High-order nonlinear optical response of a polymer nanocomposite film incorporating semiconductor CdSe quantum dots

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Abstract: We report on observation of high-order optical nonlinearities in our recently developed photopolymerizable semiconductor CdSe quantum dot (QD)-polymer nanocomposite films at various volume fractions of CdSe QDs as high as 0.91 vol.% (3.6 wt.%). We performed Z-scan and degenerate multi-wave mixing (DMWM) measurements using a 532-nm picosecond laser delivering single 35 ps pulses at a repetition rate of 10 Hz. Using the uniformly cured polymer nanocomposite films, we observed the third- and fifth-order nonlinear optical effects in closed-aperture Z-scan measurements by which it was found that saturable nonlinear absorption (light-induced transparency) and large negative nonlinear refraction were induced. We also measured dependences of the effective third- and fifth-order nonlinear refraction constants on CdSe QD volume fraction. Based on the Maxwell-Garnett model, we estimated the third- and fifth-order nonlinear optical susceptibilities of CdSe QD and discussed a contribution of the third-order effect to the fifth-order one due to the cascaded (local-field) effect. Coexistence of the third- and fifth-order nonlinear refraction was also confirmed by DMWM.

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References and links


1. Introduction

Recently, we have developed a new polymer nanocomposite material system, the so-called photopolymerizable nanoparticle-polymer composites, where either inorganic-oxide or organic nanoparticles are uniformly dispersed in photopolymerizable monomer hosts [1]. As a result of holographic assembly of nanoparticles in polymer [2], dispersed nanoparticles at high volume fractions redistribute and provide a significant increase in refractive index modulation of a recorded volume hologram under holographic exposure. Simultaneously, they improve mechanical/thermal stability of the hologram [3]. Nanoparticle-polymer composites possessing these advantages are used for applications such as holographic data storage [4,5] and holographic diffractive elements for neutron quantum beams [6,7]. If semiconductor quantum dots (QDs) [8], also referred to as semiconductor nanocrystals, that confine optically excited electron-hole pairs in all three space dimensions are employed as nanometer-size constituents in nanoparticle-polymer composites, we expect the realization of novel photonic materials being capable of optically constructing multi-dimensional and functional (e.g., nonlinear) photonic lattice structures by the holographic nanoparticle assembling technique. Indeed, we recently demonstrated holographic assembly of semiconductor CdSe QDs (the average size of ~3 nm) in a photopolymerizable monomer host for constructing volume Bragg grating structures with diffraction efficiency near 100% [9].

QDs have interesting characteristics such as fluorescence tunability, enhanced photosensitivity and large optical nonlinearities: The electronic states of QDs are strongly influenced by the quantum confinement effect when the radius of QDs is smaller than approximately three times of the exciton Bohr radius [10]. The band gap ($E_g$) of QDs increases with decreasing their size and the quantum confinement effect can strongly enhance the third-order optical nonlinearity [11,12]. The II-VI bulk semiconductor CdSe has the direct band gap $E_g = 1.74$ eV at 300 K and has the exciton Bohr radius of 5.6 nm [12]. Therefore, the strong quantum confinement effect of CdSe QDs plays an important role in a large enhancement of the optical nonlinearity as compared with that of the bulk CdSe. For this reason it would be of great interest to investigate the nonlinear optical properties of uniformly cured and holographically patterned CdSe QD-polymer composites for their photonic applications such as optical switching/limiting, signal/image processing and nonlinear photonic crystals [13,14].

Over the past two decades intensive studies have been done to investigate optical nonlinearities in various semiconductor QDs such as CdSe [15–25], CdS$_{1-x}$Se$_x$ [26–32], CdS [33, 34], CdTe [35–37], GaAs [38] and PbS [39, 40] that were uniformly dispersed in either liquid or solid hosts. Because these semiconductor QDs are randomly dispersed, they possess the inversion symmetry so that they possess optical nonlinearities of the odd orders. Although most of reported experiments with semiconductor QDs discussed the third-order effect, high-order optical nonlinearities in CdS$_{1-x}$Se$_x$ QDs doped glasses [27–32] and colloidal CdTe QDs [37] were also reported. Other nonlinear optical materials exhibiting high-order optical nonlinearities include silver nanoparticles in aqueous solution [41,42], organic solutions [43–45], chalcone and its derivatives [46], chalcogenide glasses [47] and InN thin films [48]. Saturation of the cubic Kerr nonlinearity due to such high-order nonlinearities arising at high optical intensities provide interesting nonlinear phenomena such as the formation of stable multi-dimensional optical solitons, but it sometimes causes a detrimental effect in, for example, optical switching applications [32]. For this reason it is necessary to investigate the third- and, if any, high-order optical nonlinearities in nanocomposite materials.

