Polarization spectroscopy of single CdSe quantum rods

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Excitation and emission spectra of CdSe single quantum rods with aspect ratios of 2 and 4 were investigated by far-field microscopic technique. Typical spectral linewidths of the rods are less than 60 meV at room temperature. Both excitation and emission of the single rods exhibit strong polarization dependence, indicating that dipole moment exists along the long axis of the rods, e.g., the unique axis c of the wurtzite structure.

Colloidal CdSe quantum dots have received much attention in recent years.[1-4] Their relatively reproducible and controllable synthetic chemistry and their strong size-dependent optical properties with band edge tunable through the visible wavelength range make them of particular interest for fundamental studies as well as potential applications. The spectroscopy of single quantum dots has revealed many interesting physical phenomena such as ultranarrow line shapes, luminescence intermittence, shifting of emission spectra, and a highly polarizable emitting state in the presence of strong local electric fields.[5]

Wurtzite CdSe nanocrystal is intrinsically an anisotropic material. Measurements of the dielectric dispersion of CdSe nanocrystals have shown the existence of large dipole moments along the unique c axis of the wurtzite structure.[6] Quantum-confined Stark effect measurements in single CdSe dots also implied the presence of a permanent dipole.[7] More direct measurements using electrostatic force microscopy (EFM) determined that the static dielectric constant of single CdSe nanocrystals is uniform, although the charge per nanocrystal is nonuniform.[8] Due to the prolate shape and wurtzite crystal structure, calculations have predicted two potential dipole orientations for the CdSe nanocrystals.[9] One is oriented parallel to the wurtzite c axis, and the other is in the plane perpendicular to the c axis. Polarized emission of quantum dots suggested that degenerated dipoles are only formed in the plane.[10] Recent theoretical treatments have found very large dipole moments along the c axis, which strongly depend on the exact structure of the nanocrystals and may vary significantly with small structural changes.[11] However, polarized absorption was also observed in single CdS nanocrystals, which is unexpected since CdS nanocrystals have a tetrahetral structure.[12] All these previous results indicate the importance of polarization studies for understanding the basic electronic and optical properties of nanocrystals. Consequently, studies of polarization properties will explore another dimension for device applications of colloidal nanocrystals.

Recently, it has been demonstrated that the shape of CdSe nanocrystals can be manipulated by controlling the growth kinetics.[13,14] The resulting nanoparticles can be from a nearly spherical morphology to a rodlike one. The successful growth of these rod- and wire-like structures provides a testing ground for studying the shape-dependent electronic and optical properties of nanocrystals and the quantum confinement effects in one-dimensional (1D) and quasi-1D regimes. CdSe quantum rods have well-defined shape: their long axis is preferably grown along the unique c axis.[13,14] This unique feature is helpful to determine nanocrystal orientation and make them particularly interesting for studying dipole formation and polarization effects. Polarization-dependent emissions have been observed in an ensemble multirod system, in which a certain degree of alignment of being parallel along their long axis of the rods is obtained by stretching PVB polymer embedded with the rods. A stronger polarized emission was observed along the long axis of the rods.[13] This was tentatively assigned to the level crossover of the two highest occupied electronic states due to the elongation of the nanocrystals along their c axis. A recent empirical pseudopotential calculation has shown that, due to energy level crossover, elongated dots will emit linearly polarized light instead of plane-polarized light as the aspect ratio of the elongated dots (or rods) becomes larger than 2.[15]

In this paper, we report our experimental studies of the polarization dependence of both emission and excitation (or absorption) photoluminescence (PL) spectra of single quantum rods with aspect ratios of 2 and 4. Such studies can eliminate uncertainties in ensemble multirod measurements and be used to make comparisons with theoretical predictions. Measurements of the excitation polarization dependence in single quantum rods are particularly significant since they are fundamentally different from measurements done with single quantum dots.[10]

Colloidal CdSe quantum rods were prepared using a method as described by Peng and Peng.[14] 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 $(CH_3)_2$ and Se in TBP were prepared and rapidly injected into the hot solution of HPA or TDPA in TOPO. These colloidal rods were examined by transmission electron microscopy (TEM) to determine their sizes and to analyze the size and shape distributions. Figure 1 shows the TEM pictures of two quantum rod samples. The first rod sample, shown in Fig. 1(a), has a length of about 8 nm with an average aspect ratio of about 2. The second sample, shown in
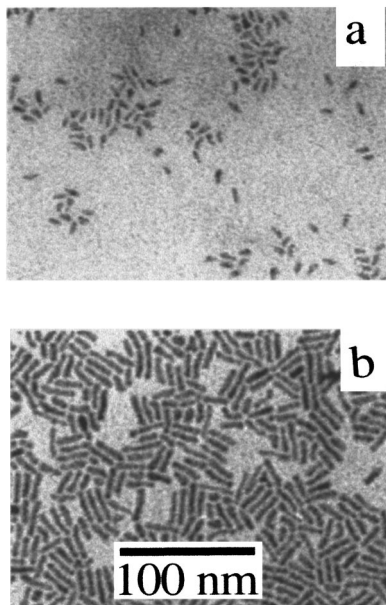
FIG. 1. TEM pictures of CdSe nanocrystals. (a) Short quantum rods with an aspect ratio of 2 on average and (b) long quantum rods with an aspect ratio of 4 on average.

