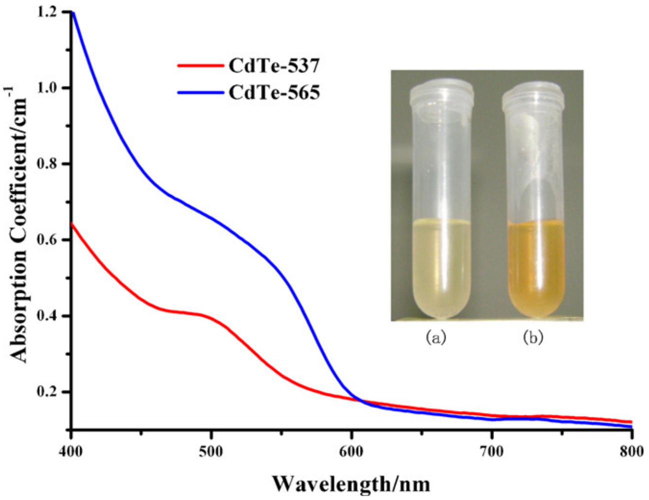

Fig. 1. Absorption spectra of CdTe-537 and CdTe-567 aqueous solution. The insert photographs of (a) and (b) show CdTe-537 and CdTe-565 aqueous solutions under the radiation of room light.

Ar and the resulting hydrogen. After approximately 8 h, the black tellurium powder disappears and sodium tetraborate white precipitation appears on the bottom of the flask instead. The resulting NaHTe in clear superstratum is placed for 0.5 h, which is used to synthesize CdTe QDs.

In a typical synthesis, 0.0655 g $Cd(ClO_4)_2{\cdot}6H_2O$ is dissolved in 100 mL water, then 30 μL TGA is added under stirring, followed by adjusting the pH to 11 by dropwise addition of 1 M NaOH solution. The solution is placed in a three-necked flask of 250 mL and deaerated by Ar bubbling for about 30 min. 0.3 mL NaHTe is added under stirring. The resulting mixture is then subjected to a reflux in an oil-bath that controlled the growth of the CdTe QDs. Finally, the reacting system is continually stirred overnight.

The CdTe QDs are precipitated by ethanol addition, washed with absolute ethanol for three times and then redissolved into pure water at pH 11 for fluorescence determination. Two kinds of water-soluble CdTe QDs with emission peaks at 537 nm and 565 nm are obtained, and they are labeled CdTe-537 and CdTe-565, respectively.

2.2. *Characterization*

Absorption spectra are recorded with a JASCO V-570 UV/Vis/NIR spectrophotometer. Excitation and emission spectra of the samples are recorded on a JASCO FP-6500 spectrofluorometer equipped with a xenon lamp source. A regenerative amplified Ti: sapphire laser with an operating wavelength of 800 nm, a repetition rate of 1 kHz, and pulse duration of 120 fs, is used as an infrared femtosecond laser excitation source. The pulse energy stability is about 10%. An optical lens with a focal length 100 mm is used to focus the laser beam and the samples are placed about 10 mm from the focal point of the laser beam. The upconversion emission spectra of CdTe are recorded on a Zolix SBP-300 spectrofluorometer with errors of about 5%. All the measurements are carried out at room temperature.

3. Results and discussion

Fig. 1 shows the absorption spectra of CdTe-537 and CdTe-565. The average sizes of CdTe QDs can be estimated from the first absorption peak by using the formula: $D = (9.8127\times10^{-7})\lambda^4 - (1.7147\times10^{-3})\lambda^2 + 1.0064\lambda - 194.84$, where D (nm) is the size of the QD, λ (nm) is the wavelength of the absorption peak [16]. The two QDs aqueous solutions have their first absorption peaks at 505 nm and 545 nm, respectively, as shown in Fig. 1. The sizes of the CdTe QDs are about 2.8 nm and 3.2 nm, respectively. The inserts (a) and (b) are photographs of CdTe-537 and CdTe-565 under the irradiation of room light. We can see that the quantum dots have been solved in the water absolutely, and no precipitation is observed after the solution is stayed for several days.

