Two-photon-enhanced three-photon absorption in transition-metal-doped semiconductor quantum dots

X B Feng, G C Xing and W Ji

Department of Physics, National University of Singapore, Singapore 117542, Singapore

E-mail: phyjiwei@nus.edu.sg

Received 25 July 2008, accepted for publication 16 September 2008
Published 14 January 2009
Online at stacks.iop.org/JOptA/11/024004

Abstract
We report the observation of two-photon-enhanced three-photon absorption (3PA) in transition-metal-doped semiconductor quantum dots (d-QDs) in the near-infrared spectral region. Due to the degeneracy between two-photon transitions to the states of metal ions inside the bandgap and three-photon transitions to the excitonic state, the 3PA cross-section is greatly enhanced in comparison with the predictions by the 3PA theory derived under the four-band approximation. Together with the enhancement in their photoluminescence, such an enhancement mechanism is highly desirable in the design and optimization of fluorescent d-QDs for potential applications based on three-photon-excited fluorescence.

Keywords: transition-metal-doped semiconductor quantum dots (d-QDs), three-photon absorption, two-photon absorption, defect state

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, semiconductor quantum dots (QDs), or nanocrystals (NCs), have received considerable attention due to their potential applications in optical switching for optical communications, three-dimensional optical data storage, optical limiting for protection of optics sensors from laser-induced damage, three-dimensional confocal imaging for biological specimens, and photodynamic therapy [1–6]. In these applications, semiconductor QDs play an essential role in laser excitation through multi-photon absorption, namely, two-photon absorption (2PA) or three-photon absorption (3PA). Compared with 2PA, longer excitation wavelengths may be utilized in 3PA-based applications to provide deeper penetration depths in absorptive media and higher spatial resolution [7, 8]. Therefore, the understanding of 3PA in semiconductor QDs is of key importance to 3PA-related technologies as well as of academic interest.

There have been tremendous advances in experimental investigations into 3PA in colloidal semiconductor QDs. Since 2004, there have been many reports [6, 9–12] on the characterization of 3PA in wide-gap semiconductor QDs made of CdS, CdSe, ZnS and ZnSe, some of which are simply capped by an organic layer in order to be dissolvable and stable in liquid; and others are made into core–shell structures for the improvement of light emission properties. With femtosecond pulsed excitation, Chon and his co-workers [9] measured the three-photon-excited band-edge and trap-state emission of colloidal organic-capped CdS QDs, and concluded that the 3PA cross-sections are on the order of $10^{-79}$ cm$^6$ s$^2$ photon$^{-2}$, which is three to four orders of magnitude higher than for previously reported common UV fluorescent dyes. The 3PA of glutathione (GSH)-capped ZnS QDs in water was determined to be $\sim 2.7 \times 10^{-78}$ cm$^6$ s$^2$ photon$^{-2}$ [10] using both Z-scan and transient transmission techniques with femtosecond laser pulses at 780 nm. The 3PA of organic-capped CdSe QDs in hexane solution of five different dot sizes was investigated systematically with femtosecond laser pulses at 1300 nm [6]. Very recently, Lad et al [11] and Xing et al [12] reported their measurements of 3PA cross-sections for organic-capped ZnSe QDs and/or core–shell ZnSe/ZnS QDs in solution. Furthermore, the 3PA cross-section of colloidal copper-doped ZnSe/ZnS QDs was also observed to be $3.5 \times 10^{-77}$ cm$^6$ s$^2$ photon$^{-2}$, which is the largest value reported up to now for semiconductor QDs with femtosecond laser pulses.
Theoretical studies, however, have lagged behind, with only two reports [13, 14] up to now. We have developed a frequency-degenerate 3PA theoretical model [14], based on the strategy employed by Fedorov et al [15] for treatment of 2PA in semiconductor QDs. It is found that our model is in good agreement with the measured 3PA cross-sections of undoped ZnS and CdSe QDs, within one order of magnitude. The model predicts the increase in the 3PA cross-section with the size of QDs in the strong confinement regime (QD radius < or \( \approx \) a\(_b\), the exciton Bohr radius). Such an insightful knowledge is of direct relevance to engineering and optimizing colloidal semiconductor QDs for 3PA-related technologies.

