High-order optical nonlinearities in nanocomposite films dispersed with semiconductor quantum dots at high concentrations

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Abstract. We describe the nonlinear optical properties of inorganic-organic nanocomposite films in which semiconductor CdSe quantum dots as high as 6.8 vol.% are dispersed. Open/closed Z-scan measurements, degenerate multi-wave mixing and femtosecond pump-probe/transient grating measurements are conducted. It is shown that the observed fifth-order optical nonlinearity has the cascaded third-order contribution that becomes prominent at high concentrations of CdSe QDs. It is also shown that there are picosecond-scale intensity-dependent and nanosecond-scale intensity-independent decay components in absorptive and refractive nonlinearities. The former is caused by the Auger process, while the latter comes from the electron-hole recombination process.

1. Introduction

Semiconductor quantum dots (QDs) that confine optically excited electron-hole pairs in all three space dimensions are of considerable interest in semiconductor physics and nonlinear optics \[1, 2, 3\]. In 2005 we suggested the possibility of optical bistable/multi-stable operations with nonlinear photonic lattice structure holographically recorded in a semiconductor QD dispersed nanocomposite film \[4\]. Later, we successfully demonstrated the holographic fabrication of fixed Bragg grating structure in a photopolymerizable nanocomposite film dispersed with CdSe QDs at the concentration up to 0.34 vol.% \[5\]. Such holographic patterning was made possible by holographic assembly of nanoparticles \[6\], resulting in the diffraction efficiency near 100%. We also reported the nonlinear optical response of uniformly cured nanocomposite films dispersed with CdSe QDs at concentrations as high as 0.91 vol.% \[7\]. Such a photopolymerizable nanocomposite material, the so-called photopolymerizable nanoparticle-polymer composite (NPC) \[8\], is prepared very differently from conventional inorganic nanocomposite materials that are generally fabricated by deposition/sputtering methods \[9\]. These nanocomposites can take advantage of the local field effect and the nanostructuring properties to control the linear optical, laser gain and nonlinear optical properties \[9, 10\]. Because of the syrup form of photopolymerizable NPCs they can be coated on any surfaces of substrate materials and...
can also be infiltrated in nanophotonic device structures. In this summary we describe the fabrication of photopolymerizable inorganic-organic nanocomposite films, as a nonlinear optical version of NPCs, at CdSe QD concentration as high as \( \sim 6.8 \text{vol.\%} \), approximately 7 times higher than our previous report [7]. We also describe the transient and steady-state nonlinear optical properties of the uniformly cured nanocomposite films that exhibit the cascaded fifth-order optical nonlinearity. We perform Z-scan measurements, degenerate multi-wave mixing (DMWM) and femtosecond pump-probe measurements to evaluate absorptive and refractive nonlinearities in the transient and steady-state responses.

2. Experiments

2.1. Material preparation

We employed the aqueous synthetic method [5] to prepare colloidal CdSe QDs in water [see Fig. 1(a)]. The average core size of the synthesized CdSe QDs coated with 2-(dimethylamino)ethanethiol was estimated to be approximately 3 nm by a transmission electron microscope. It was followed by the extraction of CdSe QDs into an ionic liquid monomer possessing one methacryloyl group. The addition of colloidal CdSe QDs to the ionic liquid monomer resulted in the liquid-liquid phase separation by which the aqueous solution appeared on the monomer layer as shown in the upper photograph of Fig. 1(b). The CdSe QDs were extracted from the aqueous solution to the ionic liquid monomer layer by stirring action [see the lower photograph of Fig. 1(b)]. Such a repeated extraction procedure finally gave the CdSe QD-ionic liquid monomer mixture at the concentration of CdSe QDs as high as \( \sim 10 \text{vol.\%} \) [see Fig. 1(c)]. Visible photoinitiator (Irgacure 784, Ciba) was then added to the mixture for green-light sensitization. In order to obtain high crosslinking networks during polymerization, we added an aliphatic urethane hexaacrylate monomer (Ebecryl 8301, Cytec) as a co-monomer to the mixture. Such mixed syrup was cast on a glass substrate with a polyester-film spacer and was covered with another glass substrate. It was then uniformly cured by green LED at 532 nm for our nonlinear optical measurements [see Fig. 1(d)]. The cured nanocomposite film exhibited the quantum-confined excitonic transition peak at 489 nm, independently of concentrations of CdSe QDs as shown in Fig. 2. Note that it is also possible to record a thick volume (Bragg) grating near 100% diffraction efficiency in such a uncured nanocomposite film [5, 8].

![Figure 1](image.png)

**Figure 1.** (a) Aqueous colloidal CdSe QDs; (b) Extraction of CdSe QDs from the aqueous CdSe QD solution (the yellowish layer) to an ionic liquid monomer (the transparent layer); (c) Photopolymerizable monomer syrup after repeated extraction of CdSe QDs; (d) A cured nanocomposite film sample dispersed with CdSe QDs.

