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Direct observation of highly polarized non-linear absorption dipole of single semiconductor quantum rods

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ABSTRACT

Polarization fluorescence microscopy was used to study the nature of the emission and nonlinear absorption dipole of single CdSe/ZnS quantum rods. Rods, with aspect ratios ranging from 2.75 to 15, showed strongly polarized emission consistent with previous one-photon studies. Non-linear excitation showed a sharp angular dependence fully consistent with the predicted two-photon absorption process. Two-photon absorption probes different transitions than linear absorption due to modified parity and angular momentum selection rules. The two-photon absorption dipole was found to be parallel to the emission polarization, and allows achieving highly orientation selective excitation of quantum rods. This is yet a further demonstration of single molecule measurements in unraveling basic principles of light-matter interaction that are otherwise masked by ensemble averaging.

INTRODUCTION

Single particle microscopy and spectroscopy are valuable methods for revealing phenomena that are otherwise shielded by the ensemble averaging, such as fluorescence intermittency, spectral diffusion [1,2], and single particle polarization [3,4,5,6]. Two-photon excitation is a method used to probe a different transition manifold than one-photon excitation due to a different parity and angular momentum selection rules [7,8,9]. Another use of two-photon excitation is imaging of biological environments by use of dye or luminescent nanocrystals, as demonstrated recently in in-vivo imaging [10].

Shape control of colloidally prepared nanostructures has been recently achieved by modifying the synthesis to obtain rod shaped particles - quantum rods (QRs) [11]. QRs exhibit electronic and optical properties different than quantum dots (QDs) [12]. For example, unlike the spherical dots, QRs have linearly polarized emission as demonstrated by fluorescence measurements on single rods and ensemble [13], leading also to polarized lasing [14].
In this work we report of direct observation of highly polarized absorption dipole of single colloidal CdSe/ZnS rod/shell nanoparticles under two-photon excitation by the use of polarization microscopy techniques. This study provides a further manifestation of the unique optical and electronic properties of colloidal semiconductor quantum rods.

EXPERIMENTAL DETAILS

The quantum rods were grown using the well-developed methods of colloidal nanocrystals synthesis utilizing high-temperature pyrolysis of organometallic precursors in coordinating

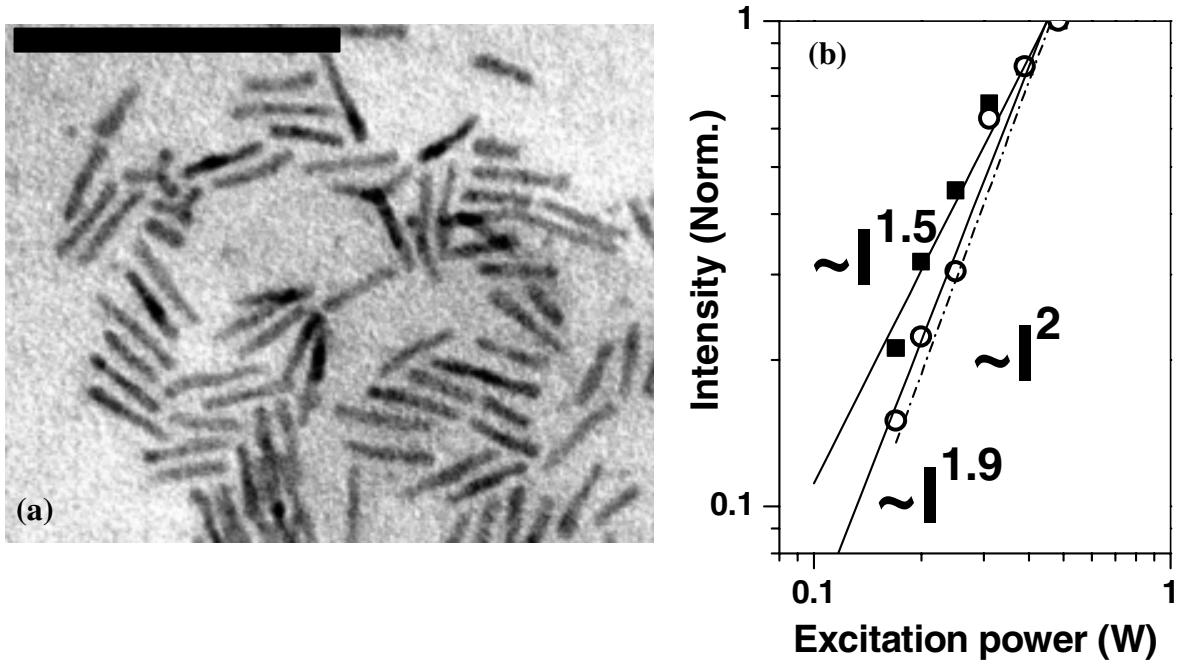

Figure 1. (a) TEM image of 4x25nm CdSe/ZnS QRs (scale bar=100nm). (b) Intensity response of two single QRs under two-photon excitation on log-log scale with linear fit.

