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Multi-wavelength intermittent photoluminescence of single CdSe quantum dots

Yuichi Yamasakib,*, Harumi Asami¹,a,c,d, Takashi Isoshimaa, Itaru Kamiya,a,c, Masahiko Harad

¹Frontier Research System, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
²Supramolecular Science Laboratory, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
³Nanotechnology Laboratory, Mitsubishi Chemical Corporation, 1000 Kamosida-cho, Aoba-ku, Yokohama 227-8502, Japan
⁴Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatuda, Midori-ku, Yokohama 226-8502, Japan

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Abstract

A single chromophore detection using video-microscopy is one of the latest methodologies to reveal unique characteristics, which could not be obtained from ensemble measurements. Among many kinds of subjects, dynamic optical properties observed in colloidal semiconductor nanoparticles are attractive and important not only for the basis of photo-physics but also for application studies, e.g. biological labeling, electronic devices. In this study, fluorescence video-microscopy was performed on cadmium selenide (CdSe) quantum dots (QDs) spin-coated on a glass substrate. From single CdSe QDs detection, emissions at wavelengths separated over 60 nm were observed for the first time. This spectral feature was attributed to the existence of double-emissive relaxation processes in CdSe QDs. Photoluminescence intermittency was also observed both from relaxation processes. Fluorescence video-microscopy, which was advanced in biology, can be applicable for the real-time monitoring of dynamic properties in semiconductor photo-physics.

Keywords: Single chromophore detection; Luminescence; Emission; Nanoparticle; Cadmium selenide; Quantum dot; Quantum confinement; Intermittency; Semiconductor; Exciton

1. Introduction

In the past decades, colloidal semiconductor nanoparticles have attracted considerable attention as quantum dots (QDs) whose unique electronic properties exhibit characteristics of artificial atoms [1,2]. They have been considered as possible candidates for substituting organic fluorescent dyes for biological applications [3], or for electronic devices, such as light emitting diodes [4,5]. This trend was accelerated when a novel synthetic method for colloidal dots of cadmium chalcogenides with high yield of photoluminescence (PL) at room temperature was reported by Murray et al. [6]. Studies on the physical aspects of semiconductor QDs have since increased extensively. In addition, a synthesis of narrow size-distributed dots enables the study of the correlation of electronic properties with their size [6]. This size-dependent optical property, so-called quantum confinement effect, arises when nanoparticles become smaller than the exciton Bohr radius of a bulk material. As the difference in the quantum-confined energy levels vary roughly with the inverse of the square of the particle radius [2,7], both absorption and emission maximum wavelengths corresponding to the interband transition shorten with decreasing particle size [6,8,9].

Such size-specific features of QDs disappear due to ensemble averaging when they are inhomogeneous in size. Thus, an assessment of the optical properties of individual QDs by single chromophore detection is more favorable for clarifying the mechanisms underlying the photoemissive process. Hence, we performed single QD detection to study both quantum effects and emissive behaviors. Nirmal et al. reported an interesting feature called fluorescence intermittency in which the emission intensity switches distinctly between on and off [10]. This feature is not apparent from ensemble measurements. It is widely accepted that QD prepared by the hot soap method is an ideal material due to
efficient surface passivation, allowing us to study the electronic properties of a three-dimensional quantum-confined structure in single particles [11].

As described above, a series of sophisticated investigations has clarified the outstanding physical features of single QDs [10,12]. However, these studies regarding the emission of semiconductor QDs appear to have been limited to excitonic luminescence. In this study, we performed fluorescence video-microscopy on single cadmium selenide (CdSe) QDs, and observed double-emissive relaxation originating from the same single QDs. In our system, intermittency was observed in both emissions.

2. Experimental

CdSe QDs were synthesized by the hot soap method reported previously [6]. To obtain wider size-distributed dots, precursor compounds, bis(tributylphospine)selemin and dimethylcadmium were slowly added into the vigorously stirred reaction flask with hot melted tri-n-octylphosphine oxide (TOPO). The QDs were purified by precipitation with anhydrous methanol and collected by centrifugation.

The exciton recombination model gave results consistent with both experimental data and theoretical predictions regarding the relationship between electronic properties and the particle size [2,6,7]. Thus, the absorption spectra were compared to those in the literature to estimate the particle size. Dilute solutions of QDs in toluene were used for optical characterization. The absorption spectra were acquired by a Shimadzu UV-3100PC spectrometer, and the PL spectra by a Hitachi F-4000 spectrometers.

Transmission electron microscope (TEM) observation of QDs was performed to confirm the size distribution using JEOL FX-2000 electron microscope operated at 100 kV. A drop of dilute particle solutions was placed on carbon-coated copper grids (200 mesh) with a supporting collodion film.

To obtain the samples for fluorescence video-microscopy, 0.05 wt% QD solution in toluene was spin-coated on a microscope coverslip. An epi-illumination inverted microscope (Olympus IX-70) equipped with a mercury lamp and an oil-immersed objective (Olympus, UPlan Apo 100×) was used to observe the luminescence from individual dots at room temperature. Excitation wavelengths were chosen by changing bandpass filters and dichroic mirrors. Both blue (460–490 nm) and yellow-green (545–580 nm) excitation filters were used with corresponding dichroic mirrors. For the detection, long-pass (cutoff wavelength at 610 and 515 nm) and green-bandpass filters (520–550 nm) were used. Thus, we carried out the observations using four filter configurations (Fig. 1).