In this paper we report on an observation of high-order optical response of photopolymerizable semiconductor CdSe QD-polymer nanocomposite films in the Z-scan [49] and degenerate multi-wave mixing (DMWM) [26] measurements with a 532-nm picosecond laser at a low repetition rate. We study dependences of effective third- and high-order nonlinear refraction constants on volume fraction of CdSe QDs in the Z-scan.
measurement, by which, based on the Maxwell-Garnett model, we extract the third- and fifth-
order nonlinear susceptibilities of CdSe QD and discuss a cascaded (local-field) contribution
to the fifth-order nonlinearity. Coexistence of the third- and fifth-order optical nonlinearities
is also examined by the DMWM measurement.

2. Sample preparation

Photopolymerizable semiconductor CdSe QD-polymer composites were prepared by the
aqueous synthetic method followed by extraction of QDs into a polymerizable ionic liquid
monomer at their high concentration [50]. Detailed descriptions of the synthesis of water-
soluble CdSe QDs and the method of adding colloidal CdSe QDs to the ionic liquid monomer
having one methacryloyl group, 2-(methacryloyloxy)ethyltrimethylammoniumbis
(trifluoromethanesulfonyl)imide (MOETMA-TFSI, Piotrek) were given in our previous work
[9]. In this study we could achieve the dispersion of CdSe QDs in the ionic liquid monomer as
high as 0.91 vol.% (3.6 wt.%). To the best of our knowledge, it is the highest doping
concentration of CdSe QDs in monomer. 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 (TEM) measurement, indicating our synthesized CdSe QDs
in the strong quantum confinement region. The estimated average core size of CdSe QDs was
compared with the theoretical formula providing the relationship between the diameter \(D\)
and the linear refractive index \(n_{\text{CdSe}}\) of a CdSe QD as given by [51]

\[
1.2 \left( \epsilon - 1 \right) / \left[ 1 + \left( 7.5 / D \right)^{12} \right],
\]

where \(\epsilon\) is the relative dielectric constant of the bulk CdSe at high frequencies, which is set
6.2 to equal the experimental value [51], and \(D\) is measured in Å. When we used \(n_{\text{CdSe}}\) of
2.318 at 546.1 nm measured by an Abbe refractometer, the calculated value for \(D\) was found
to be 3 nm, consistent with our TEM measurement. To make photo-cured solid film samples
for nonlinear optical measurements, we mixed the CdSe QD dispersed ionic liquid monomer
with 1 wt.% titanocene photoinitiator (Irgacure 784, Ciba) and a comonomer, aliphatic
urethane hexaacrylate monomer (Ebecryl 8301, Cytec), for high crosslinking
photopolymerization under green light illumination. The volume concentration of the
comonomer was chosen to be 9 vol.% since it gave the high refractive index modulation when
a plane-wave volume hologram was recorded in this film sample [9]. The mixed syrup was
cast on a glass substrate loaded with a polyester-film spacer and was covered with another
glass substrate. Such a photopolymerizable nanocomposite film sample was exposed by a
green LED to prepare a uniformly cured polymer nanocomposite film sample for our
nonlinear optical measurements. Figure 1 shows spectral linear absorption coefficients \(\alpha_0\)
for cured polymer nanocomposite film samples measured at room temperature. It can be seen that
the polymer nanocomposite film samples clearly exhibit excitonic absorption peaks at
approximately 480 nm, independently of concentrations of CdSe QDs. These peaks
correspond to the lowest quantum-confined electron-hole transition of CdSe QDs. A value for
\(\alpha_0\) with the highest CdSe QD volume fraction of 0.91 vol.% was 88 cm\(^{-1}\) at a measurement
wavelength of 532 nm, implying that the skin depth of the film sample was approximately
114 µm. This depth was thicker than the sample thicknesses (10 µm and 50 µm), so that the
linear absorption did not cause any negative effect on our measurement.
Fig. 1. Spectral linear absorption coefficients for cured polymer nanocomposite film samples at different volume fractions of CdSe QDs.