Here we present the observation of enhancement in the 3PA of doped QDs (d-QDs): two-photon-enhanced three-photon absorption. Within the bandgap of wide-gap semiconductor QDs, there inevitably exist some energy levels relating to surface/interface/defect states, or impurity states can be intentionally or unintentionally introduced, as shown in figure 1. If d-QDs are chosen in such a way that the excitonic energy matches the energy of three photons (3\( \bar{\omega} \)) and the energy difference between the ground states and the impurity (or the dopant, if it is intentional) states is equal to the energy of two photons (2\( \bar{\omega} \)), the 3PA should be enhanced by the 2PA. Similar enhancement has been observed in the four-photon absorption of polydiacetylene-PTS [16] due to the degeneracy of three-photon and four-photon transitions. Normally, the density of states of the surface/interface/defect/impurity in semiconductor QDs is largely dependent on the synthesis processes. However, it is well established that intentional doping is an effective method in semiconductor electronics or optoelectronics to alter the electronic or optical properties. In addition, suitable dopants in semiconductors can also significantly enhance the photoluminescence, which is highly desirable for bio-imaging applications.

In section 2, we first present the derivation of the 3PA theory for direct wide-gap semiconductor QDs without consideration of the existence of energy levels inside the bandgap. In section 3, we report the experimental details of the synthesis of organic-capped core–shell ZnSe/ZnS QDs, that are undoped or doped with Mn ions, and the femtosecond Z-scan experiment employed to measure the 3PA. By comparing the experimental findings with the 3PA model, we highlight the two-photon-enhanced 3PA cross-sections in section 4. Finally, the conclusions are presented in section 5.

2. Theory for 3PA in ZnSe QDs

Third-order time-dependent perturbation theory furnishes the following equation for the transition probability rate per unit volume of electrons in an initial state \( i \) being excited to a final state \( f \) by the simultaneous absorption of three photons, each of energy \( h\bar{\omega} \) [17]:

\[
W^{(3)} = \frac{2\pi}{\hbar} \sum_{i,f} |M_{fi}|^2 \delta(E_f - E_i - 3h\bar{\omega})
\]

(1)

\[
M_{fi} = \sum_{m,n} \left( E_m - E_n - 2h\bar{\omega} - ih\gamma_m (E_n - E_i - h\omega - ih\gamma_n) \right).
\]

(2)

where \( E_i, E_f \) and \( E_m (E_n) \) represent the energies of the initial, final and intermediate states of an electron, respectively. \( H_{int} = (e/\epsilon_0)A \cdot \mathbf{p} \) describes the electron–photon interaction. \( A = A\mathbf{e} \) is the vector potential of a light wave with amplitude \( A \) and polarization vector \( \mathbf{e} \), \( \mathbf{p} \) is the electron momentum operator, and \( \gamma \) is the inverse of the lifetime in each excited state. The energy states can be calculated from the Schrödinger equation in the effective-mass approximation for the four-band model of a semiconductor QD with an isotropic and parabolic electronic spectrum, neglecting the coupling of three valence bands (heavy hole: hh, light hole: lh, spin-orbit-split hole: so) and the coupling between the valence band and the conduction band.

As for direct bandgap semiconductor QDs, four independent bands are taken into consideration, explicitly including the doubly degenerate conduction band and two-fold degenerate bands of hh, lh, and so; all the effective masses are constants, and there is no band mixing between the light and heavy holes in the valence bands [15]. It is also assumed that electrons and holes are located in a spherical potential well of radius \( R \) with infinitely high barrier. Under the condition of strong confinement (\( R < \approx a_b \)), the Coulomb electron–hole correlation is negligible.

Since frequency-degenerate 3PA is a process wherein three photons whose energies are the same are absorbed by the QD simultaneously through two virtual states to reach the excited state, each integrated 3PA process \( h_f \rightarrow c \) contains two intraband transitions and one interband transition. Figure 2 illustrates three possible scenarios. Under the groundwork of interband and intraband transition matrix elements of the electron–photon interaction in QDs in Fedorov’s 2PA theory [15], considering the orientations and size distribution.
of QDs, the 3PA coefficient $\alpha_3$ for an ensemble of QDs is related to the average three-photon generation rate $\bar{W}^{(3)}$ by

$$\alpha_3 = \frac{6\hbar \omega}{N} \int \bar{W}^{(3)} f(R) \, dR,$$

where $N$ is the QD concentration and $I$ is the incident light intensity, $I = \frac{\varepsilon_{\omega}^2}{8\pi^2 c^2} A^2 (2\pi c)^{-1}$, where $\varepsilon_{\omega}$ is the dielectric constant of the semiconductor at the light frequency. In the experimental studies, the inhomogeneous size dispersion is characterized by a size-distribution function $f(R)$, the shape of which results from the conditions of sample preparation. Usually, the Gaussian function [18] and the Lifshits–Slezov distribution [19] are mostly used. For an arbitrary function $f(R)$, using the properties of the $\delta$ function, the 3PA coefficient can be expressed as the product of an envelope amplitude and an average form function,

