Wavelength scaling for multiphoton absorption in semiconductor quantum dots

Wei Ji[1], Yingli Qu[1], Jun Mi[1], Yuangang Zheng[2], and Jackie Y. Ying[2]

[1] *Department of Physics, National University of Singapore, Singapore 117542, Republic of Singapore*

[2] *Institute of Bioengineering and Nanotechnology, Singapore 138669, Republic of Singapore*

We report direct measurements of both magnitude and spectral dispersion of two-photon absorption in organic-capped CdSe quantum dots and three-photon absorption in organic-capped ZnO quantum dots by the use of open-aperture Z-scan technique with femtosecond laser pulses in the wavelength range of 720–950 nm. We find that these nonlinear coefficients are at least an order of magnitude greater than their bulk counterparts. Our experimental data are compared with theories and the rules for wavelength scaling are discussed.

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Recently, semiconductor quantum dots (QDs) in colloidal form have attracted attention due to their applications in multiphoton microscopy. Multiphoton absorption (MPA) in QDs has been investigated by multiphoton excitation spectroscopy[1−4]. With such a technique, the MPA action cross sections are measured, which is the product of the MPA cross section and the quantum efficiency of multiphoton-excited fluorescence, and is of direct relevance to applications of three-dimensional (3D) fluorescence imaging. However, such measurements are ambiguous to determination of absolute MPA coefficients and to understanding of the physics of MPA in QDs. Here we report direct measurements of both magnitude and spectral dispersion of two-photon absorption (2PA) in organic-capped CdSe QDs and three-photon absorption (3PA) in organic-capped ZnO QDs by the use of open aperture Z-scan technique with femtosecond laser pulses in the wavelength range of 720–950 nm.

The CdSe QDs investigated in this report were capped with a layer of glutathione, while the ZnO QDs were coated with oleic acid. The diameters of the CdSe and ZnO cores were 2.2 and 5.0 nm, respectively. The CdSe QDs were dispersed in water, while the ZnO QDs were in chloroform. These solutions were contained in 1-mm-thick quartz cells for the following optical studies at room temperature. The 2PA and 3PA coefficients of the QDs were measured with Z-scan technique[5]. The sample cell was moved through the focus of a laser beam and the transmitted laser power was detected completely (open aperture). The laser beam was provided by a Ti:sapphire laser with pulse durations of 120–150 fs, depending on the laser wavelength, which was tunable from 720 to 950 nm.

From the Z-scans, we extract the 2PA coefficient of the NC-liquid composite (β') with standard procedure described in Ref. [5]. The 2PA coefficient of QDs (β) is inferred by the use of

$$\beta = \frac{n_{\rm liquid}^2 \beta'}{n_{\rm QD}^2 f_\nu |f|^4},$$

where f_ν is the volume fraction of QDs, $|f|^4$ is the local-field correction facto, and $n_{\rm liquid}$ and $n_{\rm QD}$ are the refractive indices of the liquid and QD, respectively. In Fig. 1, the normalized 2PA coefficient is plotted as a function of the ratio of the photon energy ($\hbar\omega$) to the fundamental absorption edge (E_g). For comparison, we have also measured the 2PA coefficient of bulk CdSe crystal under the same experimental condition. The 2PA coefficient of bulk CdSe are in excellent agreement with the theoretical expression, $(2\hbar\omega/E_g - 1)^{3/2}(2\hbar\omega/E_g)^{-5}$ derived from a two-parabolic-band theoretical model[6,7]. We compare the normalized 2PA coefficient of the CdSe QDs to a spherically-confined, effective-mass model which has been used by Schmidt *et al.*[3] to numerically simulate the 2PA cross section for CdSe QDs (3.2 ± 1 nm in diameter). We convert their calculations to the normalized 2PA coefficients with a volume fraction of 0.18% and a density of NCs of 3.0×10^{17} cm^{-3}. Within an order of magnitude, agreement can be reached as shown in Fig. 1. It should be emphasized that the model of Schmidt *et al.*[3] excludes the effects of surface states, and hence, its conclusion may be regarded for the ideal case. The data in Fig. 1 demonstrate that the magnitude of 2PA in our CdSe QDs approaches to the ideal situation.