FIG. 2. Imaging spectra of single CdSe short rods, which were taken at room sample temperature with a CCD integration time of 60 sec.

Fig. 1(b), has similar short axis dimension and an average aspect ratio of about 4. The PL 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.

Samples for PL measurements were prepared by spin-coating dilute solutions of nanocrystals in toulene with 1% polymethyl methacrylate (PMMA) onto fused silica cover-slips, which were examined to ensure no dominating background luminescence prior to the sample deposition. The rod density on the coverslip substrate was less than one rod per square micrometer in order to have spatial resolution of individual nanocrystals for far-field optical microscopy.

The PL images and imaging spectra of single rods were obtained by using conventional optical microscopic techniques.[5] The 514.5-nm line of an argon-ion laser was used as excitation source. The laser beam was reflected by a 5% beam splitter and directed through a high-magnification microscope objective ($50\times$, NA$=0.55$) onto the sample. Luminescence was collected by the same objective and directly projected into the spectrometer, and then detected by a liquid-nitrogen-cooled charge-coupled device (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 under the excitation intensity of about 80 W/cm^2. All measurements were carried out at room sample temperature. The polarization of the excitation beam at the sample surface was greater than 200:1.

Figure 2 shows the imaging spectra of the short rods shown in Fig. 1(a), which were taken with 60 sec of CCD integration time. Typical linewidths of the short rods are around 60 meV, which are about the same as that of high-quality CdSe/CdS core/shell single quantum dots.[16] The
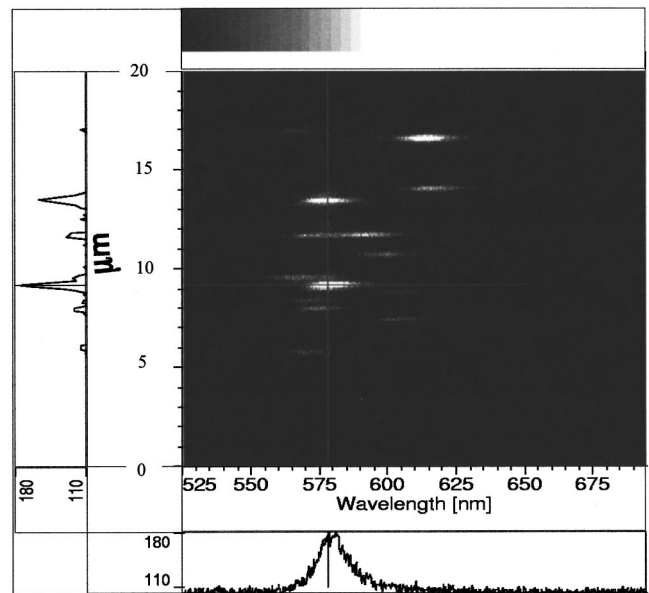
overall luminescence intensity is about several times weaker than that of the core/shell dots, which is consistent with the measurements on ensemble dots in solution. This is reasonably expected because of the lack of CdS shell barrier for the rod samples.[16,17] Based on the rod density, luminescence intermittence (which is a typical signature of single nanocrystals), and observed linewidth, we could safely assume that the observed luminescence spectra are from single quantum rods, which is consistent with other studies of single nanocrystals.[10,15,18]

Polarization studies were carried out by using luminescence imaging method. The luminescence of the single rods shows the similar blinking feature as observed in single quantum dots.[5,16,18] The intermittence on-off time intervals varied from less than 1 sec to few minutes. To reduce or avoid uncertainty in detected luminescence intensity due to the intermittence of a single nanocrystal, several repeated data acquisitions and long integration time of the CCD camera were used to average out such a blinking effect. The emission spectra of some representative rods were taken before and after the polarization measurements to ensure no significant changes of the emission intensity and photo-oxidation. Figure 3 shows typical pictures of the excitation
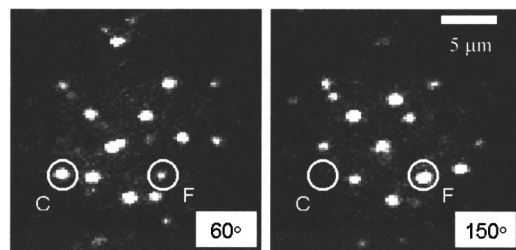

