Tunable Photoluminescence of CdTe Nanocrystals over Wide Spectral Range via Microwave-assisted Surface Modification

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An easy and fast microwave-assisted method of tuning the photoluminescence properties of CdTe nanocrystals in aqueous phase is presented. The photoluminescence could be tuned covering almost the whole visual spectral range (537-680 nm), and even partially extending to the near-infrared spectral range. The effect is probably related to the formation of core/shell structure and complex nano-assemblies. These results provide a promising means of tuning the photoluminescence of CdTe nanocrystals, leading to potential applications in biomedical labeling, solar cells, lasers, and other fields.

Key words: Microwave-assisted synthesis, CdTe, Nanocrystal, Photoluminescence

I. INTRODUCTION

Semiconductor nanocrystals (NCs) show unique size-dependent optical properties and are currently of utmost importance both for basic research in physics, chemistry, biology, and colloidal science [1-4] and for application in biomedical labeling, light emitting diodes (LEDs), solar cells, lasers, and other fields [5-19]. CdTe nanostructures are among the best-studied semiconductor quantum systems. CdTe nanoparticles (NPs) synthesized in organic systems are passivated by long chain organic surfactants such as trioctylphosphine oxide (TOPO) [20] and alkylamines. Nanocrystals soluble in an aqueous medium have been investigated for their potential applications, because of their many advantages such as compatibility with biomaterials and low toxicity [21]. Recently, researchers have studied numerous methods to synthesize water-soluble semiconductor nanoparticles, which can be obtained mainly by two different methods. The first way is to replace the surface-capping ligands on the particles prepared by the TOPO (trioctylphosphine oxide) method with water-soluble thiols or a silica shell [22-25]. But this method brings about another problem. After the substitution of the surface-capping molecules by hydrophilic molecules, the nanocrystals photoluminescence decreases markedly [26,27]. Another choice is to directly synthesize semiconductor nanoparticles in aqueous solution using water-soluble stabilizers such as thiols. One of the most successful cases was the TGA (thioglycolic acid)-capped CdTe nanocrystals prepared through this synthesis route.

The achievement of photoluminescence (PL) spectra covering the largest possible range is one of the key aims for chemically prepared nanocrystals as an emitting material. It is well known that the PL peak of CdTe nanocrystals shifts to longer wavelength with increasing particle size by prolonging the refluxing time. It had been demonstrated that it took 2-3 days to shift the PL maximum to 650 nm in the presence of TGA [28]. Beside the time-consuming manipulation, it should be mentioned that distinct asymmetric PL spectra often occurred during these excessively long refluxing processes because of Ostwald Ripening. Other approaches to tune the optical properties of the nanocrystals were through surface modification, for example, creating inorganic shells or compensating for surface defects with organic molecules. However, these processes generally controlled the optical properties in a very narrow spectral range [29].

Here, a simple and convenient approach to tuning the PL of CdTe nanocrystals over a wide spectral range using microwave-assisted surface modification is presented. The approach is dominated by the interaction of the dipole moment of the molecules with the high frequency electromagnetic radiation [30]. The surface modification makes it possible for the further reconstruction of nanostructures. PL, UV-Vis, XPS, and TEM were used to investigate the changes of the spectra properties and nanostructures. The results showed that the method provided a useful means to tune the PL of the CdTe nanocrystals while yielding a stable product with more complex nanostructures.

II. EXPERIMENTS

A. Preparation of CdTe nanocrystals

Thioglycolic acid (TGA, 99%), CdCl₂, NaBH₄ (96%), and tellurium powder (99.999%, about 0.07 mm) were obtained from Sigma, Inc. Ultrapure water with
18.2 MΩ/cm (Millipore Simplicity) was used in all syntheses.

The CdTe nanocrystals were prepared following the method described in the authors’ previous papers with some modification [31,32]. In brief, sodium borohydride (38.4 mg) and tellurium powder (25.6 mg) were mixed in a three neck flask under N₂ protection. Then a little water (about 1 mL) was injected into the flask, which was heated slightly under a nitrogen stream, to form NaHTe. Then the N₂-saturated cadmium chloride solution with TGA as capping ligand, which was prepared by mixing a solution of CdCl₂ (4 mL 0.1 mol/L stock solution) and stabilizer (TGA) solution and adjusted to pH=11 with 1 mol/L NaOH, was injected into the NaHTe solution. The concentration of Cd²⁺ was 2 mmol/L in the solution, and the typical molar ratio of Cd²⁺:Te²⁻:TGA was 1:0.5:2.5. To achieve CdTe nanocrystals with desired size, the reaction proceeded in a microwave oven (2.45 GHz, 650 W) in air with an output power of 50% and heat time of 10-60 min, depending on the diameter of CdTe NPs needed. Aliquots of the reaction solution were taken out at regular intervals for further fluorescence spectra characterization.

B. Surface modification of CdTe nanocrystals

5 mL Na₂S solutions, prepared by dissolving different amount Na₂S in ultrapure water with various concentration (the final concentrations of Na₂S were 0.000, 0.133, 0.266, 0.333, 0.400, 0.533, and 0.667 mmol/L respectively), were mixed with 5 mL as-prepared CdTe nanocrystals while keeping the concentration of the CdTe nanocrystals as a constant. Meanwhile, in order to exclude the effect of pH, 1 mol/L NaOH solution was used to adjust the mixed solution to pH=11, the same as the control sample. These samples were marked as sample a to sample g, respectively. All these mixed solutions were further heated for 10 s in the microwave oven with output power set at 50%. For the purposes of comparison, the CdTe nanocrystals without Na₂S added were used as a control (sample a). All samples were characterized with no further purification.

