Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Photochemistry and Photobiology A: Chemistry 178 (2006) 156–161
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Luminescent properties of CdS nanoclusters dispersed in solution—Effects of size and surface termination

Masayuki Okamura [a], Kojiro Ebina [a], Seiji Akimoto [b], Iwao Yamazaki [b], Kohei Uosaki [a,*]

[a] *Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*
[b] *Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

Available online 7 December 2005

Abstract

Steady-state and ultrafast transient luminescent properties of CdS nanoclusters prepared by the Aerosol-OT (AOT)/*n*-heptane reverse micelle method and those modified with 2-mercaptoethanesulfonate were investigated in heptane and water, respectively. A very short luminescence component (∼200 fs) was observed for the first time for CdS nanoclusters dispersed in solution. The luminescence mechanism of CdS nanoclusters is proposed.

Keywords: CdS nanocluster; Ultrafast transient luminescence measurement

1. Introduction

Metal and semiconductor nanoclusters have recently attracted much interest because of their unique optical and electronic properties, which are different from those of bulk materials [1–12]. Semiconductor nanoclusters, the radii of which are smaller than the bulk exciton Bohr radius, constitute a class of materials of intermediate nature between molecular and bulk forms of matter. Quantum confinement of both electrons and holes in all three dimensions leads to an increase in the effective band gap of the material with decreasing cluster size. Consequently, both optical absorption and emission of nanoclusters shift to blue (higher energy) with decrease in sizes of the clusters [13]. There are numerous reports on dynamics of electron–hole recombination using ultrafast transient absorption spectroscopy [14–18].

II–VI semiconductor nanoclusters are known to be photoluminescence materials and are used for nonlinear optics and laser applications [14]. Although many studies on luminescent properties of II–VI semiconductor nanoclusters have been published in the last two decades [13,19–26], the luminescence mechanism in nanoclusters has not been fully elucidated. Based on results of detailed investigations of the excitonic emission by various groups, it is considered that at least one of the charge carriers involved in the recombination process is trapped in very shallow traps [20,27,28]. O'Neil et al. [20] and Eychmuller et al. [27] suggested that the electrons are first trapped and then recombine with free holes after thermally returning to the conduction band. On the other hand, Bawendi et al. [28] postulated that there is a strong resonance between free holes and holes in shallow traps. The luminescence, which is strongly red shifted from the absorption, is usually assigned to the recombination of trapped holes.

Optical and luminescent properties of semiconductor nanoclusters are very sensitive to the surface chemical structure and the environment around nanoclusters [29]. Chemical modification of the surface of semiconductor nanoclusters by capping with organic reagents seems to be one of the most effective methods to control these properties. It is therefore very important to clarify the effect of the capping agent on various properties of semiconductor nanoclusters [30].

In this study, we investigated the steady-state and ultrafast transient luminescent properties of CdS nanocluster prepared by the Aerosol-OT (AOT)/*n*-heptane reverse micelle method (AOT–CdS nanoclusters) as well as those of CdS nanoclusters modified with 2-mercaptoethanesulfonate (SO_3–CdS nanoclusters), which can be used as a building block for the construction of mono- and multilayers on a substrate using a cationic polymer or other cationic groups [31]. A model for luminescence from CdS nanoclusters and the cause of the change in luminescence characteristics by surface modification are proposed.

* Corresponding author. Tel.: +81 11 706 3812; fax: +81 11 706 3440.
E-mail address: uosaki@pcl.sci.hokudai.ac.jp (K. Uosaki).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.10.036

2. Experimental

2.1. Materials

Ethanol (superpure grade), pyridine (superpure grade), diethyl ether (superpure grade), 1-butanol (superpure grade), acetone (superpure grade), bis(2-ethylhexyl) sodium sulfosuccinate (AOT, pure grade) and $Na_2S{\cdot}9H_2O$ were purchased from Wako Pure Chemicals, and $Cd(ClO_4)_2{\cdot}6H_2O$ was obtained from Kishida Chemicals. 2-Mercaptoethanesulfonate (97%) was obtained from Aldrich, and toluene (spectroscopy grade), *n*-heptane (spectroscopy grade) and methanol (spectroscopy grade) were purchased from Dojindo Laboratory. All chemicals were used without further purification. Ultrapure water was obtained using a Milli-Q water purification system (Millipore). Ar (99.999%) and N_2 (99.99%) were obtained from Air Water.

2.2. Preparation of CdS nanoclusters

CdS nanoclusters were prepared in AOT/heptane reversed micelles [9,32–35]. Typically, 100 ml *n*-heptane solution of 0.2 M AOT was prepared in two separate Schlenck tubes. An aqueous solution of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.4 M) was added to one solution, while an aqueous solution of $Na_2S{\cdot}9H_2O$ (0.3 M) was added to the other solution with a molar ratio of $W = [H_2O]/[AOT]$ for both solutions [36]. After each solution had been stirred individually for 1–2 h, they were mixed together and stirred for another 1 h, resulting in the formation of CdS nanoparticles in the reversed micelles.

