Abstract

Hybrid composites of CdSe nanocrystals embedded in allyl diglycol carbonate (CR39) matrices have been prepared and characterized. The measurements show that the linear refractive index of the composite decreases as the CdSe nanocrystal’s weight-percentage concentration increases at the laser wavelengths of 632.8 nm and 532 nm. The room temperature nonlinear optical properties of the hybrid composites were investigated using a single-beam Z-scan technique with femtosecond laser pulses at the wavelengths of 794 nm and 397 nm. The experimental data reveals that the Kerr nonlinear refractive index $n_2$ of the composite increases as the concentration increases at these wavelengths when the CdSe nanocrystal’s weight-percentage concentration is increased. Also, the nonlinear refractive index $n_2$ of the CdSe/CR39 hybrid composites exhibit dispersion from a positive value at 794 nm (below the band gap) to a positive value at 395 nm (above the band gap). The measured dispersion of $n_2$ is roughly consistent with the Sheik-Bahae’s theory for the bound electronic nonlinear refraction resulting from the two-photon resonance.

Keywords: CdSe/CR39 filter; Nonlinear refraction index

1. Introduction

Owing to their unique size-dependent optical and electrical properties, colloidal semiconductor nanocrystals are considered as a class of very promising materials for the next generation of electronic and optoelectronic devices such as light emitting diodes (LEDs), solar cells, lasers, printing of integrated circuits, biological detection, etc. A major advantage of using nanocrystals is that they can be embedded into organic, polymeric, and even glass matrices to make nanocomposite materials. In particular, the nanocrystal/polymer composites have the combined advantages of inorganic and organic materials, e.g. low-production cost and flexible possibilities, etc. However, studies on the refractive properties of those nanocrystal/polymer nanocomposite materials are very limited.

Traditional optical filters rely on light absorption, interference or both [1]. Semiconductors that exhibit a very rapid transition from opacity to transparency edge are particularly useful for such application, making excellent long-pass optical filters. However, the fixed edges of absorption (band gap energy) of a given semiconductors significantly limit their applications. On the other hand, the designs and fabrications of interference-based bandpass filters can be a very complicated and expensive process. Therefore, there is a need to develop new types of nanocrystal-based polymer thin-film optical filters that can be easily fabricated with high quality stability, and tunable wavelength. The composite filters with CdSe nanocrystals embedded in polymer (CR39) matrix described in this work
have a weak nonlinearity. The third-order susceptibility of these composite materials is two-orders of magnitude smaller than the CdSe-doped inorganic glass filters [2]. Also, such system can be easily expanded to other semiconductor nanocrystals like CdS and CdTe, since they have similar a nonlinear refractive index [2–7a].

Taking advantage of the unique size-dependent feature of semiconductor nanostructures, we developed a technique of homogeneously dispersing CdSe nanocrystals into CR39 polymers and then fabricated thin films using an in situ polymerization process instead of the well-established polymer processing technique such as extrusion or “heat and press” process. We performed optical characterizations of such nanocrystal-based thin film filters, including measuring linear refractive index and nonlinear refraction index by single-beam Z-scan technique. Such detailed studies are important in developing practical nanocrystal-based optical filters with improved optical characteristics. For high power applications of such nanocrystal/polymer optical filters, the nonlinear optical characteristics need to be investigated. Also, such nonlinearity might be used to make optical limiters for applications in certain wavelength regions.

2. Sample preparation

CR39 is a plastic polymer that is widely used in manufacturing eyeglass lenses. It is transparent in visible spectrum and almost completely opaque in infrared and ultraviolet wavelength ranges. Because of the presence of the two allyl functional groups (Fig. 1), CR39’s monomers can not only polymerize but also cross-link with each other which result in a thermoset plastic characterized by being hard, infusible and insoluble in all solvents. In addition, CR39 homopolymer is a high-grade optical plastic whose linear index of refraction is just slightly less than that of the crown glass.

Disopropyl peroxycarbonate (IPP) is usually used to catalyze CR39’s polymerization. However, due to its extremely pyrophoric nature, commercial IPP is only available for industrial uses but not for research purpose. Because of this, an alternative catalyst, benzyl peroxide, is used to initialize the polymerization of CR39.