3. Experimental method

A passively and actively mode-locked and frequency-doubled Nd:YAG laser operating at a wavelength of 532 nm and at a repetition rate of 10 Hz was employed. The output laser pulse having the FWHM pulsewidth of 35 ps and the beam diameter of approximately 3 mm was focused on a polymer nanocomposite film sample of 10-µm thickness by a convex lens of a 200-mm focal length, forming a beam spot with the beam waist radius \( \omega_0 \) of approximately 32 µm determined by a commercial beam profiler. The single-beam Z-scan technique was used to measure the nonlinear absorption and refraction of polymer nanocomposite film samples at various volume fractions of CdSe QDs exhibiting the optical nonlinearity. In this setup the polymer nanocomposite film sample placed on a computer-controlled translation stage was moved along the beam propagation direction (\( z \) axis). An aperture and a detector placed behind it were set at a distance far away from the diffraction length \( z_0 (=6 \text{ mm}) \) of the focused pulse laser beam, where \( z_0 \) is given by \( k \omega_0^2 / 2 \) with \( k \) being the wavenumber of the incident beam. Linear transmittances of the aperture were set to be unity and 0.06 in the open- and closed-aperture Z-scan measurements, respectively. The normalized transmittance \( T(z) \), defined as the ratio of the detected pulse energy to the incident pulse one normalized by the linear transmittance, was evaluated as functions of the sample position \( z \) and an incident pulse intensity \( I_0 \) at the polymer nanocomposite film sample. Individual transmitted pulses at a given pulse energy within ± 10% were selected and used to measure \( T(z) \) in order to avoid unwanted intensity fluctuations of the incident laser pulses at a repetition rate of 10 Hz.

The forward DMWM measurement was also performed to study the third- and high-order optical nonlinearities in the polymer nanocomposite film samples of 50-µm thickness since the DMWM setup could spatially separate self-diffracted beams caused by the third- and high-order optical nonlinearities. The experimental setup is shown in Fig. 2. The same green pulse laser as that used in the Z-scan measurement was employed in this measurement. Either two s-polarized or cross-polarized beams were focused on the polymer nanocomposite film sample by a convex lens of a 700-mm focal length. The angle between two interacting beams was approximately 0.77° in the air. The beam radius in the focal plane was approximately 119 µm. The delay line was used to adjust the zero time delay between two incident beams. Self-diffracted beams were observed in the screen placed away from the polymer nanocomposite film sample.
Fig. 2. Experimental setup for forward DMWM. BS, a beam splitter; L, a convex lens; S, a polymer nanocomposite film sample; P, a prism. \( k_1, k_2, k'_1 \) and \( k'_2 \) indicate wavevectors of self-diffracted beams.

4. Experimental results and discussions

4.1 Open-aperture Z-scan

Figure 3(a) shows a typical open-aperture Z-scan data for a polymer nanocomposite film sample with 0.91 vol.% CdSe QDs at \( I_0 = 1.8 \text{ GW/cm}^2 \). It can be seen that \( T(z) \) is more or less peaked at the focus (\( z = 0 \)). A similar trend was observed at other incident pulse intensities up to 2.5 GW/cm\(^2\) in our measurement. We also found that a neat polymer film without CdSe QDs did not exhibit any nonlinear absorption. Therefore, the observed light-induced transparency originates from the optical nonlinearity of CdSe QDs. We speculate that the physical origin of the observed nonlinear transparency at a laser wavelength of 532 nm below the exciton bandgap (~480 nm) is attributed to transient bleaching of the excitonic transitions as a result of the state filling effect [52] in CdSe QDs as observed by pump-probe spectroscopic measurements [53]. The data are fitted better by theoretical models of the open-aperture Gaussian-beam Z-scan for saturable absorption (SA) [54] than by a model for two-photon absorption (TPA) [49] with a negative TPA coefficient \( \beta \). The two models for SA consider different intensity-dependent absorption coefficients \( \alpha(I) \) as given by [54]

\[
\alpha(I) = \begin{cases} 
\frac{\alpha_0}{1 + I/I_s} & \text{for a homogeneous broadening system (SA1)} \\
\frac{\alpha_0}{\sqrt{1 + I/I_s}} & \text{for an inhomogeneous broadening system (SA2)},
\end{cases}
\]

(2)

![Graph](image)

