Observation of enhanced two-photon absorption in ZnS quantum dots at an ultraviolet wavelength

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Two-photon absorption (2PA) in zinc sulphide (ZnS) and Mn$^{2+}$-doped ZnS (ZnS:Mn) quantum dots (QDs) have been found to be potential materials because of their visible luminescence and interesting nonlinear optical (NLO) properties$^{[5−8,10−12]}$. Reports on the multi-photon absorption properties of ZnS QDs have been published previously. For example, two-photon absorption (2PA) has been reported by Zheng et al. with picosecond laser radiation at 532 nm in 0.5% Mn$^{2+}$-doped ZnS QDs$^{[7]}$. Some enhancements in 2PA have been reported in ZnSe/ZnS core/shell at 806 nm and in ZnS quantum structures at 532-nm laser pulses$^{[13,14]}$. However, to date, there has been no report on the measurement of NLO properties of ZnS and ZnS:Mn QDs in the ultraviolet (UV) region. In this letter, we present our observation of 2PA in undoped ZnS and ZnS:Mn QDs at an UV wavelength of 355 nm. The obtained values of the 2PA cross section of all the samples are 10$^6$ times larger than that of bulk ZnS$^{[11]}$.

The samples used in this work are freshly prepared through the chemical precipitation method$^{[11]}$. The synthesized undoped ZnS and 1% and 2.5% Mn$^{2+}$-doped ZnS samples are henceforth denoted as R$_I$, R$_{II}$, and R$_{III}$, respectively, unless otherwise specified. The UV-visible absorption characteristics of the samples, as obtained from the measurement in a spectrophotometer (Hitachi U-3010), are shown in Fig. 1. An X-ray diffraction measurement of the samples ensures the average particle size (radius) to be $\sim$1.5 nm$^{[10]}$.

The experimental z-scan set-up used for the measurement of NLO properties is a standard one$^{[2,8,15]}$. However, in the present experiment, the excitation source of 355-nm radiation is obtained through a third harmonic generation from a Q-switched Nd:YAG laser (10 ns, 10 Hz repetition rate). To avoid the absorption of the input beam in the lens material itself, a quartz lens with a focal length of 7.5 cm is used to focus the 355-nm radiation. The beam waist ($w_0$) and the confocal parameter ($z_0$) at the focus are 7 and 350 $\mu$m, respectively. After they are dispersed in methanol, the as-synthesized nanopowders are kept in a quartz cuvette with a path length ($L$) of 2 mm for the z-scan measurement, satisfying the thick sample condition ($L > n_0z_0$) in the present experiment. Here, $n_0$ is the linear refractive index of the samples at a 355-nm wavelength. In Fig. 1, the values of the linear absorption coefficient ($\alpha$) of R$_I$, R$_{II}$, and R$_{III}$ samples are 0.50, 0.33, and 0.47 cm$^{-1}$, respectively, at the excitation wavelength of 355 nm.

In the present experiment, the medium length is larger than the confocal parameter. Therefore, nonlinear refraction (NLR) should be considered in such type of thick medium, i.e., when a Gaussian beam is allowed to pass through the sample. According to the distributed lens model, the on-axis normalized open aperture (OA) transmittance ($T_{OA}$) can be written as$^{[14]}$

$$T_{OA} = \frac{1}{1 + 0.5C_0[\tan^{-1}(p + l) - \tan^{-1}(p)]} - 1,$$

(1)

where $p = z/n_0z_0$, $l = L/n_0z_0$, $C_0 = q_0(1 + \tanh(l/2)) \times [(3g_0/10) + (q_0^2/8)]$, $g_0 = \beta_{2PA}I_0n_0z_0$, and $q_0 = 2\pi\gamma n_0z_0/\lambda$. Here, $I_0$, $\beta_{2PA}$, and $\gamma$ are the on-axis peak irradiance at focus in W/cm$^2$, the 2PA coefficient, and the NLR coefficient of the sample, respectively, and $\lambda$ is the wavelength of the radiation used.

