Photoluminescence from single CdSe quantum rods

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Abstract

We report here the first observation of photoluminescence from single CdSe quantum confined nanorods (quantum rods). Luminescence imaging spectra of individual rods were obtained for two samples, with average aspect ratio of 2 and 4, respectively. Typical room-temperature luminescence spectral line widths of the rods in both samples are less than 60 meV, which are about the same as that of high-quality CdSe/CdS core/shell single quantum dots. Single quantum rods also exhibit luminescence intermittence as observed in single-dot systems.

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Colloidal semiconductor nanocrystals have received much attention in recent years [1–4]. Their size-dependent optical properties with band edge tunable through visible wavelength range make them of particular interests for fundamental studies as well as potential applications. Single quantum-dot spectroscopy has been used to eliminate the effects of inhomogeneous broadening and ensemble averaging in a number of nano-sized semiconductor systems [5–7] and has revealed many new physical phenomena in single CdSe based nanocrystals, such as ultra-narrow line-shapes, luminescence intermittence, shifting of emission spectra, and a highly polarizable emitting state in the presence of strong local electric fields [8]. The strong polarized emissions have been observed in single CdSe [9] and CdS [10] nanocrystals.

It has been recently demonstrated that the shape of CdSe nanocrystals can be manipulated by controlling the growth kinetics [11]. The resulting particles can be from a nearly spherical morphology to a rod-like one. The rods can grow up to 200 nm long with an aspect ratio of up to 50 [12]. Studies of CdSe quantum dots suggested that electronic structures and optical properties of band edge have strong dependence not only on the size but also on the shape of nanocrystals [13]. The measurements on CdSe ensemble quantum rods have shown that Stokes shift is noticeably larger than that of the corresponding quantum dots, and being even larger with the increase of rod lengths [11]. Also the polarization of the emission of these rods exhibits significant difference in comparison with the CdSe dots [11]. Studies of these rod- and wire-like structures can provide a testing ground
for the shape-dependent electronic and optical properties of nanocrystals and the quantum confinement effects in one-dimensional (1D) and quasi-1D regime, and in comparison with much characterized zero-dimensional (0D) structures. Furthermore, such studies should provide a good fundamental basis for the applications of these technically important quantum rods due to their rod morphology. CdSe quantum rods may be used as polarized emitters for light-emitting diodes [14,15] and biological labeling reagents [11,16,17].

In this paper, we report our preliminary results of photoluminescence imaging spectra of single CdSe quantum rods using far-field microscopic spectroscopy technique [8]. The imaging method provided information not only about individual rods but also about rod distribution on the substrate and their overall spectral distribution. In order for us to calibrate our optical detection system and to have quantitative measurements, CdSe/CdS core/shell quantum dots were prepared and investigated under the same experimental conditions in comparison with the quantum rods.

Colloidal CdSe rods were prepared using the method as described by Peng et al. [12]. Briefly, trioctylphosphine oxide (TOPO) and a strong Cd ligand, either hexylphosphonic acid (HPA) or tetradecylphosphonic acid (TDPA), were heated to 320–360°C. Various stock solutions of Cd(CH₃)₂ and Se in TBP were prepared and rapidly injected into the hot solution of HPA or TAPA in TOPO. All procedures were carried out with standard air-free techniques. The reaction was monitored by UV–visible absorption and photoluminescence spectra recorded with aliquots taken from the reaction. These colloidal rods were examined by transmission electron microscopy (TEM) to determine their sizes and to analyze the size and shape distributions. Fig. 1(a) and (b) show TEM pictures of two high-density quantum-rod samples, which were chosen for our photoluminescence studies. The rod sample, shown in Fig. 1(a), has a length of about 8 nm with an average aspect ratio of about 2. The other sample shown in Fig. 1(b) has similar short axis dimension and an average aspect ratio of about 4 [12]. As shown in Fig. 1, the quantum rods still have certain size and aspect ratio distribution although their uniformity should be considered quite good in general. The photoluminescence quantum yield (measured by ensemble rods in solution by comparison with R6G) of the rod samples used in this work is about a few percent at room temperature. The CdSe/CdS core/shell quantum-dots were synthesized using the method reported previously [18] and the photoluminescence quantum yields of the particular core/shell dot sample used in this study is about 20–30% at room temperature. The size of the core/shell nanocrystals used in the present study is 5 nm in average grown from 4 nm CdSe cores. All the rods and dots synthesized are surrounded by a passivating layer of organic ligands [11,18].

