Size dependence of nonlinear optical absorption and refraction of Mn-doped ZnSe nanocrystals

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Nonlinear refractive index and nonlinear absorption coefficient of high-quality Mn:ZnSe nanocrystals are measured by z-scan technique at 800 nm wavelength. The synthesized nanocrystals with nucleation doping have tunable wavelength (between 565–610 nm), high quantum yield (~50%), and high thermal as well as photochemical stabilities. The unique nanocrystal structure (with a MnSe core, Zn1−xMnxSe diffusion region, and an outer ZnSe layer) shows size-dependent nonlinear effects, which can be qualitatively explained by a simple model using crystal field. Studies of nonlinear optical properties are very important and necessary for high-power optical applications (such as light-emitting diodes and lasers) of such Mn-doped ZnSe nanocrystals. © 2007 American Institute of Physics. [DOI: 10.1063/1.2811713]

Although doped semiconductor nanocrystals have been synthesized more than twenty years ago, the developments in the synthesis of high quality Mn- and Cu-doped ZnSe,1–4 and Mn-doped CdS/ZnS core/shell5 nanocrystals have stirred new excitement in this field of making colloidal nanocrystals. Such transition metal-doped nanocrystals (d-dots) have many superior properties compared to the traditional semiconductor quantum dots,5–10 such as reduced self-quenching due to large Stokes shift, greatly suppressed host emission, and improved stabilities over thermal, chemical, and photochemical disturbances.1 Such greatly improved optical properties of d-dots, specifically those not containing any heavy metal ions, can be used to advance practical applications in biomedical labels,11 light-emitting diodes (LEDs),12 beads-based bar coding,13 and lasers.14

The traditional synthetic approaches for doping nanocrystals usually put both dopant ions and competitive host ions in the reaction systems, which result in large portion of nanocrystals without dopants. The recently developed technique is to decouple the doping from nucleation and/or growth through nucleation-doping and growth-doping strategies.1,4,5,10 By using such synthetic technique to prepare Mn2+:ZnSe d-dots, the resulting samples have very high dopant emission (>99% in intensity), tunable wavelength from 565 to 610 nm, and high photoluminescence (PL) quantum yield (QY) of about 40%–70%.1

With nucleation-doping procedure,1,4 the dopant uniformity can be well controlled and the PL spectrum shows a sharp emission peak (mainly from Mn2+ dopant) near 580 nm, which is separated from the host (ZnSe) absorption band, as shown in Fig. 1(a).1 Such large separation between host absorption band and dopant emission peak (Stokes shift) greatly reduces the reabsorption of the PL and is very important in certain applications. Since such d-dots can have potential high-power applications to improve next generation LEDs and nanocrystal lasers, the nonlinear optical properties of such d-dots can be very important and need to be investigated. In this work, we report our experimental measurements of nonlinear (two-photon) optical absorption and refraction of such Mn-doped ZnSe d-dots by using z-scan technique. Since the dot size and overcoating larger thickness can both greatly modify the QY and other optical properties,1 we specially investigate the dependence of nonlinear optical coefficients of samples on the thickness of the ZnSe overcoating layer with the same doped core.

The nanocrystalline Mn-doped ZnSe samples with particle sizes of 3.5, 5.0, 6.0, 7.0, and 8.0 nm in diameter (according to transmission electron microscopy images) are prepared using the nucleation-doping procedure as described in Ref. 1. The resulting Mn:ZnSe nanocrystals have the structure shown in Fig. 1(b), with a fixed small MnSe nanocluster core (~1.5 nm) and a diffused interface region between the nanocluster core and the ZnSe overcoating layer. For the same core size, samples with different ZnSe coating layers.

FIG. 1. (Color online) (a) The UV-Vis and PL spectra of the nucleation-doping Mn-doped ZnSe nanocrystals. Mn:Zn=1:22, T=280 °C for overcoating. (b) Theoretical structure model for Mn-doped ZnSe nanocrystal grown by nucleation doping. Here, a is the radius of the MnSe core, b is the radius of MnSe core plus Zn1−xMnxSe diffusion region, and c is the radius of the total Mn-doped ZnSe nanocrystal sphere.

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TABLE I. The radii of the core sizes, diffusion layers, and overcoating layers for the five samples, respectively.

<table>
<thead>
<tr>
<th>2c (nm)</th>
<th>a (nm)</th>
<th>b (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.745</td>
<td>0.924</td>
</tr>
<tr>
<td>5.0</td>
<td>0.743</td>
<td>0.983</td>
</tr>
<tr>
<td>6.0</td>
<td>0.740</td>
<td>1.042</td>
</tr>
<tr>
<td>7.0</td>
<td>0.736</td>
<td>1.116</td>
</tr>
<tr>
<td>8.0</td>
<td>0.731</td>
<td>1.206</td>
</tr>
</tbody>
</table>

The nonlinear optical measurements were done with the single-beam z-scan technique. The light source is a modelocked Ti:Sapphire laser with a high repetition rate of 82 MHz at the wavelength of 800 nm, which has a temporal width of about 565 fs and a peak power of up to 40 kW. The spatial profile of the laser beam was determined to be approximately Gaussian. The beam was then focused by a lens with the focal waist radius of $\omega_0 \sim 11 \mu m$ ($z_0=0.5 \text{ mm}$) at 800 nm, as determined from the measured beam divergence. To reduce the effect of the fluctuations in the pulse energy, another detector was used to monitor the pulse energy as a reference. All measurements were conducted at room temperature. All closed-aperture (CA) z-scan measurements were performed with a fixed linear transmittance of $S=4\%$, defined as the fraction of the beam energy passing through the far-field aperture. The open-aperture (OA) and CA z-scan traces may be fitted by two corresponding numerical programs based on Ref. 16 to obtain the nonlinear refractive indices. The sample’s parameters of $\alpha$ (linear optical absorption coefficient) and $L$ (sample thickness), as well as the laser’s parameters of $R$ (repetition rate), $t_{FWHM}$ (full width at half maximum of pulse’s duration), and AP (average incidence power of the laser beam), are required as the inputs for these numerical programs.