Femtosecond laser is a powerful tool to induce many nonlinear phenomenons. When we focus the femtosecond laser beam (800 nm) to the solution, bright visible emission is observed. So upconversion luminescence (UCL) occurs when the 800 nm femtosecond laser is used as excitation source. Generally, the CdTe QD is excited by the ultraviolet or near-ultraviolet light, which can also make the CdTe QD emit visible light. The emission spectra of CdTe QDs excited by an 800 nm femtosecond laser and 400 nm monochromatic light from a xenon lamp are shown in Figs. 2 and 3. The spectral profiles of CdTe QDs excited by 400 nm monochromatic light and 800 nm femtosecond laser are almost the same. The full widths at half-maximum (FWHM) of the photoluminescence (PL) spectra of the different sized CdTe QDs used for the measurements are 62 nm and 60 nm, respectively. The inserts are photographs of CdTe QDs excited by 405 nm diode laser and 800 nm femtosecond laser. Figs. 2(a) and 3(a) show the luminescence of CdTe-537 and CdTe-565 excited by 405 nm laser diode. Figs. 2(b) and 3(b) depict the upconversion luminescence of CdTe-537 and CdTe-565 by 800 nm femtosecond laser. We can see that the colors of the CdTe QDs excited by 405 nm laser diode and 800 nm femtosecond laser are the same. This implies that the luminescence of CdTe QDs excited by 400 nm monochromatic light and 800 nm femtosecond laser maybe come from the same origin.

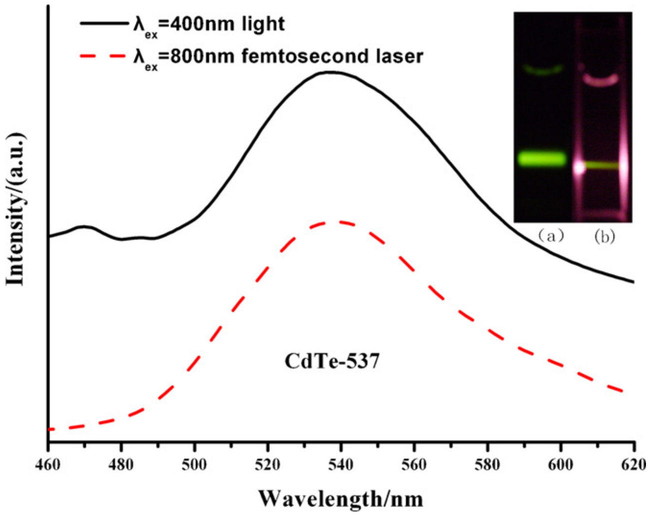

Fig. 2. Emission spectra of CdTe-537 aqueous solutions excited by 400 nm monochromatic light and 800 nm femtosecond laser. The inserts are photographs of CdTe-537 excited by 405 nm laser diode and 800 nm femtosecond laser.

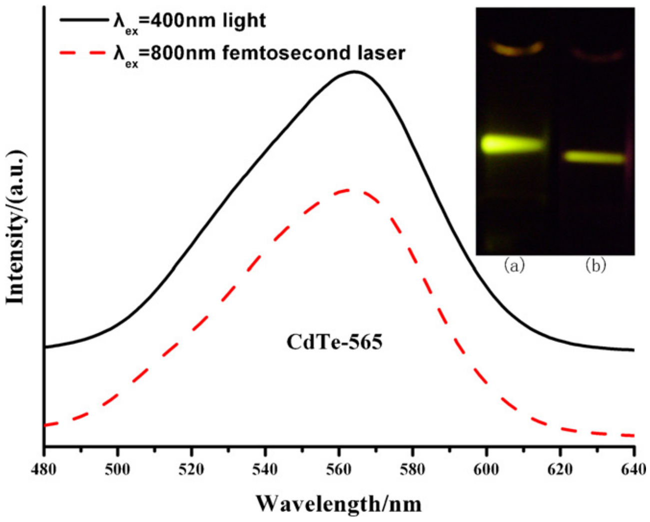

Fig. 3. Emission spectra of CdTe-565 aqueous solutions excited by 400 nm monochromatic light and an 800 nm femtosecond laser. The inserts are photographs of CdTe-565 excited by a 405 nm laser diode and an 800 nm femtosecond laser.