solvents [11,15,16]. The rod/shell configuration was chosen since the growth of ZnS on the organically coated CdSe quantum rods enhances the fluorescence quantum yield [14,17,18]. Both the rod growth process and shell growth were monitored by the absorption spectrum and the emission spectrum (shell growth only). Transmission electron microscopy (TEM) was used for size determination as well as to confirm the formation of rod shaped nanocrystals and once more after shell growth to confirm a maintained rod shape.

A TEM image of CdSe/ZnS rod/shell is presented in Figure 1(a). showing good size and shape monodispersivity. The average rod/shell length is 25 nm, with an average diameter of 4 nm.

The sample for single rod optical studies was prepared by spin coating a dilute solution of QRs in toluene onto a precleaned quartz substrate placed in front of the objective. For the two-photon excitation source we used a mode locked Ti:sepphire laser with 150 fs FWHM pulsewidth and a 76 MHz pulse repetition rate (Coherent Mira). Fluorescence images were collected with a commercial high numerical aperture long working distance objective (100x N.A.=0.70). Both images and spectra were taken by the same CCD (Lavision Imager QE) by means of switching between a mirror and an appropriate grating in the monochromator. Both parallel and perpendicular components were imaged simultaneously by use of polarization displacing cube placed in front the entrance of the monochromator. All optical elements were carefully examined to avoid polarization effects.

RESULTS AND DISCUSSION

We studied three main QR samples all with the average diameter of 4 nm and lengths of 11nm, 25 nm to 60 nm. Polarization effects were observed for more than 50 single QRs within each sample. Fluorescence intermittency (blinking) was observed at various time scales providing further evidence for observation of single quantum rods. Spectra of the single particles were collected within each sample and throughout the measurements. The measured spectra of the single rods clearly span the spectrum of the ensemble, showing the significance of single particle spectroscopy in uncovering ensemble-averaging effects. Figure 1(b) shows nonlinear response of emission intensities of single quantum rods as a function of two-photon excitation power. A quadratic law was fitted in agreement to two-photon excitation

Single quantum rods' emission showed strong polarized emission signifying the existence of a strong linear emission dipole consistent with previous reports. Figure 2(a) shows a pair of images of single particles fluorescence taken simultaneously. Each image represents a specific polarization component, the left image marked 0^o represents the vertical polarization component whereas the right image marked 90^o represent the horizontal polarization component. The emission of the two circled-particles is visibly polarized (vertically polarized) since it appears clearly in the left frame (vertical polarization) and is greatly dimmed in the right frame (horizontal polarization), from which one can conclude that the circled rods are oriented vertically [13]. We expedited a full and comprehensive study of the emission polarization by rotating the fluorescence image polarization using a half wave plate, and acquiring a series of images for each angle and extracting the intensity counts of the two polarization-components of each particle. The polarization degree $P = \frac{I_{\perp} - I_{//}}{I_{\perp} + I_{//}}$ was plotted as a function of the analyzer angle yielding linear polarized emission. Figure 2(b) shows the polarization degree as a function of the rotation angle for two particles from the core/shell QR sample of shorter length (4 nm