Fig. 3. (a) Open-aperture Z-scan \( T(z) \) at \( I_0 = 1.8 \text{ GW/cm}^2 \) as a function of sample position \( z \) for a polymer nanocomposite film sample with 0.91 vol.% CdSe QDs. The solid curves are the least-squares fits of the TPA (curve in red), SA1 (curve in blue) and SA2 (curve in brown) models to the data. Best fit values for the TPA, SA1 and SA2 models are \( \beta = 107 \text{ cm/GW}, I_s = 0.53 \) and 0.11 GW/cm\(^2\), respectively. (b) Transmittance change \( \Delta T \) at \( z = 0 \) as a function of input intensity \( I_0 \). The solid curves are the least-squares fits of the TPA (curve in red), SA1 (curve in blue) and SA2 (curve in brown) models to the data.
where $I$ is the laser pulse intensity inside a medium, $I_0$ is the saturation intensity and $\alpha$ equals to $\alpha_0$ under the low-intensity approximation ($I \ll I_0$). Analytic expressions for the open-aperture Gaussian-beam Z-scan $T(z)$ in these models can be given by means of the Adomian’s decomposition method [54–56]. We confirmed that the summation up to the eighth term in the series expansion for $T(z)$ with the Adomian’s decomposition method was enough to obtain the convergence in our experiment. The SA1 and SA2 models give best fit values for $I_0$ to be 0.53 and 0.11 GW/cm$^2$, respectively. Figure 3(b) shows transmittance changes $\Delta T$ at $z = 0$ [defined as $T(0)-1$] as a function of $I_0$. It can be seen that the SA1 and SA2 models give best fit values for $I_0$ to be 0.54 and 0.21 GW/cm$^2$, respectively. We see that the SA1 model gives a consistent result for the parameter fitting of $I_0$ in Fig. 3(a) with that in Fig. 3(b). For this reason we consider that the saturable absorption (light-induced transparency) observed in our polymer nanocomposite film sample as that shown in Fig. 3. It can be seen that the Z-scan data exhibit the peak-and-valley configuration, indicating the negative nonlinear refraction. A similar trend was observed in the closed-aperture Z-scan measurement at incident pulse intensities up to 2.5 GW/cm$^2$. It is well known that $\Delta T_{p-v}$ [defined as a peak-to-valley difference in $T(z)$] is proportional to $I_0$ for a material possessing the third-order effect [49]. The ratio for $\Delta T_{p-v}/I_0$ is plotted as a function of $I_0$ as shown in Fig. 4(b). It can be seen that $\Delta T_{p-v}/I_0$ is not a constant, indicating that the third-order nonlinear refraction is not the sole contribution to the observed optical nonlinearity. It can also be seen that the magnitude of $\Delta T_{p-v}/I_0$ more or less linearly decreases with an increase in $I_0$. It means that the third- and fifth-order effects simultaneously contribute to $T(z)$ in the closed-aperture Z-scan measurement.

### 4.2 Closed-aperture Z-scan

Figure 4(a) shows typical closed-aperture Z-scan data at $I_0 = 1.8$ GW/cm$^2$ for the same cured polymer nanocomposite film sample as that shown in Fig. 3. It can be seen that the Z-scan data exhibit the peak-and-valley configuration, indicating the negative nonlinear refraction. A similar trend was observed in the closed-aperture Z-scan measurement at incident pulse intensities up to 2.5 GW/cm$^2$. It is well known that $\Delta T_{p-v}$ [defined as a peak-to-valley difference in $T(z)$] is proportional to $I_0$ for a material possessing the third-order effect [49]. The ratio for $\Delta T_{p-v}/I_0$ is plotted as a function of $I_0$ as shown in Fig. 4(b). It can be seen that $\Delta T_{p-v}/I_0$ is not a constant, indicating that the third-order nonlinear refraction is not the sole contribution to the observed optical nonlinearity. It can also be seen that the magnitude of $\Delta T_{p-v}/I_0$ more or less linearly decreases with an increase in $I_0$. It means that the third- and fifth-order effects simultaneously contribute to $T(z)$ in the closed-aperture Z-scan measurement.

To model the measured trend in $T(z)$ shown in Fig. 4(a), we assume the nonlinear refraction up to the fifth-order effect, so that it is expressed by $n = n_0 + n_2 I + n_4 I^2$, where $n_0$, $n_2$ and $n_4$ are the background (linear) refractive index, the third- and fifth-order nonlinear refraction constants, respectively. First, we consider a model in which the third- and fifth-order nonlinear refraction is taken into account without nonlinear absorption. The theoretical expression for $T(z)$ in this case is given by [57]

$$T(x) = 1 + \frac{4x}{(x^2 + 1)(x^2 + 9)} \Delta \Phi_0^{(3)} + \frac{8x}{(x^2 + 1)^2(x^2 + 25)} \Delta \Phi_0^{(5)},$$

(3)

![Graphs showing closed-aperture Z-scan data](image)

**Fig. 4.** (a) Closed-aperture Z-scan $T(z)$ at $I_0 = 1.8$ GW/cm$^2$ as a function of sample position $z$ for the same polymer nanocomposite film sample with 0.91 vol.% CdSe QDs as that shown in Fig. 3. Solid curves correspond to the least-squares fits of the theoretical formulae for the closed-aperture Gaussian-beam Z-scan $T(z)$ without (curve in red) and with (curve in blue) saturable absorption of the SA1 type. The best-fit values for $n_2$ and $n_4$ are $-4.0 \times 10^{-4}$ cm$^2$/GW and $+1.5 \times 10^{-3}$ cm$^2$/GW, respectively. (b) $\Delta T_{p-v}/I_0$ as a function of input intensity $I_0$. The solid line is the least-squares linear fit to the data.
where \( x = z/\Delta z_0 \), \( \Delta \Phi(2n+1) = k n_2 \int_0^{\Delta z_0} E_{\text{eff}}^{(2n+1)} \), \( E_{\text{eff}}^{(2n+1)} = \left[ 1 - \exp(-n a_0 \Delta z) \right] / n a_0 \) is the effective sample thickness related to the \((2n+1)\)th-order optical nonlinearity for a nonlinear material of the mechanical thickness \( L \). In Fig. 4(a) the least-squares fit of Eq. (3) to the data is plotted as the solid curve in red. It can be seen that this model gives a poor fitting result, showing the necessity of taking saturable absorption into account. Next, we consider the second model that takes both (the third- and fifth-order) nonlinear refraction and saturable absorption (SA1). In this cases the nonlinear phase shift at the thin sample position \( z \), the radial distance \( r \) and time \( t \) may be given by