Since CR39 is resistant to most of the organic solvents, an in situ polymerization strategy is used to prepare the composite material. To do this, various ligands were screened to identify the one that would make the nanocrystals be compatible with the CR39 monomers, and a proper one was synthesized to be compatible with the CR39 monomer. This ligand contains a thiol functional group (to bind on nanocrystal surface) and a long polyethylene-glycol (PEG) tail, which, we believe, makes the semiconductor CdSe nanocrystals compatible with the CR39 polymer. The CdSe nanocrystals with the particle size of ~3.5 nm were synthesized according to the published method [7b], and then were thoroughly purified by precipitating and washing with methanol and stored in toluene. An in situ polymerization process was used to form CdSe nanocrystal/CR39 polymer nanocomposite thin films. To form CR39 monomer-compatible CdSe nanocrystals, native trioctyolphosphate and trioctylphosphine oxide (TOP/TOPO) capped CdSe nanocrystals were mixed with an excess of poly (ethylene glycol)-terminated dihydroxypic acid (DHLA–PEG) ligand. After being incubated for several hours at room temperature, the DHLA–PEG coated CdSe nanocrystals were separated from solution via centrifuging and then re-dispersed into CR39 liquid monomer to form a homogenous solution (via overnight stirring). The CdSe nanocrystal/CR39 monomer mixture were injected into film molders and cured at temperature up to 100 °C with benzyl peroxides as initiators by a classical curing process of free-radical-addition polymerization [7c]. Fig. 2 (color online) shows the CdSe/CR39 thin films with various nanocrystal concentrations.

3. Optical measurements

3.1. Linear absorption coefficient

The UV–vis absorption spectra of all six samples with different concentrations of CdSe nanocrystals are presented in Fig. 3. The pure CR39 sample (sample a) was found to absorb only below 400 nm, hence the absorption between 400 and 700 nm in samples b–f can be attributed to the added CdSe nanocrystals. It is known that the UV absorption of semiconductor nanocrystals is due to the band gap absorption, which is blue-shifted relative to the bulk due to quantum size confinement effect [8,9]. Thus, Fig. 3 shows that the UV thresholds of all samples are blue-shifted relative to bulk CdSe at wavelength 660 nm. It is also noted that, within the same batch of samples, the absorption threshold becomes more blue-shifted as the CdSe concentration is increased. The average particle size in our samples (calculated from the equation based on the effective mass approximation [8], and compared to the experimental curve of absorption threshold versus particle diameter by

![Fig. 1. CR39’s monomer:diethyleneglycol bis allyl carbonate.](image1)

![Fig. 2. (Color online) CdSe nanocrystal/CR39 films (1.0 mm), the CdSe concentrations of each film are labeled on the top of the figure.](image2)
Henglein et al. [9]) is estimated to be about 3.5 nm that is consistent with the diameter measured by TEM image. We found that phase segregation occurs at high nanocrystal concentration, e.g., above 1%.

The linear absorption coefficient $a$ of the CR39 thin films embedded with different concentrations of CdSe nanocrystals are shown in Fig. 4 from the transmittance spectra using the relation

$$a = \frac{\ln(1/T_a)}{l},$$

where $T_a$ is the interference-free transmittance [10] of the thin film after subtracting the substrate’s absorption, and $l$ is the thickness of thin film. The linear absorption coefficient $a$ of the composite film depends on CdSe nanocrystal concentration in polymer CR39 at a given wavelength, higher concentration makes $a$ to be larger. The films have very small $a$ value in the infrared wavelength region. The linear absorption coefficients ($a$) of the composite films drop sharply in the visible region and the zero edges of $a$ are located at different wavelengths: 290 nm, 340 nm, 420 nm, 480 nm, 570 nm, 585 nm for CdSe nanocrystal concentrations in polymers CR39 to be 0%, 0.16%, 0.34%, 0.5%, 0.92% and 1.48%, respectively.

### 3.2. Linear refractive index

By using a prism coupler system, we measured the linear optical refractive indices of these samples, which also depend on the concentration of CdSe nanocrystals in CR39 polymer. It decreases from 1.5066 to 1.4876 with increasing concentration of CdSe nanocrystals at CR39 polymer when the laser wavelength is 632.8 nm, and it decreases from 1.5122 to 1.4944 with increasing concentration of CdSe nanocrystals when the laser wavelength is 532 nm. As an example, Fig. 5 shows the variation of the refractive index versus CdSe nanocrystal concentration for these CdSe nanocrystal/CR39 polymer films. As shown in this figure, the refractive index decreases as the CdSe nanocrystal weight-percentage concentration increases.

The linear refractive index of CdSe nanocrystals of $\sim 3.5$ nm average diameter is calculated to be 2.34 with the following relation [11]

$$n_{\text{CdSe}} = \left[1 + \left(\epsilon_{\text{bulk}} - 1\right)/\left[1 + (0.75 \text{ nm}/d)^{1/2}\right]\right]^{1/2},$$

where $\epsilon_{\text{bulk}} \approx 6.2$ is the dielectric constant of bulk CdSe and $d$ is the average diameter of CdSe nanocrystals in nanometer.