Surface-modified CdS nanoparticles were prepared by the method reported by Miyake et al. [37]. Aqueous solution of 0.3 M 2-mercaptoethanesulfonate was added to 100 ml of the reversed micelles solution containing CdS nanoparticles and stirred for 2 h, resulting in the formation of CdS nanoparticles covered with 2-mercaptoethanethiol. The thiol-covered CdS nanoparticles were obtained as precipitate after being dried under vacuum. The nanoparticles were sequentially washed with pyridine, *n*-heptane, diethyl ether, 1-butanol, acetone and methanol.

2.3. UV–vis spectroscopy, fluorescence spectroscopy and luminescence lifetime measurement

UV–vis spectra of CdS nanoparticles in solution were obtained using a Hitachi U-3300 spectrometer. Steady-state luminescence measurements were carried out using a Hitachi F-2000 spectrometer.

Ultrafast luminescence lifetime measurements were carried out by using a femtosecond luminescence up-conversion system, the details of which have been given elsewhere [38]. Briefly, the second harmonic of a Ti:Sapphire laser (Spectra-Physics, Tsunami, 840 nm, 80 MHz) pumped with a diode-pumped solid state laser (Spectra-Physics, Millennia X) was used as an excitation source. The fundamental pulses are split into two beams: one is frequency-doubled by a BBO crystal (420 nm) to excite the sample and the other beam serves as a gate pulse. The gate pulse traverses a variable optical delay of 2 μm/step (6.7 fs), while the excitation pulse traverses a fixed delay before being focused into a 1 mm sample cell. The fluorescence emission and the gate pulse are focused into a 0.5 mm thick BBO crystal in a type-1 phase matching geometry. To avoid polarization effects, the angle between the polarizations of the excitation and probe beams was set to the magic angle by a λ/2 plate. The sum-frequency signal of the Raman line in pure benzene excited with the second harmonic yielded an instrumental response function of 200 fs FWHM. All measurements were carried out at room temperature.

3. Results

3.1. Luminescent properties of AOT–CdS nanoclusters

Fig. 1(A and B) show absorption spectra and steady-state luminescent spectra excited at 380 nm, respectively, of AOT–CdS nanoclusters with various AOT/*n*-heptane ratios (*W*:

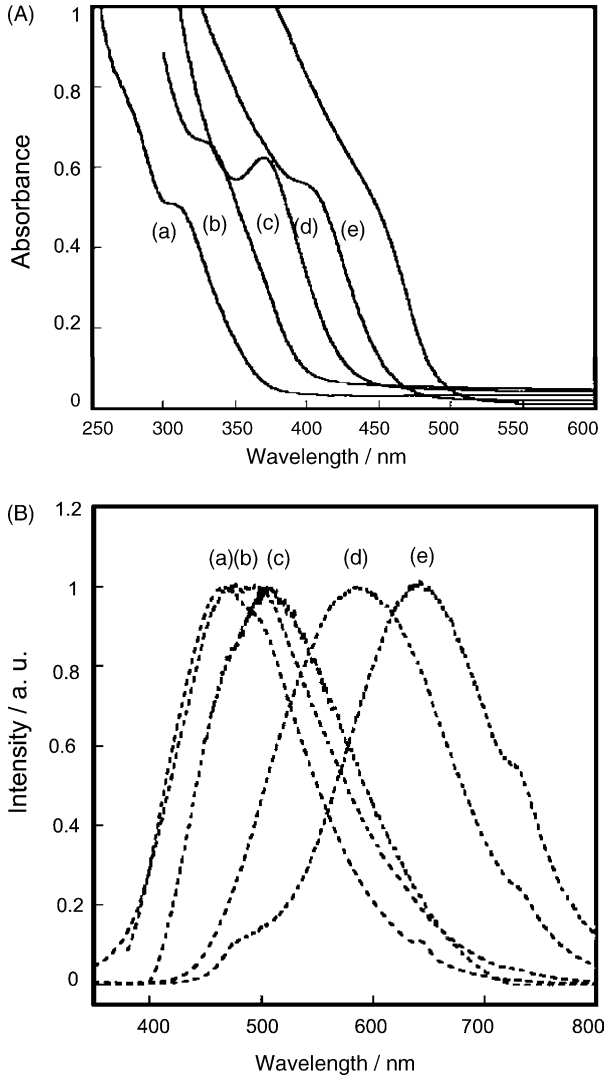

Fig. 1. (A) Absorption and (B) luminescence spectra of AOT–CdS nanoclusters of various sizes: (a) $W = 1$, (b) $W = 3$, (c) $W = 4.5$, (d) $W = 6$ and (e) $W = 8$. Luminescence spectra were obtained at 350 nm excitation.