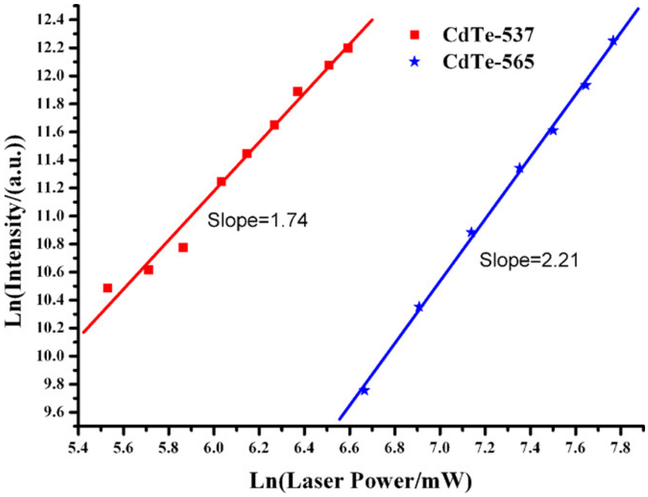

Fig. 4. ln–ln plots of integral intensity from upconversion luminescence of CdTe QDs versus pump power of the femtosecond laser.

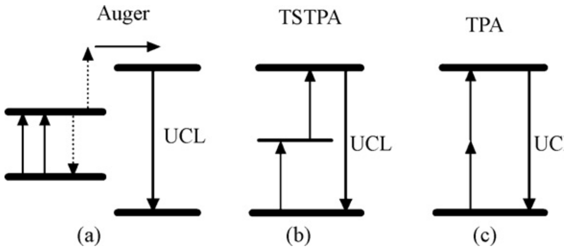

Fig. 5. Possible upconversion luminescence mechanism in semiconductor quantum dots. (a)–(c) represent the Auger process, two-step two-photon absorption process (TSTPA) and two-photon absorption process through a virtual intermediate state (TPA), respectively.

The upconversion intensity and pump power usually have the following relationship [15,17–20]:

$$I \propto P^n,$$

where I is the integral intensity of upconversion emission from CdTe QDs, P is the pump power of the femtosecond laser and n corresponds the number of photons involved in the multiphoton absorption process [15]. The ln–ln plots of integrated intensity of CdTe QDs versus the excitation power of the 800 nm femtosecond laser are shown in Fig. 4. The slopes of the ln–ln plots of CdTe-537 and CdTe-565 are 1.74 and 2.21, respectively. This indicates that the upconversion luminescence of CdTe by femtosecond laser is a two-photon assisted process.

Auger recombination and two-photon absorption have been proposed to explain the UCL of semiconductor quantum dots [15]. In Auger process, the energy transfers from an excited electron–hole pair upon recombination to another electron or hole, creating a high excited carrier. Then the carriers can recombine at a higher energy [21]. The Auger recombination process is shown in Fig. 5(a) [15]. Auger process occurs frequently in heterostructures, and it requires the incident photon energy exceeds the band gap to produce initial electron–hole pairs. In CdTe QDs, the incident photons cannot excite electron–hole pairs or other carriers [15]. So it cannot be used as the possible mechanism to explain the upconversion luminescence of CdTe QDs here. There are two ways to induce two-photon absorption: process through an intermediate state within the band gap, which can be termed two-step two-photon absorption (TSTPA) as shown in Fig. 5(b) or process through a virtual intermediate state (TPA) as shown in Fig. 5(c) [15]. The upconversion luminescence from CdTe QDs were also measured under the excitation of both CW laser diode ($\lambda_{ex} = 808$ nm) and femtosecond laser ($\lambda_{ex} = 800$ nm). No upconversion luminescence was observed under the excitation of a focused CW laser diode. At the same time, obvious upconversion luminescence (UCL) can be observed when exciting the CdTe QDs with femtosecond laser. So we can conclude that the mechanism of upconversion luminescence of CdTe QDs is through a two-photon excitation via a virtual intermediate state.

4. Conclusions

Water-soluble CdTe QDs with strong luminescence were synthesized by hydrothermal method. The upconversion luminescence (UCL) of CdTe QDs under the excitation by an 800 nm femtosecond laser was investigated. And the mechanism of UCL proved to be a two-photon assisted process via a virtual state. Thus, CdTe QDs appear to be potentially useful as biological labels with much weaker autoluminescence background.

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