\[
\Delta \phi(z, r, t) = kn_2 \int_0^z I(z', r, t)dz' + kn_2 \int_0^z I^2(z', r, t)dz',
\]

where \( I(z', r, t) \) is the intensity inside the nonlinear medium and its analytical solution can be found by the Adomian’s decomposition method [54]. The electric field \( E_z(z, r, t) \) at the exit surface of the nonlinear medium including the nonlinear phase shift given by Eq. (4) is expressed as

\[
E_z(z, r, t) = \sqrt{I(L)} \exp[i \Delta \phi(z, r, t)].
\]

When Eq. (5) is decomposed into a summation of many Gaussian beams by a Taylor series expansion as done in the original Z-scan theory [49], an individual Gaussian beam independently propagates along \( z \) axis toward an aperture in free space. As a result, the electric field of the laser beam in front of the aperture positioned at the distance \( d \) from the medium is obtained by a summation of the propagating individual Gaussian beams such that

\[
E_z(z, r, t) = \sqrt{I(L)} \sum_{m=0}^{\infty} \left[ i \Delta \phi(z, r = 0, t) \right]^m w_m^2 \exp \left( - \frac{r^2}{w_m^2} \right) \left[ 1 + \frac{ikr^2}{2R_m} + \frac{i\theta_m}{2} \right].
\]

In Eq. (6) \( w_m^2 = w_0^2/(2m+1) \) and \( w_m^2 = w_m^2 \left[ g^2 + (d/d_m)^2 \right] \) in which \( w_0^2 = w_0^2(1 + z^2/\Delta z_0^2) \), \( g = 1 + d(z(1 + z^2/\Delta z_0^2)) \), and \( d_m = k w_m^2/2 \). Also, \( R_m = d[1 - g(g^2 + d^2/d_m^2)]^{-1} \) and \( \theta_m = \tan^{-1} \left[ d(d_m g^2) \right] \). The normalized Z-scan transmittance \( T(z) \) for the nonlinear medium possessing the saturable absorption (SA1) and the simultaneous third- and fifth-order nonlinear refraction in the closed-aperture Z-scan measurement can be found by the following formula [49]:

\[
T(z) = \frac{\int_{-\infty}^{\infty} P_t(z, t)dt}{\int_{-\infty}^{\infty} P(t)dt},
\]

where the transmitted pulse power \( P_t(z, t) \) through the aperture is given by

\[
P_t(z, t) = 2\pi \int_0^{r_0} I_z(z, r, t)rdr = c \epsilon_0 n_2 \pi \int_0^{r_0} \left| E_z(z, r, t) \right|^2 rdr,
\]

the incident pulse power \( P(t) \) is given by \( \pi w_0^2 I_0(d_0/t)/2 \), and the linear transmittance of the aperture \( S \) is given by \( 1 - \exp(-2r_0^2/w_0^2) \) with \( r_0 \) and \( w_0 \) being the aperture radius and the Gaussian beam radius at the aperture, respectively. Also, \( c \) and \( \epsilon_0 \) are the speed of light in vacuum and the vacuum permittivity, respectively. Equation (7), together with Eqs. (4), (5), (6) and (8), was numerically calculated to extract \( n_2 \) and \( n_4 \) by the curve fitting to the data shown in Fig. 4(a). Note that \( I_0 \) of 0.53 GW/cm\(^2\) found in the open-aperture Z-scan measurement (see Fig. 3) is used for this fitting procedure. It can be seen in Fig. 4(a) that the second model is in good agreement with the data. As a result, the best-fit values for \( n_2 \) and \( n_4 \) were found to be \(-4.0 \times 10^{-3} \) cm\(^2\)/GW and \(+1.5 \times 10^{-3} \) cm\(^2\)/GW\(^2\), respectively, at \( I_0 = 1.8 \) GW/cm\(^2\).