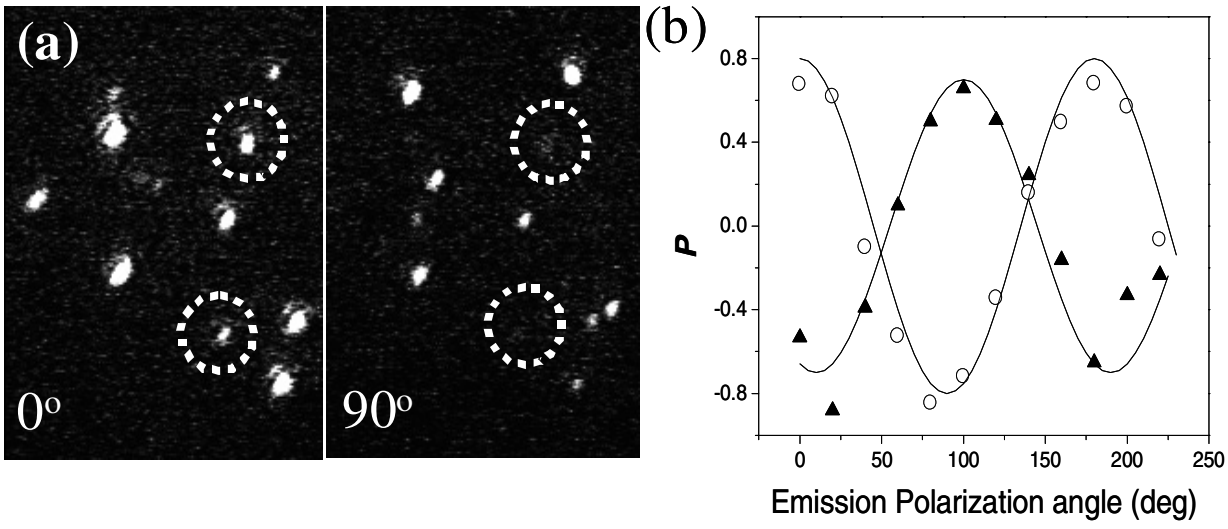

Figure 2. (a) Split image of the emission polarization components (0^o-vertical, 90^o-horizontal) showing linearly polarized emission (circled particles) (b) Emission anisotropy ratio P (see text) as a function of the emission polarization angle fitted with a sinusoidal function.

diameter, 11 nm length) and fitted with a sinusoidal function.
All QRs samples showed strong polarized emission with polarization degree ranging from 0.7 to 0.9 as reported previously [13], while the dots showed little to no polarization dependence.

More interestingly, the two-photon non-linear absorption polarization was investigated. Two-photon absorbance probes a transition manifold unlike linear absorbance due to different parity and angular momentum selection rules [9]. The emission intensity induced by two-photon excitation is proportional to $\left|EE:T\right|^2$ (eq. 1) yielding enhanced angular selectivity compared to the linear absorption case proportional to $\left|\vec{\mu}\bullet\vec{E}\right|^2$ (eq. 2), where $\vec{E}$ is the polarization of the exciting light, T is the two-photon absorptivity tensor, and $\vec{\mu}$ is the transition dipole moment [19,20].
Fig 3 shows two pairs of fluorescence images of the same quantum rods taken from the sample of shorter rods mentioned above, the left pair represents the emission components of both polarizations, while the exciting laser is in a vertical polarization (i.e. 0^o), while the right pair shows the same image component with the exciting laser changed to horizontal polarization (i.e. 90^o). The brackets in the corner of each image point out first the laser polarization and second the emission polarization, i.e. (Laser,Emission), so that (0^o,90^o) means that the laser is polarized vertically and the emission component is the horizontal component. The fluorescence of two particles is circled and marked as (I), and (II), by which one can track their behavior due to change of exciting laser polarization. In the left pair, the QR marked as (I) has a stronger horizontal fluorescence component indicating that the QRs orientation is more to the horizontal, while the QR marked as (II) has a stronger vertical component indicative of orientation closer to vertical. This is further indicated in the right pair, from which one can see that by changing the laser polarization the horizontal direction yields fluorescence enhancement of the particle with orientation closer to the horizontal (particle (I)), while the fluorescence of the particle which is oriented more to the vertical (particle (II)) can bee hardly seen. This behavior is fully consistent with a two-photon absorption dipole, which is oriented parallel to the QR long axis. This property was investigated systematically in all three samples. The laser orientation was rotated by a small angle and a pair of emission images was acquired. By analyzing a series of images for each sample, and extracting the emissions' intensity counts as a function of the exciting laser polarization angle we resolved the full character of quantum rods' polarized two-photon absorbance. The normalized intensity counts were plotted for each particle as a function of the excitation angle as shown for two particles in figure 4 (a) (4x11 nm sample) and 4(b) (4x24 nm

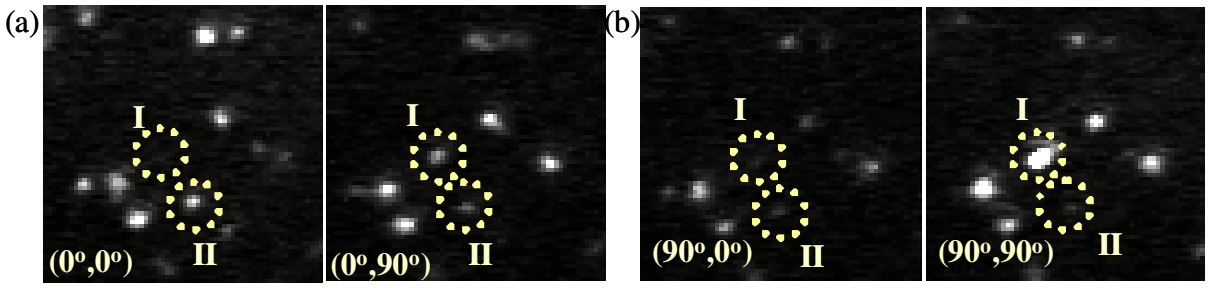

Figure 3. Split image acquired simultaneously of both polarization components for vertically polarized excitation (a) and horizontally polarized excitation (b). The two circled particles, one oriented more vertically (I) and the other horizontally (II) show strong response to changed laser polarization.