Thus, the refractive index of the dopant semiconductor nanocrystals (2.34) is higher than that of the host polymer ($\approx 1.5$) in our samples, one would naturally anticipate that embedding nanocrystals into polymer matrix would cause the increase in the refractive index [12,13]. The observed slight decrease of $n_0$ with increasing nanocrystal concentration (shown in Fig. 5) may be attributed to the poor crystalline structure due to relaxation rate difference between nanocrystals and the polymer host [13]. The decreased trend in $n_0$ as increasing nanocrystal concentration could also be due to the change in polymer’s morphology upon embedding nanocrystals. This phenomenon is currently still under investigation.
3.3. Nonlinear refractive index

The quantum confinement and dielectric confinement effects make semiconductor nanocrystals a promising class of nonlinear optical materials [14–17]. We performed the nonlinear optical measurements of the CdSe/CR39 composite samples by using the single-beam Z-scan technique [18]. The nonlinear refractive index at both the wavelengths of 794 nm and 397 nm were measured to show dispersion properties. The light source is a mode-locked Ti:Sapphire laser with a high repetition rate of 81 MHz at the wavelength of 794 nm, which has a temporal width of about 565 femtosecond and a peak power of up to 40 kW. The 397 nm pulse laser beam was generated by frequency doubling the 794 nm laser pulses with a peak power of up to 4.9 kW. The output beam was collimated, expanded and the spatial profiles of these laser beams were determined to be approximately Gaussian. The beam was then focused into the sample using a lens with the focal waist radius of 0.5 mm at 794 nm (or 0.4 mm at 397 nm). To reduce the effect of fluctuations in the pulse energy, another detector was used to monitor the input pulse energy as a reference. 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 that passed through the far-field aperture. The open-aperture (OA) and CA Z-scan traces are fitted by two corresponding numerical programs based on Ref. [19] to obtain the nonlinear refractive indices. The sample’s parameters (\( \alpha \) linear optical absorption coefficient and \( L \) sample thickness), as well as the laser’s parameters (\( R \) repetition rate, \( t_p \) FWHM, FWHM of pulse’s duration, and AP average incident power of the laser beam) are required as the inputs for these numerical programs.

We can use the equations [18] below to calculate the nonlinear refraction indexes \( n_2 \) of the films by the Z-scan traces as following

\[
\begin{align*}
    n_2 &= \frac{\Delta T_{p-v}}{0.406(1-S)\kappa L_{\text{eff}}I_0}, \\
    k &= \frac{2\pi}{\lambda}, \\
    L_{\text{eff}} &= (1-e^{-\alpha d})/\alpha,
\end{align*}
\]

where \( L \) is the sample thickness, \( \alpha \) is the linear absorption coefficient, and \( \Delta T_{p-v} \) is the peak-valley transmittance change.

A typical CA Z-scan curve of the CdSe/CR39 thin film (with CdSe weight concentration of 0.16%) is shown in Fig. 6, which gives the characteristic shape for a positive nonlinearity. Assuming that the nonlinear refractive index of this sample is dominated by the third-order only, the experimentally measured data (solid line) is fitted with the standard Z-scan theory to extract the nonlinear refractive index. The measurement in Fig. 6 was done at a fixed input irradiance with the laser wavelength of 397 nm and the pulse duration of 565 fs. From the fitting results the observed nonlinear refractive index is determined to be about \( 1.0 \times 10^{-4} \text{cm}^2/\text{GW} \), which is of the same magnitude as the ones reported in Refs. [2,3]. Seo et al. [3] measured the third-order nonlinear optical susceptibility of CdSe nanocrystals to be \( 1.8 \times 10^{-5} \text{~cm}^2/\text{GW} \) for various concentrations of CdSe quantum dots (\( 1.2 \times 10^{-6} \text{~mol/m}^3 \)) in a toluene host at the wavelength of 532 nm by using nanosecond degenerate four-wave mixing with 8 ns laser pulses. Yao et al. [2] got the value of \( 1.1 \times 10^{-7} \text{esu} \) (\( 9.1 \times 10^{-4} \text{cm}^2/\text{GW} \)) for \( |\chi(3)| \) of CdSe-doped PHEMA films (the absorption coefficient of the film is \( 20.7 \text{cm}^{-1} \) at 460 nm), indicating low concentration of doped nanocrystals. The reflectivity of their signal was about two-orders of magnitude smaller than that for CdSe-doped inorganic glasses [4].