![Figure 2](image.png)

**Figure 2.** Spectral linear absorption coefficients \( \alpha \) of cured nanocomposite film samples at various CdSe QD concentrations.
2.2. Nonlinear optical measurements

A frequency-doubled, passively and actively mode-locked picosecond Nd:YAG laser operating at a wavelength of 532 nm and at a repetition rate of 10 Hz was used in Z-scan and DMWM experiments. The normalized transmittance $T_{\text{norm}}(z)$, defined as an energy ratio of a detected pulse to an incident pulse normalized by the linear transmittance, was evaluated as a function of the film sample’s position $z$ measured from the incident beam focus. Individual incident pulses at a given pulse intensity $I_0$ (measured at $z=0$) were selected within ±3% errors, and averaging over tens of detected pulses was done to avoid unwanted errors in $T_{\text{norm}}(z)$. Figure 3 shows $T_{\text{norm}}(z)$ as a function of $z$ for a cured film sample dispersed with 6.8 vol. % CdSe QDs at $I_0=100$ MW/cm$^2$. A generic theoretical model [11, 12] taking both saturable absorption for a homogeneous broadening two-level system [13] and third- and fifth-order nonlinear refraction into account was used to perform curve fitting to the measured data. We found that the effective third- and fifth-order nonlinear refraction coefficients $(n_2)_{\text{eff}}$ and $(n_4)_{\text{eff}}$ were found to be $-1.5 \times 10^{-2}$ cm$^2$/GW and $+7.0 \times 10^{-2}$ cm$^4$/GW$^2$, respectively, with the saturation intensity of 0.17 GW/cm$^2$. The origin of the observed nonlinear transparency is considered to be transient bleaching of the excitonic transitions as a result of the state filling effect [1] in CdSe QDs as observed by pump-probe spectroscopic measurements [14, 15].

We also found that a measured dependence of $(n_4)_{\text{eff}}$ on the fill fraction $f_i$ of CdSe QDs was well fitted to the following form of a quadratic dependence on $f_i$:

$$(n_4)_{\text{eff}} = f_iL^4 L^2 (n_4)_{\text{CdSe}} + f_i^2 L^4 L^2 (n_2)_{\text{CdSe}} - f_i(1 - f_i)L^4 L^2 [2L^2 (n_2)_{\text{CdSe}} + |L^2|(n_2)_{\text{CdSe}}]$$,

where $(n_2)_{\text{CdSe}}$ and $(n_4)_{\text{CdSe}}$ are the third- and the fifth-order nonlinear refraction constants of a CdSe QD, respectively, and $L$ is the local-field correction factor of Maxwell-Garnett composites [9, 10]. The first term in the right-hand side of the above equation corresponds to the direct fifth-order contribution, while the second and third terms correspond to the macroscopic and microscopic cascaded ones from the third-order nonlinearity, respectively [16, 17].

![Figure 3](image_url)

Figure 3. (a) Open- and (b) closed-aperture Z-scan data for uniformly cured nanocomposite film sample. The solid curves are the least-squares fits of the theoretical models [11, 12] to the data.

Transmitted and diffracted beam patterns in DMWM measurements are shown in Figs. 4(a) and 4(b) for incident pump and probe beams at parallel and orthogonal polarizations, respectively. It can be seen from Fig. 4(a) that nonlinear diffraction originated from the third- and fifth-order optical nonlinearities take place for co-polarized pump and probe beams. The existence of the fifth-order nonlinearity is consistent with our Z-scan measurement described above. The observed third-order nonlinearity with cross-polarized pump and probe beams [see Fig. 4(b)] results from the non-zero component of the third-order nonlinear optical susceptibility tensor $\chi^{(3)}_{1221}$ of centro-symmetric media such as our nanocomposite films.
We also performed femtosecond pump-probe measurements of absorptive and refractive nonlinearities induced in uniformly cured nanocomposite film samples. Figures 5(a) and 5(b) show the decay dynamics of the induced nonlinear refraction and transparency, respectively, in a nanocomposite film sample dispersed with 6.8 vol.% CdSe QDs, by means of the femtosecond transient grating method [18]. It can be seen that there are picosecond-scale intensity-dependent and nanosecond-scale intensity-independent decay components in the nonlinear refraction and transparency data. The former is caused by the Auger process as observed in colloidal CdSe QDs [19], while the latter comes from the electron-hole recombination process. Figure 5(c)

Figure 4. Transmitted and diffracted beams from a uniformly cured nanocomposite film sample in the DMWM setup with incident pump and probe beams at (a) parallel and (b) orthogonal polarizations.

Figure 5. The decay dynamics of the induced (a) nonlinear refraction and (b) transparency in a nanocomposite film sample (6.8 vol.% CdSe QDs) at different pump intensities at 488 nm with a probe pulse at 775 nm. Double exponential fits are shown in red. (c) The differential transmission spectra of a nanocomposite film sample (0.9 vol.% CdSe QDs) for various probe time delays, where $\Delta \alpha$ is a change in $\alpha$ and $L$ is the film thickness.
shows differential transmission spectra as a function of probe time delay for a nanocomposite film sample dispersed with 0.9 vol.% CdSe QDs at a 488-nm pump intensity of 260 MW/cm². It can be seen that saturable absorption takes place in the broadband spectral region around the first quantum-confined electron-hole transition wavelength as similar to results seen in Figs. 3(a) and 5(b).

3. Conclusion
We have studied the nonlinear optical properties of uniformly cured inorganic-organic nanocomposite films dispersed with CdSe QDs at high concentrations. We found that CdSe QD dispersed nanocomposite films exhibits negative third- and positive fifth-order nonlinear refraction with saturable absorption. We have also confirmed the fifth-order optical nonlinearity by DMWM. The observed quadratic dependence of the fifth-order nonlinearity on \( f_i \) indicates a contribution from the macroscopic and microscopic cascaded processes of the third-order effect in composite films. Such observed high-order nonlinear responses are interesting from a fundamental viewpoint of optical nonlinearities in nanocomposite structures [9]. In addition, aside from their straightforward applications of ultrafast switching, limiting and processing by film and nanophotonic device structures, the observed fifth-order nonlinearity may find applications in quantum-information science and manipulations of nonlinear optical pulses such as light bullets and spinning/multi-dimensional optical solitons.

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