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Synthesis and time-resolved photoluminescence spectroscopy of capped CdS nanocrystals

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Abstract

Here, we report the synthesis of colloidal CdS nanoparticles by capping with starch, phenol and pyridine. We also study the photophysical properties of CdS nanoparticles by steady state and time-resolved photoluminescence spectroscopy. The experimental results show that the relaxation of the excited state of CdS nanoparticles is composed of two different components. Our analysis suggests that the fast and slow components decay times of these capped CdS nanocrystals are due to trapping of carriers in surface state and e–h radiative recombination processes, respectively.

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1. Introduction

Semiconductor nanocrystals have attracted much attention in both fundamental research and technological applications, owing to their unique size dependent optical and electronic properties [1,2]. The size dependence of the bandgap is the most identified aspect of quantum confinement in semiconductors; the bandgap increases as the size of the particles decreases. When the dimensions of nanocrystalline particles approach the exciton Bohr radius, a blue shift in energy is observed due to the quantum confinement phenomenon. The effective mass model is commonly used to study the size dependence optical properties of quantum dots (QD) system [3]. Due to high surface area of nanoparticles, surface defects play an important role in their quantum efficiency. The tunability of the properties of nanoparticles by controlling their size and shape may provide an advantage in formulating new composite materials with optimized properties for various applications [4–10]. To date, there has been much progress in the fabrication of quantum dots for devices but the relaxation dynamics of the electronic states in quantum dots remain an open fundamental debate. Carrier dynamics in nanocrystals are significantly different from those in bulk materials because of large energy level spacing and an enhanced surface-to-volume ratio. A variety of radiative and nonradiative mechanisms occur during the relaxation process. The most important processes completing with radiative recombination are carrier trapping at surface/interface states and Auger recombination [11–14]. A variety of relaxation processes may occur on a wide range of time scales. Electron and hole trapping were found to occur on the 300 and 30 ps time scales, respectively [15,16]. Electron–phonon coupling is another dominant mechanism for relaxation of electronic states in semiconductors. In quantum dots, the electronic energy levels are discrete with spacing far exceeding the phonon energies and the slow relaxation by phonons is called the "phonon bottleneck" effect [17,18]. However, applications would be restricted due to different nonradiative relaxations pathways. Due to a large surface-to-volume ratio, electron and hole wave functions in nanocrystals are strongly affected by nanocrystal surface

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properties. One of the most important nonradiative pathways is surface related defects. Uncoordinated surface atoms give rise to trap states that lie within the band gap and reduce the quantum yield by providing alternative pathways of excited-state relaxation. The interaction of the CdS nanocrystals with its environment or capping agents plays a crucial role in determining its luminescent properties. To overcome the above-mentioned difficulties, organic and inorganic capping agents are used to passivate the free quantum dots. Polymers, amines, TOPO, thiols and silica are used during the wet-chemical synthesis for capping the surface of the particles to prevent nonradiative recombination at surface sites and also control of growth kinetics to prevent the aggregation via steric hindrance [19–25]. It is also believed that the capping agent on the surface of the particles plays an important role on transfer of the photogenerated electrons and holes to capping agents [26,27]. Wuister and Meijerink [28] reported detail photophysical properties of silica capped CdS nanoparticles and they reported that both electron and hole trapped were involved in the recombination process. Recently, Creti and coworkers [29] reported the role of surface and interface defects on the photophysical properties of core and core/shell CdSe nanocrystals by ultrafast spectroscopy. The main purpose of this work is to understand how the photophysical properties vary with changing the capping agents. A very little attention has been paid on the role of capping agent on the photophysical properties of CdS nanocrystals by steady state and time-resolved photoluminescence (PL) spectroscopy. Here, we report the synthesis of CdS nanocrystals capped with starch, phenol and pyridine and study their photophysical properties by steady state and time-resolved spectroscopy.

2. Experimental details

2.1. Synthesis of capped CdS nanoparticles

Cadmium acetate dihydrate (Loba Chemie), thioacetamide (Spectrochem), glacial acetic acid (Merck), 2-methoxy ethanol (Merck), starch (Merck), phenol (Merck), pyridine (Merck), *N*,*N*-dimethylformamide (DMF) (Merck) were used without further purification in the present study.

Starch capped CdS: 0.1 gm of starch was dissolved in 5 ml of hot water to get a clear solution. Then 0.1 mM (0.0266 g) $Cd(OAc)_2 \cdot 2H_2O$ dissolving in 20 ml of glacial acetic acid was added into the starch solution and stirred for 5 min at room temperature. After this 0.1 mM (0.0075 g) thioacetamide in 20 ml 2-methoxy ethanol was added to the above mixture and then whole thing was stirred in an oil bath at 85–90 °C for 1 h. The resulting lemon yellow colored solid products were centrifuged, washed and finally disperse in water for optical study.

Phenol capped CdS: 5 ml phenol was added to the solution of 0.1 mM (0.0266 g) $Cd(OAc)_2 \cdot 2H_2O$ in 20 ml DMF and stirred for 10 min. Then 0.1 mM (0.0075 g) thioacetamide solution in 20 ml DMF was added dropwise into the above mixture under stirring condition. After complete addition, the reaction was carried out at room temperature for 1 h. The resulting lemon yellow colored solution was obtained.

Pyridine capped CdS: In a typical synthetic procedure, a 10 ml 0.1 mM aqueous solution of $Cd(OAc)_2 \cdot 2H_2O$ was prepared by dissolving the salt in de-ionized water. Then this aqueous solution was slowly added to the supporting solvent consisting of 5% by volume Span 80 in cyclohexane (solution:cyclohexane was 1:5, v/v) to get emulsified droplets under stirring condition. After 5 min stirring, a 10 ml 0.1 mM aqueous solution of thioacetamide was added slowly and stirred the whole reaction mixture at room temperature and finally placed in an oil bath at 85–90 °C for another 30 min. The resulting lemon yellow colored solution was cooled to room temperature and 5 ml of pyridine was added into it. Then CdS containing liquid layer was separated out and used for further characterization.

2.2. Characterization of the capped CdS nanoparticles

Room temperature optical absorption spectra were obtained with an UV–vis spectrophotometer (Model: Cary 50, Varian) in the range 200–550 nm. The emission spectra of all samples were recorded in a Fluoro Max-P (HORIBA JOBIN YVON) Luminescence Spectrometer. The transmission electron microscopy (TEM) images were taken using a JEOL-TEM-2010 transmission electron microscope operating voltage at 200 kV. Samples for TEM were prepared by making a clear dispersion of the samples in acetone and placing a drop of the solution on a carbon coated copper grid. For the time-correlated single-photon counting (TCSPC) measurements, the samples were excited at 373 nm using a picosecond diode laser (IBH Nanoled-07) at a repetition rate 900 kHz. The data is collected with a PCA3 card (Oxford) as a multi-channel analyzer. All luminescence decay curves were measured at the maximum of the emission peak. The following expression was used to analyze the experimental time-resolved luminescence decays, $P(t)$:

$$P(t) = b + \sum_{i}^{n} \alpha_i \exp\left(\frac{-t}{\tau_i}\right) \tag{1}$$

Here, n is the number of discrete emissive species, b is a baseline correction ("dc" offset), and α_i and τ_i are the pre-exponential factors and excited-state luminescence decay times associated with the ith component, respectively.

3. Results and discussion

Fig. 1a shows the TEM images of CdS nanocrystals prepared in presence of starch. This figure clearly shows the aggregated CdS nanocrystals. Fig. 1b shows the HRTEM of single particle of CdS and the measured interlayer spacing is found to be 3.38 Å, which corresponds to the

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