Different heating methods were also used to make known the effect and advantage of microwave irradiation in the study. As the CdTe nanocrystals and Na₂S were mixed together in a flask following the steps mentioned above, the flask was heated in a heating jacket for half an hour or stirred under ambient temperature overnight.

C. Characterization

The PL excitation and emission spectra data were monitored by a PE steady-state fluorescence spectrometer (LS-550). Room-temperature UV-Vis absorption spectra were achieved with a Model UV-2100s spectrophotometer (Shimadzu, Japan). The compositions of the nanoparticles were determined by X-ray photoelectron spectroscopy (XPS). All spectra reported were recorded on a PHI-5300/ESCA spectrometer employing a monochromatic Al Kα X-ray source. The peak position was internally referenced to the C1s peak at 285.0 eV. A transmission electron micrograph (TEM) was recorded by a Hitachi H800 electron microscope (Japan) operating at 200 kV.

III. RESULTS AND DISCUSSION

The preparation of CdTe nanocrystals was carried out by a microwave assisted synthesis method. As various amounts of Na₂S solutions were added to the as-prepared CdTe nanocrystals followed by 10 s microwave heating, a series of samples with different maximum emission wavelength were obtained, as shown in Fig.1(a). Without the addition of Na₂S, the PL spectrum of the control sample had a small red-shift about 5 nm (from 532 nm to 537 nm), which was mostly caused by the continuative crystal growth stage. With increas...
ing amounts of Na$_2$S injected, the PL emission of the sample gradually shifted to the longer wavelength region. All the samples had a good fluorescence intensity, and the emission could be observed by naked eye in the daylight. (The inset of Fig.1(a) shows the optical graphs of three representative samples, which emitted green, yellow, and red under 365 nm uvio lamp.) In summary, injecting more Na$_2$S solution leads to more red-shifting of the PL spectra. The maximum peak of sample g even reached 680 nm, while the control sample had a characteristic band-edge PL spectrum at 537 nm. Figure 1(b) shows the UV-Vis absorption spectra of these samples treated with different amounts of Na$_2$S, and all absorption spectra shifted to lower energy. The spectra are very consistent with the PL spectra shown in Fig.1(a). When low concentration of Na$_2$S was added, the absorption spectrum roughly maintained its overall shape, with a slight broadening feature. While high concentration of Na$_2$S was added (e.g., samples f and g), the first electronic transition of the CdTe nanocrystals became poorly-resolved. Although some of the samples showed a characteristic absorption of CdS clusters below 500 nm, the possibility to form independent CdS nanocrystals through the microwave modification reaction between the sulfide ions and cadmium ions could be excluded, because no deep trap luminescence and characteristic luminescence of independent CdS nanocrystals were detected in this study. All the above results imply the formation of CdTe@CdS core/shell structure [33-35].

XPS technique was used to examine the changes of the surface of TGA-capped CdTe nanocrystals, shown in Fig.2. All measured samples were purified by 2-propanol precipitation procedure before measurement. The characteristic Cd 3d$_{5/2}$ peak of all the samples was at 405.3 eV and Te 3d$_{5/2}$ peak was at 572.2 eV, both identical to the peaks for the CdTe nanocrystals [36]. In contrast, the binding energy (162.7 eV) of S2p from CdTe NCs, which demonstrates the existence of chemical bonds (Cd-SR) between thiols and cadmium ions on the surface, shifted to lower energy (162.1 eV), indicating the coordination situation of S from modified NCs was different from that of Cd-SR. As the binding energy (162.1 eV) of S2p was much closer to the binding energy of CdS, the new S2p could be attributed to the S from CdS. All these results can therefore further confirm the above proposed core-shell structure in which CdS acted as a shell encapsulating the CdTe core [37,38].

The difference of the structures was further investigated using TEM. Some representative TEM images are shown in Fig.3. The original CdTe nanocrystals were nearly monodispersed and separated particles (Fig.3(a)). When low concentration of Na$_2$S was added, they spontaneously organized into nanowires (sample b), as shown in Fig.3(b). And with the higher concentration of Na$_2$S added, such as sample f, they tended to organize into larger and more complex aggregation (shown in Fig.3(c)).

![TEM images](image)

**FIG. 3 TEM images of original CdTe nanocrystals (a), samples b (b) and f (c), showing that they tended to spontaneously organize into nanowires, and larger and more complex aggregation after surface modification.**

Although the exact mechanism behind the PL spectra and nanostructure is not yet well-known, we here make some speculations based on previous knowledge and present experiments (shown in Fig.4). When Na$_2$S was added, sulfide ions could react with cadmium ions of CdTe nanocrystals so that the complex of TGA-Cd$_2$S$_y$ would form on the surface of CdTe nanocrystals, along with many surface defects at the very beginning [39]. For example, the surface was compensated by organic ligands became disordered, and many Cd, Te, and S sites with hanging bonds came into being on the surface of the CdTe nanocrystals. This situation would cause two aspects of influence. On one hand, it is well-known that the PL spectra are highly sensitive to the change of surface structure (PL quenched immediately as the Na$_2$S was added, shown in Supporting Information), because these surface defects would provide many non-radiative relaxation pathways to make the PL of CdTe nanocrystals quench nearly completely. On the other hand, these surface defects decreased the mutual electrostatic repulsion of the nanoparticles from the TGA.
IV. CONCLUSION

In summary, microwave-assisted surface modification could significantly affect the PL properties of CdTe nanocrystals, covering almost the whole visual spectral range. The results here demonstrated that the large change of the PL should be attributed to the change of their surface properties and nanostructures. It provides a new strategy for the control of the optical properties over a wide spectral range based on the microwave-assisted surface modification and the intrinsic physical properties of CdTe nanocrystals. The technique may have some implications for the tailored synthesis of nanostructures with tunable properties, along with potential applications in the biological, light emitting diodes, solar cell, and other fields.

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