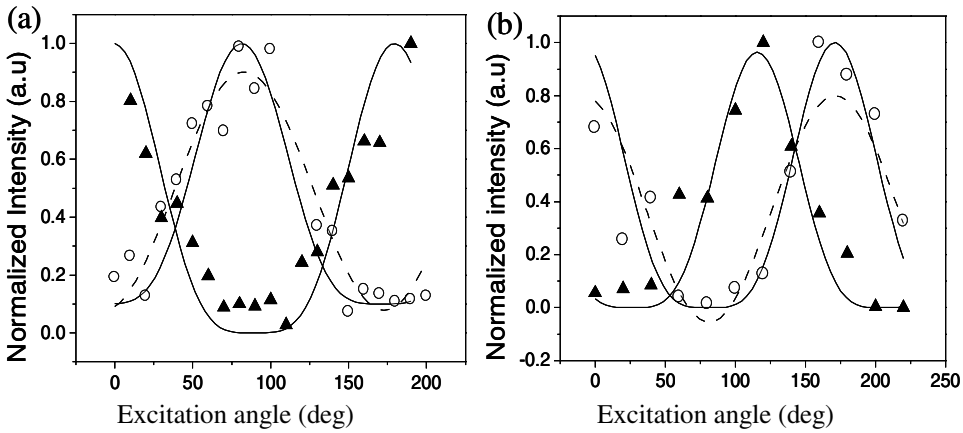

Figure 4. Emission intensity dependence of excitation angle, for two single QRs from the 4x11 nm sample (a) and 4x24 nm sample (b) fitted with $\cos^4(\phi)$ (lines) verifying theoretical predication. Dotted line shows a $\cos^2(\phi)$ behavior of one photon excitation which obviously serves as a poor fit here.

sample) revealing the unique two-photon absorption angular dependence.

Using eq. 1, we consider a linearly x - polarized field propagating along z, where the QR transition dipole lies in the x-y plane (sample plane) at an arbitrary orientation. Taking into account linear absorption dipole behavior, the two-photon absorptivity tensor has a reduced form of a single diagonal element T_{11} in the rod frame. This leads to a two-photon induced fluorescence intensity dependence of $\sin^4(\theta)\cos^4(\phi)T_{11}^2$ where θ is the angle between the dipole and the normal to the sample plane (x-y) and ϕ is the angle between the laser polarization and the two-photon transition dipole [19,20]. The dependence on θ and ϕ is separable, and the polarization measurement is sensitive to the projection of the dipole in the sample plane so the $\cos^4(\phi)$ dependence should be seen for any value of θ. Moreover, in our case, since the QRs were deposited directly on the substrate without the use of a thin layer of a polymer, the attractive rod-substrate interaction will clearly favor θ angles close to 90^o. We therefore consider the intensity dependence of $\cos^4(\phi)$, providing good agreement with the experimental angular dependence as seen in Figure 4 (solid lines). It is important to note that the observed $\cos^4(\phi)$ dependence for the two-photon excitation case is different from the $\cos^2(\phi)$ dependence observed for the single-photon excitation case [21]. For comparison we present in dashed line also fits to a $\cos^2(\phi)$ dependence for some of the traces. It is seen, although there is noise, that $\cos^2(\phi)$ does not fit the data well, especially in the flat regions where the excitation is minimal. This is also reflected in the objective fit quality parameters.

CONCLUSIONS

Two-photon polarization microscopy of single CdSe/ZnS nanorods revealed strong polarization behavior of both non-linear absorption and emission. The emission polarization is observed to be linear and parallel to the QRs axis as reported previously [21]. The two-photon absorption dipole of single QRs found to be highly polarized in full agreement with theoretical predication. This unique polarized absorption behavior being more sensitive than the one photon

polarized absorption, could serve as potential material in many applications including optical study of biological specimens and optoelectronic devices, where the sharp polarization behavior can serve as a useful tool in tracking and controlling optically active environments. This method enables us the specifically locate the dipole axis in the plane, and facilitates selection of a certain dipole axis with the laser polarization. The observed property reveals the quasi one-dimensional nature of the QRs even for aspect ratios as small as three with length above ~ 10 nm. This ability is of significant importance for future nanotechnology applications of QRs.

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