Figure 2 shows our experimental and theoretically fitted OA z-scan transmission traces of all the samples measured at the maximum input beam intensity of 27.4 GW/cm$^2$. Here, the symbols are the experimental points,

![Fig. 1. UV-visible absorption characteristics of undoped ZnS and ZnS:Mn QDs dispersed in methanol.](image-url)
The value of the intrinsic 2PA coefficient ($\beta_{2PA}^{int}$) of the samples is deduced using the relation $\beta_{2PA}^{int} = (n_0^{QDs})^2 / (n_0^{soln})^2 \times 4\pi / \lambda^4$, where $n_0^{QDs}$ is the refractive index of the QDs, and $n_0^{soln}$ is the refractive index of the solvent which depends on the dielectric constant of the solvent and QDs [12]. The refractive index $n_0^{QDs}$ of the QDs of radius $R$ can be obtained using the relation $n_0^{QDs} = \sqrt{1 + \frac{\lambda^2 \sigma_{2PA}}{4 \pi R}}$. The wavelength-dependent refractive index ($n$) of the bulk ZnS is calculated using the Sellmeier dispersion relation [10],

$$n^2 = 4.4175 + 1.7396\lambda^2 / (\lambda^2 - 0.07166). \quad (2)$$

Using the relation $\sigma_2 = \hbar c / 2\beta_{2PA}/N_0$ and $N_0 = 6.2 \times 10^{17}$ cm$^{-3}$, the 2PA cross section ($\sigma_2$) of all samples is calculated. The experimentally obtained values of $\beta_{2PA}^{int}$, $\sigma_2$, etc. for all the samples obtained in this work, along with the literature data for bulk ZnS and ZnS QDs, are summarized in Table 1. The obtained values of $\sigma_2$ of all samples are $\sim 10^7$ times larger than that of bulk ZnS, and they are at least one order of magnitude larger than those of ZnSe/ZnS core/shell and ZnSe QDs [12]. In Table 1, the calculated values of the NLR coefficient ($n_2$) of all samples are almost the same and of the same order of magnitude as that of bulk ZnS.

As the values of the incident photon energy ($E_p$) and the bandgap energy ($E_g$) of the sample are $\sim 3.5$ and $\sim 5.16$ eV, respectively; the condition $2E_p > E_g$ is satisfied in all samples. This finding clearly confirms the dominance of 2PA in the present experiment [13]. In another calculation, using the dispersion scaling rule given by Sheik-Bahae et al., the normalized 2PA maxima (peak) near the wavelength of 355 nm is obtained by taking the bandgap of the material of 5.2 eV (Fig. 3(a)) [15]. In Fig. 3(a), the curves correspond to the normalized 2PA coefficients with different semiconductor bandgap energy values of 3.6, 4, 4.5, 5.2, 5.5, and 6 eV, respectively. At $E_p = 5.2$ eV, the curve shows that the maximum (peak) of the normalized 2PA appears near 355 nm. Conversely, the other curves (i.e., for different bandgaps) show that the position of the maxima (peak) deviates from 355 nm, indicating the higher probability of occurrence of 2PA at 355 nm at the bandgap energy $E_g = 5.2$ eV. Thus, the suitable choice of the bandgap of the semiconductor and that of the corresponding wavelength is the best combination for obtaining a large 2PA.

OA z-scan transmittance traces are also collected at four different values of the input intensities for the R$_I$ sample. All the experimental data are theoretically fitted as described above. Based on the theoretical fitting, the intensity dependent values of $\beta_{2PA}^{int}$ are calculated, as shown in Fig. 3(b). In the same figure, the solid curve is obtained by a second-order polynomial fitting of the experimental data (symbols) to show only the trends of variation of the experimental data. In Fig. 3(b), with the increasing intensity $I_0$, the 2PA coefficients initially increase and then decrease with increasing $I_0$. The observed variation of the NLA coefficient with the intensity demonstrates the presence of two-photon-generated free-carrier nonlinearities resulting in the effective fifth-order nonlinearity under strong excitation [7,17–19]. The value of the free-carrier absorption (FCA) cross section induced by the 2PA in the R$_I$ sample is calculated from the measured intensity-dependent OA z-scan traces using the fast analytical procedure of Gu.