Figure 5 shows the extracted best-fit values for \( n_2 \) [Fig. 5(a)] and \( n_4 \) [Fig. 5(b)] as a function of \( I_0 \). It can be seen that \( n_2 \) and \( n_4 \) are more or less independent of the input intensity.
Fig. 5. (a) Extracted values for (a) \( n_2 \) and (b) \( n_4 \) as a function of input intensity \( I_0 \) for a polymer nanocomposite film sample doped with 0.91 vol.% CdSe QDs.

in the measured intensity range; the average values for \( n_2 \) and \( n_4 \) are \( -4.0 \times 10^{-3} \text{ cm}^2/\text{GW} \) and \( +1.5 \times 10^{-3} \text{ cm}^4/\text{GW}^2 \), respectively. The magnitude of \( n_2 \) for the polymer nanocomposite film sample with 0.91 vol.% (3.6 wt.%) CdSe QDs is approximately two orders of magnitude larger than that \( (\approx -1.45 \times 10^{-5} \text{ cm}^2/\text{GW}) \) of a bulk CdSe at 1064 nm [58] and is approximately one order of magnitude larger than that \( (+4.3 \times 10^{-4} \text{ cm}^2/\text{GW}) \) at 794 nm for the polymer CR39 composite film dispersed with 1.5 wt.% CdSe QDs [23]. We note that the sign of \( n_2 \) (also, that of nonlinear absorption) is not necessarily consistent in past literatures [15–25] that were different material parameters and experimental conditions such as the size of QDs, types of host materials (liquid and solid hosts) and operating wavelengths. We also note that a contribution of the third- and fifth-order nonlinear refraction to the nonlinear refractive index change is comparable at \( I_0 \) of the order of GW/cm².

Two physical mechanisms mainly contribute to the optical nonlinearities: electronic and thermal effects. The thermal effect is based on heat transformation from absorptive nanoparticles to the transparent polymer host material, giving negative \( n_2 \) [18,25]. There are two parameters related to the thermal lens effect that might have occurred in the \( Z \)-scan measurement; the rise and relaxation time constants in the thermal lens effect. The rise time constant is determined by the transit time \( \tau_{\text{rise}} \) of generating acoustic phonons over the beam area, which is given by \( \alpha_0/V_s \) [49] with \( V_s \) being the sound velocity, respectively. Using \( \alpha_0 = 32 \text{ } \mu \text{m} \) and \( V_s = 2730 \text{ m/s} \) [59] in our experiment, we find \( \tau_{\text{rise}} \) to be approximately 12 ns, which is approximately two orders of magnitude larger than the pulse duration (35 ps). The relaxation time \( \tau_{\text{relax}} \) is given by \( \omega_0^2/\rho C_v/4\kappa \) [18,25], where \( \rho \) is the density, \( C_v \) is the specific heat and \( \kappa \) is the thermal conductivity. Using \( \rho = 1200 \text{ kg/m}^3 \), \( C_v = 1466 \text{ J/kg.K} \) and \( \kappa = 0.2 \text{ W/m.K} \) for typical polymer materials [60], we find \( \tau_{\text{relax}} \) to be 2.3 ns. This time constant is much shorter than the pulse repetition time (100 ms). Therefore, we find that the generated heat does not accumulate over the beam area per pulse in our experiment. In addition, the nonlinear refractive index \( n_{\text{thermal}} \) induced by the thermal effect is given by [49]

\[
n_{\text{thermal}} = \frac{dn}{dT} \frac{F_0 \alpha_0}{2 \rho C_v I_0},
\]

where \( dn/dT \) is the thermo-optical coefficient and \( F_0 \) is the pulse fluence. Using \( dn/dT = -1.3 \times 10^{-3} \text{ °C}^{-1} \) [3, 61], \( F_0 = 0.033 \text{ J/cm}^2 \) at \( I_0 = 1.8 \text{ GW/cm}^2 \) and \( \alpha_0 = 88 \text{ cm}^{-1} \) for the polymer nanocomposite film with 0.91 vol.% CdSe QDs, we find \( n_{\text{thermal}} \) to be \( -5.9 \times 10^{-5} \text{ cm}^2/\text{GW} \), which is approximately two orders of magnitude smaller than our experimental results. Therefore, it can be concluded that the thermal contribution to the observed optical nonlinearities is negligible and the dominating nonlinear response has the electronic origin.