Imaging was carried out under Köhler illumination which allows uniform excitation over a visual field. Throughout the experiments, fluorescence images of CdSe QDs obtained by an SIT tube (Hamamatsu Photonics C2400-08) were recorded on a video tape through an image processor (Hamamatsu Photonics Argus-10) at 30 frames per second. Successive image analyses of both spatial and intensity distributions were performed using macroprograms for NIH Image [13] developed by us.

3. Results and discussion

Fig. 1 shows room-temperature optical properties of the CdSe QDs used in this study, indicating that the electronic state of exciton is strongly quantum-confined and that the mean size of the QDs is on the order of several nanometers, with a wider size distribution. In fact, the histogram of size distribution measured by TEM shows that the mean size of QDs is 4.38 nm with a standard deviation of about 0.78 nm (Fig. 2).

![Fig. 2. Histogram of QD diameter used in this study, obtained by measuring the diameter of more than 100 particles by TEM.](image-url)
between absorption maximum and mean size matches those reported by Murray et al. [6].

A fluorescence micrograph of the CdSe QDs spin-coated on a microscope coverslip is shown in Fig. 3. To obtain this image, a blue filter and a long-pass filter with a cutoff wavelength at 515 nm were used for excitation and detection, respectively (Fig. 1(d)). In this image, the size of each bright spot appears to be diffraction-limited, indicating that the fluorescent objects are well separated on the substrate. Although a QD density detected through the above filter set is 28 dots in $10 \times 10 \mu m^2$ area, less dots are observed due to the on–off behavior or fluorescence intermittency of individual dots. As indicated by the fluorescence intermittency, individual bright spots shown in Fig. 3 arise from single QDs, which is one of the strong evidence for single QD detection. Fig. 4 clearly indicates the intermittency, but with a very short on-period due to incomplete surface passivation of organic cap. Several reports concluded that Auger photoionization, which is proposed as an essential process of on–off switching, occur frequently in the organically capped dots, while inorganic capping reduces the ionization frequency and leads to longer on-period. Nirmal et al. reported that CdSe/ZnS core-shell QDs exhibit long on-periods [10]. Not only the on-period but also PL quantum efficiency is affected by the degree of surface passivation [14]. Thus, the PL intensity of individual QDs varies due to randomness in the degree of their surface passivation as shown in Fig. 3 despite the Köhler illumination.

We confirmed the observed results on the same visual field using different filter configurations with a band-pass-filtered mercury lamp. Typical transients of PL intensity observed from the same single dot are shown in the time trace plots in Fig. 4. While frequencies of intermittency, or blinking, are different, a distinct on–off behavior was observed using all filter sets from (a) to (c). It should be noted that intermittent PLs were observed both at wavelengths over 610 nm (Fig. 4(a) and (b)) and between 520 and 550 nm (Fig. 4(c)). It means that a single QD can emit light that is separated by as much as 60 nm in wavelength or 220 meV. Since complete experimental confirmations of single QDs detection were not carried out, there might be a possibility that the emitter is a dimer made of two nanocrystals of different size, or that two nanocrystals locate at the same diffraction-limited spot. In the recent reports, however, both observations of diffraction-limited spots and of the intermittency are believed to be strong evidences of single QDs detection. Although a spectral diffusion has been observed in single-nanoparticle and single-molecule systems [15,16], such a wide jump in the emission wavelength has not been reported. For example, several studies reveal that the emission bandwidth of single QDs is within 30 meV (6 nm at 500 nm) at cryogenic [12] and 60 meV at room temperature [17], and that the spectral diffusion is in the range of 10 meV [18]. The spectral variation of 220 meV which we observed is far too large to be account for by thermal effects.
Generally, the dominant radiative process of CdSe QDs is believed to be the transition between $^1S(e)$ and $^1S_{3/2}(h)$ state. Possible causes of the double-emissive feature observed in this study are (1) phonon bottleneck effect, and (2) trap states of QDs. In the strong 3D quantum-confined systems such as semiconductor QDs, phonon bottleneck effect is theoretically predicted due to energy level spacing larger than phonon energy [19]. Although several groups reported observations of phonon bottleneck effect in III–V QDs fabricated by epitaxial techniques [20,21], it has so far not been reported in colloidal CdSe QDs. The trap state model is more plausible, supporting evidences include report by Hines and Guyot-Sionnest here the fluorescence spectrum of CdSe/TOPO has a broad tail arising from what they assigned as surface trap sites in the red region of excitonic luminescence [14]. Thus, the emission observed between 520 and 550 nm can be attributed to excitonic luminescence and those over 610 nm to the emission from surface trap sites. Here, intermittent emission are observed in both excitonic recombination and surface trap related processes. Although our results strongly suggest the double-emissive feature of single CdSe QDs, more precise experimental systems which include emission spectroscopy, lifetime and statistic measurements, scanning probe technique, etc. should be build up to confirm these results.

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