### Table 1. 2PA Coefficients, 2PA Cross Sections, and NLR Coefficients of All Samples Measured at 355 nm Wavelength at 27.4-GW/cm$^2$ Intensity

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_{2PA}^{int}$ (cm/GW)</th>
<th>$\sigma_2$ (GM)</th>
<th>$\gamma$ ($\times 10^{-14}$cm$^2$/W)</th>
<th>$n_2$ ($\times 10^{-12}$ e.s.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Work</td>
<td>Lit. Data</td>
<td>This Work</td>
<td>This Work</td>
</tr>
<tr>
<td>R$_I$</td>
<td>3.8 $\times 10^6$</td>
<td>1$^a$, 1.18$^b$, 1±0.3$^c$</td>
<td>2.12 $\times 10^5$</td>
<td>5.14 $\times 10^{-26}$</td>
</tr>
<tr>
<td>R$_{II}$</td>
<td>4.4 $\times 10^5$</td>
<td>2.47 $\times 10^5$</td>
<td>1.47</td>
<td>8.6</td>
</tr>
<tr>
<td>R$_{III}$</td>
<td>5.7 $\times 10^5$</td>
<td>3.20 $\times 10^5$</td>
<td>1.50</td>
<td>8.7</td>
</tr>
</tbody>
</table>

$^a$Bulk ZnS at 610 nm [11]. $^b$ZnS QDs at 532 nm [7]. $^c$ZnS QDs at 795 nm [12].
relation and FCA cross section (the slope (below the analytical procedure elaborated in Ref. [18], \( \beta \)) which corresponds to shown in Fig. 4, where the symbols denote the experimental data. From Eq. (3), the value of the NLA coefficient \( (\beta_{2\text{PA}}) \) for higher values of the incident peak irradiances \( (I_0) \). This plot is calculated by the fitted straight line is related to the FCA cross section \( (\sigma_a) \) of the sample by the following expression\[18\]:

\[
\sigma_a = -\frac{1.36 s E_p \times 10^{-9}}{\tau_e} \left( \frac{1 + 0.59 (\tau/\tau_e)^{1/3}}{0.59 (\tau/\tau_e)^{1/3}} \right) \sqrt{1 + 0.59 (\tau/\tau_e)^{1/3}}. \tag{4}
\]

By substituting \( E_p=3.5 \text{ eV}, s = 0.074 \), the free-carrier lifetime in ZnS(\( \tau_e=0.8 \text{ ns} \)[19]), and the duration of the incident laser pulse \( \tau = 10 \text{ ns} \) in Eq. (4), we obtain \( \sigma_a = -0.04 \times 10^{-18} \text{ cm}^2 \).

The average particle size of 1.5 nm of the QDs is less than the exciton Bohr radius of 2.2 nm in bulk ZnS. The huge enhancement in the 2PA cross section is attributed to the quantum confinement effects as well as to the large surface to volume ratio of the QDs. As the size is reduced, the oscillator strength is concentrated into only a few transitions, leading to the enhancement of the nonlinearity of the materials. Moreover, as described above, the use of the 355-nm wavelength in the present experiment also favors the large enhancement in the 2PA coefficient of ZnS QDs. In a QD, the absorption is determined by the confined transitions; however, in the refractive index, a large number of off-resonant but still bulk-like states are attributed\[20\].

In conclusion, we present here a 10\(^5\) time-enhanced 2PA coefficient both in the ZnS and (1–2.5\%) Mn\(^{2+}\)-doped ZnS QDs at 355 nm by the \( z \)-scan technique. This huge enhancement in the 2PA in the samples is attributed to the quantum confinement effects. The observation of intensity-dependent NLA in a sample is explained by considering the simultaneous presence of 2PA and 2PA-induced FCA in the investigated sample. As the particle size is reduced below the exciton Bohr radius of the material, the oscillator strength is concentrated into only a few transitions, leading to the enhancement of the nonlinearity of the materials. Moreover, the beneficial combination of the experimental parameters, such as the incident photon energy and the bandgap of the used samples, provides the highest probability for achieving 2PA in the investigated samples. The present observation of the enhanced NLA and NLR of the undoped and Mn\(^{2+}\)-doped ZnS samples at 355 nm, combined with our previous observations at 532 and 1064 nm\[5,8\], shows that these QDs are excellent materials for use in optoelectronic and bio-photonic devices.

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### References