$$\alpha_3 = B \sum_{j=1}^{3} \left| F_{c,b_j} \right|^3$$

where the amplitude of the envelope and the average form function are given by the following two expressions, respectively:

$$B = \frac{6\pi \alpha N}{\varepsilon_{\omega}^{3/2}} \left( \frac{8\pi e^2}{3\alpha c^2} \right)^3 (P h)^2,$$

and

$$\left| F_{c,b_j} \right| = \frac{1}{2\Delta_{b_j}} \sum_{\rho_i, \rho_0} \left( I_2 \delta_{b_j, b_{j+1}} + I_0 \delta_{b_j, b_{j-1}} \right) \times \left( I_1 \delta_{b_j, b_{j+1}} + I_0 \delta_{b_j, b_{j-1}} \right) T_{\rho_i, \rho_0}^{(b_j)} \left( R_{\rho_i, \rho_0}^{(b_j)} \right)^3 \times \frac{\xi^2 l^2}{(\xi^2 - \xi_{\rho_0}^2)^2 (\xi^2 - \xi_{\rho_0}^2)^2} \left( R_{\rho_i, \rho_0}^{(b_j)} \right)^3.$$

The transition radius has been introduced in equation (6) and it is given as follows:

$$R_{\rho_i, \rho_0}^{(b_j)} \left[ \frac{\hbar^2}{2\Delta_{b_j}} \left( \frac{g^2 \xi^2 l^2}{m c + m_{b_j}} \right) \right] \frac{1}{\sqrt{2}}$$

and $\Delta_{b_j} = 3\hbar \omega - E_{b_j}$, $m_a$ is the effective mass in the $a$ band. $\xi_{b_j} = \xi_{a,b_j}$ is the $n$th root of the $l$th-order spherical Bessel function, $j_l(\xi_{a,b_j}) = 0$.

The corresponding selection rules for a three-photon transition can be precisely obtained. Together with the one-photon-transition selection rule, it is easily found that a three-photon transition can occur from the valence band to the conduction band for which the quantum number of the electron ($l_1, m_1$), hole ($l_0, m_0$), and the intermediate state ($l_2, m_2$), satisfy the relations $l_2 - l_0 = \pm 1, l_2 - l_1 = \pm 1, m_2 - m_0 = 0 \pm 1$, and $m_2 - m_1 = 0 \pm 1$. In most experiments, 3PA is measured in terms of the 3PA cross-section, $\sigma_3$, which is defined as

$$\sigma_3 = (\hbar \omega)^2 \alpha_3 / N.$$

Following the analytical expressions derived above, we have calculated the frequency-degenerate 3PA cross-sections for ZnSe QDs, with a Gaussian size distribution [18]. Hereinafter, the calculations and discussions are for ZnSe QDs using the following parameters [20]: $E_g = 2.82$ eV, $\Delta_{so} = 0.43$ eV, $m_e = 0.14 m_0$, $m_h = 1.44 m_0$, $m_{hh} = 0.149 m_0$, and $m_{so} = 0.30 m_0$.

By applying our 3PA model to a system consisting of a large number of ZnSe QDs, their calculated 3PA spectra are shown in figure 3 with a Gaussian size distribution (FWHM = 20%) and five different average radii. It is found that the 3PA cross-sections are in the range from $10^{-78}$ to $10^{-77}$ cm$^6$ s$^2$ photon$^{-2}$ in the spectral region of interest, with the precise values depending on both the average size of the QDs and the incident light wavelength. For a given average radius in the range from 2.0 to 2.4 nm, the 3PA cross-section approaches zero as the laser wavelength is increased to or is beyond $\sim 1200$ nm, that is the triple of the center wavelength for the lowest exciton, $1S_{1/2}(e) \rightarrow 1S_{3/2}(h)$. At a fixed light wavelength, the 3PA cross-section increases with the increase of QD radius, similar to the 2PA case [21]. The positions of peaks in the 3PA spectra are determined by the energy denominators in the term $T_{\rho_i, \rho_0}^{(b_j)} \left( R_{\rho_i, \rho_0}^{(b_j)} \right)$ in equation (6), which is indirectly dependent on the QD transition radius. The larger the QD size is, the denser the energy state becomes. As
Calculated low-energy spectra of the form function $F_{c,h_1}$ for ZnSe QDs.