Fig. 1. TEM of CdSe nanocrystals (a) short quantum rods with an aspect ratio of 2 in average and (b) long quantum rods with an aspect ratio of 4 in average.
Samples for photoluminescence measurements were prepared by spin coating a dilute solution of nanocrystals in toluene with 1% poly methyl methacrylate (or in pure toluene) onto a fused silica coverslip (or formvar thin film on a standard copper grid). The substrates were examined to make sure no dominating background luminescence prior to the sample deposition. The rod density on the substrate was controlled by changing concentration of the rods in the solution before spin coating. Nominal densities of the rods are less than one rod per micrometer square, which were checked by TEM images, in order to have spatial resolution of individual nanocrystals for far-fields optics.

The photoluminescence images and imaging spectra of single rods were obtained by using conventional optical microscopic techniques. The 514.5 nm line of an Argon-ion laser was used as an excitation source. Laser beam was reflected by a 5% beam splitter and directed through a high-magnification microscope objective (either 50×, NA = 0.55 or 100×, NA = 0.7 was used) onto the sample, which was mounted on a micro-move-ment-controlled XYZ translation stage for sample positioning and imaging. Luminescence was collected by the objective and directly projected into spectrometer, and then detected by a liquid-nitrogen-cooled CCD camera. The scattered laser light was blocked by a notch filter. The luminescence images of single quantum rods were obtained by using a flat mirror in place of the grating inside the spectrometer. All the images and imaging spectra were taken at room temperature, and under the excitation intensity of around 80 W/cm².

The excitonic sharp line and distinguished LO phonon lines of single CdSe/CdS quantum dots have been observed at low temperature [19]. At room sample temperature, a typical spectral line width of the single dot is around 60 meV [19]. This homogenous line broadening is mainly due to the acoustic-mode phonon coupling [20]. We chose this well-characterized core/shell type dot sample to test the sensitivity of our experimental apparatus, and to compare with the rod samples.

The imaging spectra of single quantum dots of CdSe/CdS core/shell sample are shown in Fig. 2,
which were taken with 60 s in integration time of CCD (note that all the imaging spectra shown here were directly plotted from the data acquisition software, and CCD dark counts were not deducted). The vertical axis represents the spatial distribution of the nanocrystals. As can be seen in Fig. 2, the typical line width is less than 60 meV which is narrower than that of CdSe/CdS dots reported previously [19] As shown in Fig. 2, the spectral line center of the individual dot spreads from 578 to 626 nm. The broad distributions of emission energies are mainly ascribed to the size distribution and possible difference of the local environment of quantum dots. Light-driven spectral diffusion has been observed in single CdSe/ZnS dots at low sample temperature [5] which could contribute to the line width. As shown in Fig. 2, the spectral shapes of most dots are symmetric.