Figure 2(a) presents a typical CA z-scan trace for the small d-dots of diameter 3.5 nm. The sample was put in a quartz cell (1 mm thick) with a density of $2.7 \times 10^{-3} \text{ g/cm}^3$ in toluene solution. By fitting this trace to the standard theoretical calculation,16 we can obtain the third-order nonlinear refractive index $\beta$ to be 8.36 cm/GW. Figure 2(b) gives a typical OA z-scan trace for the same sample, which, by fitting with the theory, determines the nonlinear (two-photon) absorption coefficient $\gamma$ to be $1.37 \times 10^{-5} \text{ cm}^2/\text{GW}$. The same z-scan measurements were repeated for the d-dot samples with diameters of 5.0, 6.0, 7.0, and 8.0 nm, respectively, and the nonlinear refractive indices as well as nonlinear (two-photon) absorption coefficients were determined using the same procedures.

The measured nonlinear absorption coefficients and nonlinear refractive indices for the five d-dot samples are depicted in Figs. 3(a) and 3(b), respectively. As one can see that as the overcoating ZnSe layer increases, the nonlinear refractive index and nonlinear absorption coefficient both increase and show similar “saturation-like” behavior as the outside ZnSe layer gets thicker. The measured nonlinear refractive index and nonlinear absorption coefficient are comparable to the results obtained from Ref. 17. We have not found theoretical calculation in literature that can be used directly to describe the nonlinear optical
properties of our current d-dot system with the three-layer structure (e.g., a MnSe core, a thin Zn$_{1-x}$Mn$_x$Se diffusion region, and an outer ZnSe overcoating layer). To make a qualitative explanation of our experimentally measured results, as shown in Fig. 3, we consider a model used to treat related composite systems as a simple guidance.

We can first consider the doped nanocrystals as an effective particle inside a dielectric solution (with dielectric constant $\varepsilon_0$) in which the dielectric local field will affect the nonlinear susceptibility of the nanocrystals (NCs). The effective nonlinear susceptibility of the NCs is then given by

$$\chi^{(3)}_{\text{eff}} = p \chi^{(3)}_m,$$

where $\chi^{(3)}_m$ is the nonlinear susceptibility of the NCs, $p$ is the volume fraction of the NCs, and

$$f = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_{\text{eff}}},$$

is the modification factor due to local field of the involved dielectric medium. $\varepsilon_{\text{eff}}$ is the effective dielectric constant of the NCs. For the three-layer structure with a MnSe core (about 1.5 nm with dielectric constant $\varepsilon_1$), a diffusion region of Zn$_{1-x}$Mn$_x$Se (with dielectric constant $\varepsilon_2$), and an overcoating layer of ZnSe (with dielectric constant $\varepsilon_3$), the effective dielectric constant $\varepsilon_{\text{eff}}$ can be calculated to be

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_0(c^3 + 2B)}{c^3 - B},$$

$B$ is a function of dielectric constants ($\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$) and diameters of different layers [a, b, and c, as indicated in Fig. 1(b)]. It is clear that $f$ is a sensitive function of the diameters of different layers. Given the inner core diameter to be almost a constant for the five samples (about 1.5 nm), as the ZnSe shell layer gets thicker (d-dots get larger), the effective nonlinear index of refraction $n_2$ increases. Using the dimensions given in Table I and $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ values ($\varepsilon_1 = 5.4$, $\varepsilon_2 = 6.0$, and $\varepsilon_3 = 9.2$) obtained from literature, we plot $n_2$ as a function of d-dot diameter in Fig. 4. The square points are experimentally measured values from Fig. 3, which show remarkable agreement with the calculated curve based on Eqs. (1)–(3). Note that no free fitting parameters are used here since all the diameters of various layers and dielectric constants are either independently measured or are from literature.

The above results indicate that the size-dependences of the measured nonlinear refractive index and nonlinear (two-photon) absorption coefficient are mainly caused by the local field of the surrounding dielectric medium. Since the light emitters are the dopant Mn ions, the thickness of the overcoating ZnSe layer (or shell) acts as a protective shield to the light emitters. As determined earlier, thicker ZnSe layer can have better thermal, photochemical stabilities, and therefore higher QY. However, such thicker shell also increases nonlinear coefficient. Depending on specific applications, one needs to carefully choose appropriate overcoating ZnSe layer thickness to balance the desired high QY (and stabilities) and undesired nonlinear coefficient. In certain applications, one might demand high nonlinear coefficient for certain wavelength regions, such as optical limiting devices.

In summary, we have investigated nonlinear optical properties of high quality Mn-doped ZnSe nanocrystals and found that nonlinear index increases as the overcoating ZnSe layer gets thicker (with fixed core diameter). Such dot-size dependence of the optical nonlinearity can be explained well by the modified local field effect due to different shell thicknesses of the nanocrystals. Understanding nonlinear optical properties of the high efficient d-dots can be very important for the high-power optical applications of such d-dots and guide the desired structures for special linear and nonlinear optical applications.

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