As a consequence, this leads more three-photon transitions to be squeezed to a particular wavelength. In order to demonstrate this explanation, figure 4 depicts the low-energy spectra of the form function $F_{c,h_1}$ for three average radii of ZnSe QDs. It is obvious that there is a low-energy threshold which shifts to lower energies when increasing the average radius of the QDs. In addition, the energy density of the lines, or the number of lines per given energy range, increases with the increase in the average radius of the QDs.

3. Experimental details

The synthesis of ZnSe/ZnS QDs was based on the reaction of zinc acetate with sodium hydroselenide in dimethylsulfoxide (DMSO) as solvent. Sodium hydroselenide was prepared by mixing sodium borohydride and selenium powder in methanol under nitrogen. When the selenium powder was completely reduced by NaBH$_4$, 10 ml of freshly prepared NaHSe solution (0.4 M in methanol) was added into another solution containing 50 ml of 0.2 M of zinc acetate with vigorous stirring. Then the NaHSe precursor and 6 ml of 1 M Na$_2$S solution were injected under vigorous stirring. The resulting mixture was precipitated with 10 ml of 1 M of mercaptopropionic acid (MPA), with pH adjustment to 11 with NaOH. After centrifuging and washing, the precipitate was re-suspended in water, and then heated to 95°C for 2 h to grow MPA-capped ZnSe/ZnS QDs to a final diameter of $\sim4.4$ nm.

The synthesis of Mn-doped ZnSe/ZnS QDs is briefly described in the following. 10 ml of freshly prepared NaHSe solution (0.02 M) was added into another solution containing 50 ml of 0.01 M ZnCl$_2$/MnCl$_2$ and GSH at a pH of 11.5 with vigorous stirring. After the injection of NaHSe precursor, 0.3 ml of 1 M Na$_2$S was injected under vigorous solution. The amounts of Zn, Mn, Se, S and GSH introduced were 0.5, 0.005, 0.2, 0.3 and 0.6 mmol, respectively, in a total volume of 50 ml. The resulting mixture was heated to 95°C, and the growth of GSH-capped QDs began immediately. The final diameter was 4.1 nm on average. In the d-QDs, 1% Zn ions in the core were substituted by Mn ions.

The as-prepared QDs in aqueous solutions were examined by taking their spectra of one-photon absorption and photoluminescence (PL) excited with a wavelength of 360 nm. The crystalline structures and sizes were studied by both x-ray diffraction (XRD) measurements and transmission electron microscopy (TEM). In order to determine the 3PA cross-sections, open-aperture Z-scans were conducted. The Z-scan set-up was similar to the one used in [22]. The laser pulses, of wavelengths ranging from 850 to 1064 nm, were provided by a Coherent Legend (seeded by Mira) pumped TOPAS-C operating at 1 kHz repetition rate. The full width at half maximum (FWHM) of the laser pulse duration was 200 fs. After the spatial filter, the spatial profiles of the pulses were of near-Gaussian distribution. The pulses were then divided into two parts: one part was used as the reference, and the other part was focused with a focus lens ($f = 10$ cm) in the Z-scans. The beam radius at the focus was measured to be $12 \pm 2 \mu$m. The incident and transmitted laser pulses were monitored with two energy detectors (Laser Probe RKP 465). The QD solutions were contained in 1 mm thick quartz cells and Z-scanned along the focused laser beam in the Z-axis. All the Z-scans were carried out at room temperature. The maximum laser irradiance was controlled at 250 GW cm$^{-2}$, below which no laser-induced damage or degradation on the QD solution was observed. Furthermore, the Z-scans on pure water under the same experimental conditions confirmed that the water made no contribution to the Z-scan signals obtained from the QD solutions.

4. Results and discussion

As shown in figure 5, the one-photon absorption spectra can be fit with a series of Gaussian functions (black lines). The
as shown by the green downward arrow in figure 1, are involved in the interface/surface/defect states of undoped QDs, QDs. The origins of the PL bands are attributed to transitions d-QDs is found to be 11 times as strong as that of the undoped QDs and undoped QDs. The PL quantum yield of the d-QDs, as displayed by the red downward arrow in figure 1. Evidently, the dopant-related states of the Mn2+, -related states of the in-gap energy levels are a four-band approximation, neglecting the existence of energy levels inside the bandgap. The in-gap energy levels are a result of interfaces, surfaces, defects or impurities that are unintentionally or intentionally present in QDs. Their density is increased considerably if a significant amount of dopants is introduced on purpose. These dopant-related states play an important role in the enhancement. The enhancement is on resonance if the energy differences between the hole states in the valence band and the dopant states are equal to $2\hbar\omega$, with the excitonic energy matching $3\hbar\omega$. As illustrated by figure 7, the measured 3PA cross-section in the d-QDs is increased greatly as the energy of two photons approaches resonance. By conception, this type of enhancement is similar to resonance. By conception, this type of enhancement is similar to the one in figure 3.