FIG. 3. Photoluminescence images of single CdSe rods with excitation polarization at two angles with a 90° difference.
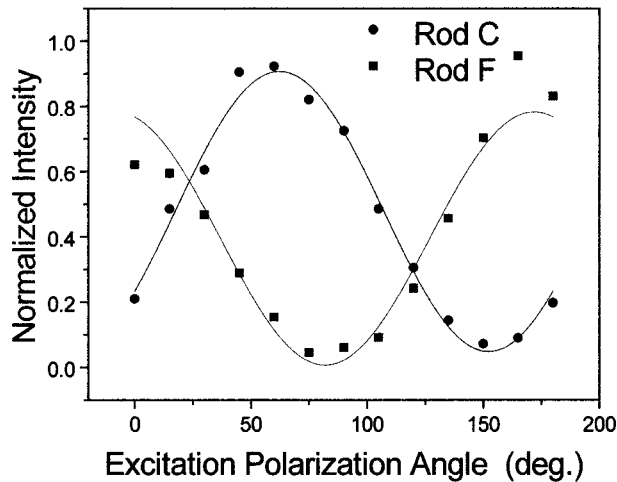
FIG. 4. Polarized excitation spectroscopy of single quantum rods. Normalized emission intensity of rods C and F as a function of excitation polarization angle. The solid lines correspond to the fit to a $\cos^2(\theta)$ function of the excitation polarization angle.
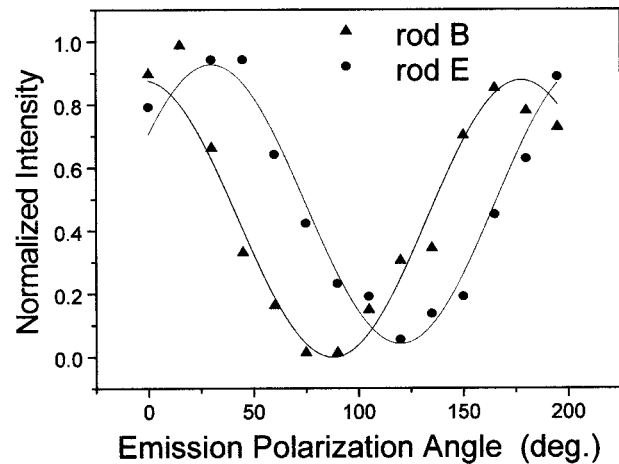

FIG. 5. Polarized emission spectroscopy of single quantum rods. Normalized emission intensities of two typical rods as a function of emission polarization angle. The solid lines correspond to the fit to a $\cos^2(\theta)$ function of the emission polarization angle.

polarization dependence, which were obtained by rotating excitation polarization angle with a 90° difference, of single quantum rods with an average aspect ratio of 2. One can see from the two highlighted single rods (C and F) that they turn from bright to dark (rod C) or dark to bright (rod F) when the excitation polarization rotates 90° (0° corresponds to vertical polarization). By rotating the polarization of excitation from 0° to 180°, almost all the rods shown in Fig. 3 exhibit the same polarization dependence as the highlighted C and F rods with the maximum absorption along one particular polarization angle, as shown in Fig. 4. We have carefully checked the polarization properties of all optical elements involved to ensure the purity of the detected polarization of the single quantum rods. Such a high-degree polarization dependence suggests that the transition dipole is formed only along one axis of the quantum rod.

The strength of the dipole transition is proportional to $|\boldsymbol{\mu}\cdot\mathbf{E}|^2$, where $\boldsymbol{\mu}$ is the dipole moment and $\mathbf{E}$ is the polarization of excitation field. In 3D space, $|\boldsymbol{\mu}\cdot\mathbf{E}|^2$ is proportional to $\cos^2(\theta)\cos^2(\varphi)$, where θ is the angle between the excitation polarization and the projection of dipole $\boldsymbol{\mu}$ onto the plane (sample plane) which is normal to the detection axis and φ is the tilted angle between $\boldsymbol{\mu}$ and the sample plane. The detected intensity oscillates between $I_{min}=0$ and $I_{max}=\mu^2\cos^2(\varphi)$ with rotation of excitation polarization angle θ. The angular dependence of the transition follows $\cos^2(\theta)$. Figure 4 plots the detected luminescence intensities of two rods versus the excitation polarization angle. The set of intensity data for each rod was normalized to $(I_{max}-I_{min})/(I_{max}+I_{min})=P$, e.g., the polarization degree for that rod. As shown in Fig. 4, both rods C and F follow the $\cos^2(\theta)$ curve and the polarization degrees of both rods are close to unity. The 15 rods shown in Fig. 3 were all examined and fitted in this way, the polarization degrees of all the rods being above 90% except one rod which is close to 80%. Measurements were also done for many other single-rod samples [such as the ones shown in Fig. 1(b) with aspect ratio of 4], and they all show similar polarization dependence

as presented here in Figs. 3 and 4.