Similar fitting procedures were performed for other film samples at different volume fractions of CdSe QDs. The extracted values for \( n_2 \) and \( n_4 \) as a function of CdSe QD volume fraction are shown in Fig. 5.
fraction are plotted in Fig. 6. We note that a neat polymer film without CdSe QDs (i.e., \( f = 0 \)) did not exhibit any nonlinear refraction (i.e., \( n_2 \approx 0 \) at \( f = 0 \)). It can be seen that the magnitudes of \( n_2 \) and \( n_4 \) increase with the increase of CdSe QD volume fraction. For a Maxwell-Garnett type nanocomposite material with nonlinear optical nanoparticles the effective third-order nonlinear optical susceptibility \( \chi_{\text{eff}}^{(3)} \) of the nanocomposite material is related to the third-order nonlinear optical susceptibility of nanoparticles, \( \chi_n^{(3)} \), as given by [12, 62]

\[
\chi_{\text{eff}}^{(3)} = f |q|^2 q^2 \chi_n^{(3)},
\]

where \( f \) is the volume fraction of nanoparticles and \( q \) is the local field factor given by

\[
q = \frac{3 \varepsilon_n}{\varepsilon_n + 2 \varepsilon_h},
\]

in which \( \varepsilon_n \) and \( \varepsilon_h \) are the relative dielectric constants of nanoparticles and a host material, respectively. Using \( \varepsilon_n = 5.38 \) and \( \varepsilon_h = 2.14 \) for CdSe QDs and the host polymer film, respectively, we find \( \chi_{\text{CdSe}}^{(3)} \) to be \(-2.55 \times 10^{-8}\) esu that is obtained by a linear curve fit with a function \( n_2 = Af \) [the solid line in Fig. 6(a)] to the data together with Eq. (10) and the conversion factor between \( n_2 \) and \( \chi_{\text{eff}}^{(3)} \) [63]. This value is comparable to that of CdSe QDs in organic solution [25]. We speculate that a deviation of the data at \( f = 5.2 \times 10^{-3} \) from the solid line is partly attributed to increased measurement errors due to lower signal levels at low volume fractions of CdSe QDs.

The effective fifth-order optical nonlinearity may generally include intrinsic, macroscopic and microscopic cascaded contributions [45]. The intrinsic contribution due to the intrinsic fifth-order nonlinear optical susceptibility of nanoparticles \( \chi_n^{(5)} \) is proportional to \( f \) and is given by [45]

\[
\chi_{\text{eff}}^{(5)} = f |q|^4 q^2 \chi_n^{(5)}.
\]

The other two contributions are proportional to \( f^2 \) [45]. By using a function \( n_4 = af + bf^2 \), where \( a \) is proportional to the pre-factor \( |q|^4 q^2 \chi_n^{(5)} \) in Eq. (12) and \( b \) is a constant related to the two cascaded contributions, to the data for \( n_4 \) shown in Fig. 6(b), we find the ratio \( b/a \) and \( \chi_{\text{CdSe}}^{(5)} \) to be 0.3 and \(+ 7.25 \times 10^{-16}\) esu, respectively. Therefore, the main contribution of the fifth-order nonlinear refraction for CdSe QD comes from the intrinsic origin. The occurrence of the intrinsic fifth-order optical nonlinearity may be mainly attributed to TPA-induced free carriers for the bulk semiconductors [58]. In our case, however, we consider that it originates from the state filling effect showing saturable absorption.

Figure 7 shows the normalized transmittances as a function of incident intensity by means of a variant of the closed-aperture Z-scan technique, the so-called intensity scan technique [64] that measures \( T(z) \) for a nonlinear medium placed at either a valley or a peak position.
away from the beam focus \((z = 0)\) in the closed-aperture Z-scan setup as seen in Fig. 4(a). This technique can be used to determine the sign and the magnitude of effective optical nonlinear constants either when a nonlinear material such as a polymer film has low damage threshold or when a transversal beam quality along the \(z\) direction is poor. It can be seen that \(T(z)\) decreases (increases) with increasing an incident intensity for the polymer nanocomposite film sample was located at the valley (peak) position. The decreasing trend of the laser power after an aperture with increasing an incident laser intensity can be used for optical power limiting; it would be more effective when a thicker film sample is employed.

![Graph showing \(T(z)\) as a function of incident intensity for a polymer nanocomposite film sample doped with 0.91 vol.% CdSe QDs when the sample is placed at the valley (\(\bigcirc\)) and peak (\(\bullet\)) positions.](image)

**Fig. 7.** Closed-aperture Z-scan \(T(z)\) as a function of incident intensity for a polymer nanocomposite film sample doped with 0.91 vol.% CdSe QDs when the sample is placed at the valley (\(\bigcirc\)) and peak (\(\bullet\)) positions.