The crystalline structures and sizes have been determined accurately by the XRD and TEM studies (not shown here). The average diameters are 4.1 and 4.4 nm, respectively, for the d-QDs and undoped QDs, with size dispersion of 20% or less. The crystalline structures and sizes have been determined accurately by the XRD and TEM studies (not shown here). The average diameters are 4.1 and 4.4 nm, respectively, for the d-QDs and undoped QDs, with size dispersion of 20% or less. The average diameters are 4.1 and 4.4 nm, respectively, for the d-QDs and undoped QDs, with size dispersion of 20% or less. The average diameters are 4.1 and 4.4 nm, respectively, for the d-QDs and undoped QDs, with size dispersion of 20% or less. The average diameters are 4.1 and 4.4 nm, respectively, for the d-QDs and undoped QDs, with size dispersion of 20% or less.

Table 1. Measured and calculated 3PA cross-sections. (Note: experimental errors are ±50%.)

<table>
<thead>
<tr>
<th>Quantum dots (QDs)</th>
<th>Diameter (nm)</th>
<th>Wavelength, $\lambda$ (nm)</th>
<th>$\sigma_3$ (cm$^6$ s$^2$ photon$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-doped ZnSe/ZnS QDs</td>
<td>4.1</td>
<td>850</td>
<td>$4.6 \times 10^{-78}$</td>
</tr>
<tr>
<td>Mn-doped ZnSe/ZnS QDs</td>
<td>4.1</td>
<td>880</td>
<td>$3.3 \times 10^{-78}$</td>
</tr>
<tr>
<td>Mn-doped ZnSe/ZnS QDs</td>
<td>4.1</td>
<td>920</td>
<td>$8.1 \times 10^{-78}$</td>
</tr>
<tr>
<td>Mn-doped ZnSe/ZnS QDs</td>
<td>4.1</td>
<td>950</td>
<td>$7.4 \times 10^{-78}$</td>
</tr>
<tr>
<td>Mn-doped ZnSe/ZnS QDs</td>
<td>4.1</td>
<td>1000</td>
<td>$1.3 \times 10^{-78}$</td>
</tr>
<tr>
<td>Mn-doped ZnSe/ZnS QDs</td>
<td>4.1</td>
<td>1064</td>
<td>$3.0 \times 10^{-78}$</td>
</tr>
<tr>
<td>ZnSe/ZnS QDs</td>
<td>4.4</td>
<td>850</td>
<td>$2.4 \times 10^{-78}$</td>
</tr>
<tr>
<td>ZnSe/ZnS QDs</td>
<td>4.4</td>
<td>880</td>
<td>$2.4 \times 10^{-78}$</td>
</tr>
<tr>
<td>ZnSe/ZnS QDs</td>
<td>4.4</td>
<td>920</td>
<td>$1.3 \times 10^{-78}$</td>
</tr>
<tr>
<td>ZnSe/ZnS QDs</td>
<td>4.4</td>
<td>950</td>
<td>$5.0 \times 10^{-78}$</td>
</tr>
<tr>
<td>ZnSe/ZnS QDs</td>
<td>4.4</td>
<td>1000</td>
<td>$4.6 \times 10^{-78}$</td>
</tr>
<tr>
<td>ZnSe/ZnS QDs</td>
<td>4.4</td>
<td>1064</td>
<td>$8.3 \times 10^{-78}$</td>
</tr>
</tbody>
</table>

Figure 6. Open-aperture Z-scans with 200 fs laser pulses. The top five Z-scans are shifted vertically for clear presentation.