Figure 5 shows the emission polarization dependence of two typical rods (rods B and E are from similar images as in Fig. 3), which was obtained by rotating a linear polarizer in the emission pathway while excitation polarization was maintained at vertical direction (0°). The emission polarization curves of two typical rods are presented in Fig. 5, which follow $\cos^2(\theta)$ as expected. The maximum intensities of the rods were detected when the emission polarization was close to the excitation polarization at 0°. These data indicate that both emission and absorption maxima are along the same direction and the quantum rods exhibit single-dipole transition behavior. The normalized plots of emission polarization dependence in Fig. 5 show that the polarization degree P of the rods is close to unity as expected. We have also studied the long rods shown in Fig. 1(b) for emission polarization, and the data show a similar polarization dependence as the short rods reported here. This observed purely linearly polarized emission with aspect ratio larger than 2 for single quantum rods is consistent with the recent results obtained in Ref. 15.

The polarization emission and absorption of single quantum rods exhibit unique dipole transitions, and the dipole moment can be only formed along one of the rod axes, either the c axis or short axis that is along the plane perpendicular to the c axis. Since the measured polarization degrees for all rods are close to unity and the samples were prepared by spin coating, the rods likely lie on the sample plane. In such a case, the dipole formed along the short axis or long axis will have the same polarization dependence as we measured. However, optical polarization measurements on ensemble rods have shown that much stronger polarized emission was along the long axis of the rods.[13] In that experiment, the rods were embedded in PVB polymer, which was then stretched up to 4 times its original length. A certain degree of rod alignment is obtained along the stretching direction. Therefore, based on the polarization studies of ensemble multirods done previously[13] and of single rods in this work, one can conclude that the c axis of the rods is the unique axis that the

dipole can be formed along when the aspect ratio of the rods is larger than 2. This conclusion is confirmed by a recent theoretical prediction.[15]

The polarization dependence of quantum rods shows significant differences from quantum dots. Polarization microscopy performed on single CdSe quantum dots suggested that degenerate transition dipoles were formed in the plane perpendicular to the c axis.[10] The c axis of the dots is a dark axis along which no polarization should be observed. These experimental data also showed that no apparent dependence on absorption polarization was observed in the single dots. Our experimental data on ensemble rods and single quantum rods have shown that the Stokes shift increases with an increase of the rod length, while in CdSe dots the Stokes shift increases with a decrease of the dot size and the Stokes shift has been ascribed to the lowest state as being a ''dark exciton'' state.[19] To find these differences and understand the underlying mechanism, it is important to study the nanostructures in a regime of dot to rod transitions and to have more theoretical studies of the electronic states involved in the optical transitions in these quantum rod systems.

The optical anisotropy of the CdSe nanocrystals can be attributed to the intrinsic asymmetry of wurtzite lattice structure. Studies of the CdSe dot system suggested that the electronic structures and optical properties of the band edge have a strong dependence on the shape of the nanocrystals.[19] Recent theoretical treatments have shown that a large dipole moment is present due to the lack of inversion symmetry and not due to the presence of a surface charge.[11] Their work also predicted that the dipole depends sensitively on the surface reconstruction and surroundings that are particularly important for wurtzite structures. Based on the above arguments,

the intrinsic crystal structure, surface reconstruction (or shaping), and surroundings all could determine and alter the electronic structure and optical properties of nanocrystals.

In summary, we carried out PL polarization studies of single CdSe quantum rods by using the far-field microscopic technique. The strong polarization dependence of both the excitation and emission indicate the existence of a unique dipole in the quantum rods. Our experimental measurements with single rods, combined with measurements of ensemble rods previously,[13] suggest that a dipole can only be formed along the long axis of the rod, i.e., the c axis of wurtzite structure, which is consistent with the results of Ref. 15. The strong excitation polarization dependence of single rods is significantly different from previous studies of slightly elongated dots. We have measured a large amount of single-rod samples prepared by different methods and different aspect ratios, which all show similar polarization behaviors. This is the first experimental study of linearly polarized excitation (absorption) of single quantum rods. Since the theoretical model used in Ref. 15 to treat the polarization of emission (which is determined by the polarization of the lowest excited state) does not apply to the polarization of the excitation (which relates to the polarization of higher excited states), our experimental observation reported here will stimulate more theoretical interest in the excitation polarization properties of elongated nanocrystals. These studies help us to understand the polarization properties of nanocrystals and will lead to some interesting biological and electro-optical applications of nanocrystals.

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