Figure 1 shows, however, that the discrete nature is less pronounced than the theoretical calculation. It is attributed to a collection of contributions from various broadening mechanisms such as size dispersion, phonon excitations at room temperature, and others. Interestingly, Fig. 1 suggests that the envelop of the 2PA spectra

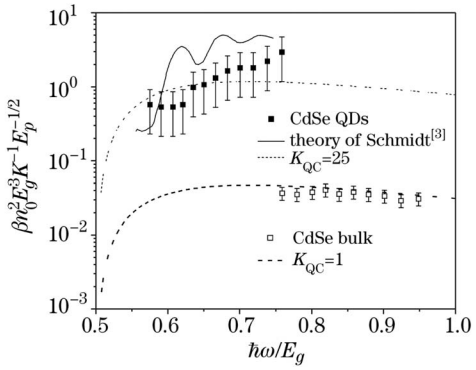

Fig. 1. Normalized 2PA coefficient versus $\hbar\omega/E_g$, where $\hbar\omega$ is the photon energy, E_g the fundamental absorption edge, n_0 the refractive index, $K = 3100$ (eV)$^{5/2}$·cm·GW^{-1}[7], $E_p = 21$ eV[7] and β the 2PA coefficient in cm/GW. The symbols are the experimental data, the dashed lines are calculated by $K_{\rm QC}(2\hbar\omega/E_g - 1)^{3/2}(2\hbar\omega/E_g)^{-5}$, and the solid line is the theoretical modelling converted from Schmidt's calculation[3].

of colloidal QDs should approximately follow the wavelength scaling predicted by the two-band model for bulk crystals with an enhancement factor, i.e., $K_{\rm QC}(2\hbar\omega/E_g-1)^{3/2}(2\hbar\omega/E_g)^{-5}$ and $K_{\rm QC}$ is the enhancement factor. This enhancement is dictated by the size, material, interfacial condition, and broadening mechanisms for excitonic transitions. Both interfacial condition and broadening mechanisms impose enormous complexity in theoretical derivation for the 2PA spectrum. But the $K_{\rm QC}$ value can be easily determined by Z-scan experiments, as demonstrated here.

From the Z-scans, we obtain the 3PA coefficients (γ) for the ZnO QDs with a volume fraction of 0.7% and a density of NCs of 1×10^{17} cm^{-3}, as shown in Fig. 2. For comparison, Fig. 2 also presents our measurement on the 3PA spectrum of bulk ZnO crystal from the same experiment. Clearly, the 3PA coefficients of the ZnO QDs are one to two orders of magnitude larger than those of bulk ZnO. To the best of our knowledge, no rigorous, first-principles calculations are available in literature for the 3PA of QDs. Therefore, we compare our data to 3PA theories for bulk semiconductors. There have been two approaches under the two-band approximation: the first one, developed by Wherrett[6], uses the first-order perturbation theory with maximum available interband excitations and de-excitations; and the second one includes a single, virtual interband transition and two self-transitions[8]. Wherrett's theory leads to a wavelength scaling of $(3\hbar\omega/E_g-1)^{1/2}(3\hbar\omega/E_g)^{-9}$, while the second approach results in a differentiated dispersion of $(3\hbar\omega/E_g-1)^{5/2}(3\hbar\omega/E_g)^{-9}$. We plot the two theoretical curves in Fig. 2, illustrating that the 3PA spectral dispersion of bulk ZnO is close to the theory of Brandi and Aroujo[8], while the 3PA spectrum of ZnO QDs follows the Wherrett's prediction[6] with an enhancement factor of $K_{\rm QC}=36$. In conclusion, we have found that the 2PA and 3PA coefficients of organic-capped QDs are at least an order of magnitude greater than their bulk counterparts. Our experimental data are compared with theories, and wavelength scaling for 2PA and 3PA in QDs is discussed. Such wavelength scaling revealed by our data should not only give valuable insight to the understanding of 2PA and 3PA processes in QDs, but also provide rules to practical designing of colloidal QDs for multiphoton microscopy.

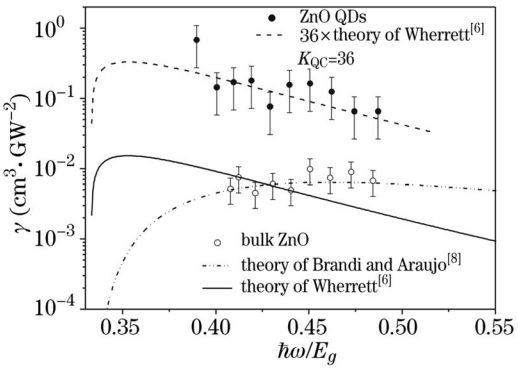

Fig. 2. 3PA coefficient versus $\hbar\omega/E_g$, where $\hbar\omega$ is the photon energy, E_g is the fundamental absorption edge, and γ the 3PA coefficient. The symbols are the experimental data, the solid and dashed lines are calculated from Wherrett's theory[6], and the theory of Brandi and Araujo[8], respectively. The log-dashed line is calculated from Wherrett's theory with a multiple of $K_{\rm QC}=36$.

W. Ji's e-mail address is phyjiwei@nus.edu.sg.

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