4.3 Degenerate multi-wave mixing

Forward DMWM measurement was also performed with uniformly cured polymer nanocomposite film samples. When two coherent plane wave pulses with wavevectors \(k_1\) and \(k_2\) interfere each other in the sample at their small incident angles, the formed interference pattern locally modifies the local refractive index and induces the periodic modulation of the refractive index (i.e., a dynamic thin grating). The two incident beams nonlinearly interact each other via the formed grating, creating a new \(n\)th diffracted beam whose wavevector \([\text{either } k_{2n+1} = (n + 1)k_1 - nk_2 \text{ or } k'_{2n+1} = (n + 1)k_2 - nk_1]\) depends on an effective \((2n + 1)\)th-order nonlinear susceptibility \(\chi_{\text{eff}}^{(2n+1)}\) via a \((2n + 2)\)-wave mixing process [44]. Therefore, the effective third- and fifth-order optical nonlinearities as observed in our Z-scan measurement are related to the first- and second-order diffracted signals with wavevectors \(k_3, k_5\) and \(k'_3, k'_5\). Such a dynamic self-diffraction phenomenon was indeed observed in the 50-\(\mu\)m polymer nanocomposite film sample with 0.91 vol.% CdSe QDs as shown in Fig. 8(a), where the induced grating spacing \(\Lambda\) was approximately 40 \(\mu\)m and the total input intensity was 1.8 GW/cm\(^2\). The diffraction is in the Raman-Nath regime because the \(Q\) factor defined as

\[
2\pi d J_0^2 (\lambda/\Lambda)^2 \quad (\lambda \text{ is a wavelength of light in vacuum}) \quad [65] \text{is 0.07. It can be seen that four diffracted beams are newly generated. These diffracted beams correspond to the third- and fifth-order nonlinear optical effects, which is consistent with our Z-scan measurement described earlier. It is indicative of the coexistence of the third- and fifth-order optical}

![Images showing far-field transmitted and diffracted beams from the polymer nanocomposite film sample with 0.91 vol.% CdSe QDs at grating spacing of (a) 40 \(\mu\)m and (b) 1 \(\mu\)m.](image)

**Fig. 8.** Far-field transmitted and diffracted beams from the polymer nanocomposite film sample with 0.91 vol.% CdSe QDs at grating spacing of (a) 40 \(\mu\)m and (b) 1 \(\mu\)m.
nonlinearities in the polymer nanocomposite film samples. Figure 8(b) shows the transmitted and diffracted beams from the dynamic grating at 1 µm that corresponds to $Q = 114$ (i.e., the Bragg regime). Unlike the case shown in Fig. 8(a) no self-diffraction is seen because the phase mismatching is significant for self-diffracted beams in the Bragg regime. We also performed the DMWM experiment with the cross-polarized input beams. The first-order diffraction was observed due to the third-order effect arising from the off-diagonal element of the third-order nonlinear optical susceptibility tensor $\chi^{(3)}_{1212}$ in isotropic media. Details on these DMWM experiments will be reported elsewhere.

5. Conclusions
We have studied the nonlinear optical properties of uniformly cured semiconductor CdSe QD-polymer nanocomposite films by means of the Z-scan technique and DMWM with a 532-nm picosecond laser at a low repetition rate. Using closed- and open-aperture Z-scan techniques, we have found that the polymer nanocomposite films at the volume fraction of CdSe QDs as high as 0.91 vol.% (3.6 wt.%) exhibit the saturable absorption (light-induced transparency) as well as the negative third-order and the positive fifth-order nonlinear refraction. We have also found that the observed high-order nonlinearity originates mainly from the intrinsic fifth-order effect and partly from the third-order one due to the cascaded contributions. The observed nonlinearity is attributed to the electronic state filling effect. Such coexistence of the third- and fifth-order optical nonlinearities has been also confirmed by DMWM measurements. The observation of cross-polarized DMWM diffraction also supports the electronic origin of the third- and fifth-order nonlinearities. The large third-order nonlinearity, the occurrence of high-order nonlinearities and the capability of holographic nanoparticle assembling make our CdSe QD-polymer nanocomposite system promising for nonlinear photonics applications. For example, let us estimate the materials (one-photon) figure of merit $W$ given by $|\Delta n|/\lambda \alpha$ [66,67] for our CdSe QD-polymer nanocomposites, where $\Delta n$ is the nonlinear refractive index change. Using $\Delta n = n_2 I + n_4 I^2 = -2.5 \times 10^{-3}$ at $I = 1$ GW/cm$^2$ and $\alpha = 30$ cm$^{-1}$ with $I_s = 0.53$ GW/cm$^2$ for the polymer nanocomposite film with 0.91 vol.% CdSe QDs, we find $W$ to be 1.5. [Thanks to the light-induced transparency, the linear value for $\alpha$ (= 88 cm$^{-1}$) is reduced to 30 cm$^{-1}$. See Fig. 3.] This value is close to 2, the threshold value required for complete all-optical switching for nonlinear guided-wave devices [66]. We expect that the further enhancement of $W$ is possible if the large nonlinearity of the CdSe QD-polymer nanocomposite system is combined with electromagnetic nonlinear feedback mechanisms [68, 69] by constructing photonic lattice structures [2,9,14]. Our study in this direction is currently under way.

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