It is interesting to notice that there are large discrepancies at longer wavelengths. At 1000 nm, the theoretical predictions should be $2.2 \times 10^{-78}$ and $1.8 \times 10^{-78}$ cm$^6$ s$^2$ photon$^{-2}$, respectively, for the d-QDs and undoped QDs. The experiments, however, show a 6-fold and 2.5-fold increase, respectively. At 1064 nm, a 100-fold increase can be found in the d-QDs. Such a large enhancement should be anticipated because the theoretical model in section 2 is derived under the four-band approximation, neglecting the existence of energy levels inside the bandgap. The in-gap energy levels are a result of interfaces, surfaces, defects or impurities that are unintentionally or intentionally present in QDs. Their density of states is increased considerably if a significant amount of dopants is introduced on purpose. These dopant-related states play an important role in the enhancement. The enhancement is on resonance if the energy differences between the hole states in the valence band and the dopant states are equal to $2\hbar\omega$, with the excitonic energy matching $3\hbar\omega$. As illustrated by figure 7, the measured 3PA cross-section in the d-QDs is increased greatly as the energy of two photons approaches resonance. By conception, this type of enhancement is similar to the one in figure 3.

lowest exciton, $1S_{1/2}(e) \rightarrow 1S_{3/2}(h)$, is peaked at 365 and 388 nm, respectively, for the d-QDs and undoped QDs. Thus, 3PA is expected to manifest itself in the spectral range from 750 to 1200 nm. The band-edge light emission is quenched, consistent with the previous reports [23, 24]. There is a broadband of PL centered at 590 and 498 nm, respectively, for the d-QDs and the undoped QDs. The PL quantum yield of the d-QDs is found to be 11 times as strong as that of the undoped QDs. The origins of the PL bands are attributed to transitions involved in the interface/surface/defect states of undoped QDs, as shown by the green downward arrow in figure 1, or are dominated by transitions involved in Mn$^{2+}$-related states of the d-QDs, as displayed by the red downward arrow in figure 1. The crystalline structures and sizes have been determined accurately by the XRD and TEM studies (not shown here). The average diameters are 4.1 and 4.4 nm, respectively, for the d-QDs and undoped QDs, with size dispersion of 20% or less.

Typical open-aperture Z-scans are depicted in figure 6. Evidently, the Z-scan signals increase with the laser wavelength. To extract the 3PA coefficient, the measured Z-scans are fit with the theory of Z-scan signal induced by 3PA [25], as shown by the solid lines in figure 6. Then, the 3PA cross-sections are inferred by equation (8). These values are summarized in table 1 and plotted as a function of the laser wavelength in figure 7. Within experimental errors, an agreement can be reached between the experiments and the theory at shorter wavelengths (<920 nm). This observation is also consistent with our previous report for colloidal ZnS QDs [14].
to the three-photon-enhanced four-photon absorption observed in polydiacetylene-PTS [16].

At wavelengths of 920 and 950 nm, the enhancement also manifests itself in the d-QDs, though these photon energies are off-resonance with the dopant states in terms of two-photon transitions. In this case, the states of the interface/surface/defect play a supplementary role in the enhancement, though their contributions to the PL signal are quenched as the excited electrons preferably relax to the dopant state in the d-QDs. In fact, the enhancement is in good agreement with the summation of the PL signals from the d-QDs and the undoped QDs, see the black dashed line, which reflect the total density of states inside the bandgap of the d-QDs.

It has been reported [23, 24] that transition-metal doping can enhance the PL quantum yield of d-QDs. In our case, we have found an increase of 11-fold in the PL quantum yield if ZnSe/ZnS QDs are doped with 1% Mn ions. More importantly, the findings presented here point out that the doping also results in the enhanced 3PA. Such double enhancements are highly desirable in the design and optimization of fluorescent QDs for applications of three-photon-excited fluorescence.

5. Conclusion

In conclusion, two-photon-enhanced three-photon absorption in organic-capped, core–shell, transition-metal-doped ZnSe/ZnS QDs has been revealed by comparing the theoretically calculated 3PA cross-sections with the experimentally measured ones in the near-infrared spectral region. Due to the degeneracy between two-photon transitions mainly to the states of dopants and the three-photon transition to the excitonic state, the 3PA cross-section is enhanced by two orders of magnitude at 1064 nm. Taking into account the enhancement in PL, such double enhancements make ZnSe/ZnS QDs doped with transition-metal ions a promising candidate for applications based on three-photon-excited fluorescence.

Acknowledgments

This work is supported by the National University of Singapore (Grant no. R-144-000-213-112). G C Xing and X B Feng would like to acknowledge the receipt of scholarships from the National University of Singapore and the China Scholarship Council, respectively. It is also acknowledged that the samples were synthesized by Y G Zheng and J Y Ying of A*Star Institute of Bioengineering and Nanotechnology, Singapore.

References