A typical photoluminescence images of the shorter rods (Fig. 1(a)) is shown in Fig. 3(a). Clearly seen from Fig. 3(a), the rods spread uniformly on the substrate, and some rods are brighter than the others. This photoluminescence image was taken with a rod density higher than the ones used later for imaging spectra of single rods to show the uniformity of the rods and blinking behaviors with some rods bright and others dark at a given time. Before taking imaging spectra, the entrance slit of the spectrometer was closed down to 150 μm as shown in Fig. 3(b). The emission spectrum of individual rods could be separated for the sample (such as Fig. 3) with the density used. However, in order to have more well-separated single rods, we used even lower rod density for studying imaging spectra. Fig. 4 shows the imaging spectra of the short quantum rods with such lower density, which were taken with 60 s of integration time. Typical line width of the short rods is about 60 meV, with some of them even narrower (note that the individual line width may not be clearly seen with the figure presented here). The overall luminescence intensity is about several times weaker than that of the core/shell dots, which is consistent with the measurements on ensemble dots in solution. This is reasonably expected because of the lack of CdS shell barrier for the rod samples. The interfacial defects are greatly reduced in core/shell type structures [19, 21]. The spreading range of the spectral line center of the rods is about the same as that of the core/shell dots (Fig. 2).

The imaging spectra of the long rods are shown in Fig. 5. The overall luminescence intensity counted by integration time of the CCD camera is weaker than that of the short rods, which is also consistent with the measurements on ensemble rods. As shown in Fig. 5, the spectral line widths of the long rods are about the same as that of the short rods and the core/shell dots, indicating the uniformity in the diameters of the rods since

Fig. 3. Photoluminescence images of single CdSe quantum rods (a) with a fully opened entrance slit of spectrometer and (b) with a narrower slit for measuring the spectra of individual rods.
the lengths of the rods are beyond the exciton Bohr radius, the size fluctuation along the rods, if severe, would provide local traps for excitons, hence the broadening of line widths. At room temperature, no such broadening has been observed. Further studies of this effect (shape uniformity on spectral line width) are needed at low temperature. Although care has been taken to eliminate luminescent background contributions, a broad emission from the substrate in this case can still be seen in Fig. 5. Since a longer integration time (3 min) is needed to observe weaker signals from the longer rods, the imaging spectra are not as sharp as the case for shorter rods as in Fig. 4. Comparing with the short rods, the center of spectral distribution shifts to the red side, and the range of spectral distribution is smaller. The imaging spectra obtained at several different positions on the sample show the similar results. The red shifting of the long rods cannot be simply explained by the quantum size effects, especially the possible fluctuation in the diameters of the rods. Based on the measurement on ensemble rods, emission peak shifts to lower energy side (red shift) with the increase of the rod length but the absorption peak remains almost unchanged. The ensemble Stokes shift observed in CdSe dot system has been ascribed to the lowest state being a “dark exciton” [13]. More theoretical analyses and experimental studies are needed to clarify the features of Stokes shift in quantum-rod structures.

One of the common features of single colloidal nanocrystals is that luminescence exhibits on and off behavior [5,19]. This luminescence intermittency may be ascribed to the ionization of nanocrystals. All our quantum-dot and quantum-rod samples have shown the emission intermittency and the on–off time scale at room temperature ranges from $<1$ s to a few minutes. The blinking feature indicates that spatial image shown in Fig. 3 and imaging spectra shown in Figs. 2, 4 and 5 are from single nanocrystals. Since the blinking behavior of single rods are similar to the ones reported for single dots [5,19], we will not present such observations in this paper. CdSe quantum rods are expected to have strong anisotropic optical properties. Our preliminary data have shown that both emission and absorption of the single quantum-rod samples are strongly polarized, which are different from that

![Fig. 4. Imaging spectra of single CdSe short rods, which were taken at room temperature with a CCD integration time of 60 s.](image-url)
observed in CdSe quantum dots [9] Detailed spectroscopic studies of the polarization dependence of the single quantum rods are undergoing.

In summary, room temperature photoluminescence imaging spectra of single CdSe quantum rods have been obtained by the conventional microscopic technique. The spectral line widths of both the short and the long rods are about the same as that of the CdSe/CdS core/shell quantum dots. Luminescence intermittency and strong polarization dependence in emission and absorption were observed in the rod samples. All these preliminary results are very encouraging for more detailed studies of these new nano-structures, especially at low sample temperatures.

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References