Also the nonlinear refractive index of the CdS–PS hybrid composites was found to increase linearly (in the range from \( -1.0 \times 10^{-4} \text{~cm}^2/\text{GW} \) to \( -3.0 \times 10^{-4} \text{~cm}^2/\text{GW} \)) as the input irradiance decreases. These values are of the same magnitude as the results obtained in Ref. [6]., in which the nonlinear refractive index of capped CdS nanocrystals in an ordered polydiacetylene host at wavelength of 532 nm was measured to be about \( 1.1 \times 10^{-4} \text{~cm}^2/\text{GW} \) using 0.09 GW/cm² laser pulses of 5 ns. In that case, the polydiacetylene host itself has a nonlinear refractive index of about \( -3 \times 10^{-4} \text{~cm}^2/\text{GW} \). In addition, Wang et al. [7] had performed the pump-probe measurements with ammonia-passivated CdS clusters in polymer. They measured the absorption of CdS at different wavelengths with excitation by 30 ps laser pulses at 355 nm and obtained the associated changes in refractive index at different wavelengths through the Kramers–Kronig relation. According to their calculation, the nonlinear refractive index of CdS at 532 nm is \( 1.41 \times 10^{-4} \text{~cm}^2/\text{GW} \), which is also in the same range as our results presented here. In our composite samples, we can attribute the nonlinearity to the CdSe nanoparticles, since the pure CR39 sample dosenot show third-order nonlinear properties in the error range of our measurements.

![Fig. 6. Measured Z-scan CA trace in CdSe/CR39 film (1.0 mm) at wavelength 397 nm. CdSe weight-percentage: 0.16%; S = 0.04; n_2 = 1.09 \times 10^{-4} \text{~cm}^2/\text{GW}.](image-url)
Sheik-Bahae et al. [19] and Krauss and Wise [20] have presented a scaling rule between the nonlinear refraction index \( n_3 \) of hybridized CdSe/CR39 nanocomposites and the ratio of the photon energy to the band gap energy \((h\nu/E_g)\). Here we found that if the mechanism for the nonlinearity in our samples is dominated by the third-order nonlinear effect, we should be able to fit the \( n_3 \) value in the Z-scan measurement at each concentration. The linear relationships between the nonlinear index and the concentrations are shown in Figs. 7 and 8 for two different wavelengths. We can see that the value of \( n_3 \) increases linearly as the nanocrystal concentration gets higher. The changing values of the nonlinear refractive index \( n_{\text{ex}} \) indicate that the nonlinear refraction has contribution not only from the third-order nonlinearity but also from higher-order nonlinearities that can be caused by free carrier effect. The nonlinear refractive index can be written as [17]:

\[
n = n_0 + n_{\text{ex}} I = n_0 + (n_2 + n_4)I,
\]

where \( n_0 \) is the linear refractive index, \( n_{\text{ex}} \) is the effective nonlinear refractive index, \( I \) represents the input laser intensity, \( n_2 \) is the normal third-order nonlinear refractive index [19,21], and \( n_4 \) denotes the fifth-order nonlinearity. Li et al. [21] found that free carrier effect (fifth-order nonlinearity) in bulk CdS is significant for longer laser pulses, which might still have contribution in our case.

Another interesting effect is due to the local field effect. When the nanocrystals (NCs) are embedded in a dielectric matrix as in the case presented here, the experimentally measured effective nonlinear optical susceptibility of the composite material \( \chi^{(3)}_{\text{eff}} \) is related to \( \chi^{(3)}_m \) through [22]:

\[
\chi^{(3)}_{\text{eff}} =pf^4 \chi^{(3)}_m ,
\]

where \( p \) is the volume fraction of NCs, and \( f = \frac{3\varepsilon_0}{2\varepsilon_0+\varepsilon} \) is the local field effect (with \( \varepsilon_0 \) and \( \varepsilon \) being the dielectric constants of the matrix and nanocrystals, respectively), \( \chi^{(3)}_m \) is the optical susceptibility of NCs. So in our samples, the change of the nonlinear refractive index \( n_{\text{ex}} \) can be caused by the change of the volume fraction of CdSe nanocrystals in CR39. It increases when the CdSe nanocrystal weight-percentage concentration increases, which has a linear dependence as shown in Figs. 7 and 8.

4. Conclusions

We have shown that the optical properties of the hybrid composite films are strongly dependent on the CdSe nanocrystal concentration in the CR39 polymer. The optical nonlinearity measurements using the Z-scan technique have shown that the hybrid materials have effective nonlinear refractive indexes ranging from \( 2.05 \times 10^{-4} \) cm\(^2\)/GW to \( 4.29 \times 10^{-4} \) cm\(^2\)/GW at 794 nm (below the band gap) and from \( 1.09 \times 10^{-4} \) cm\(^2\)/GW to \( 1.60 \times 10^{-4} \) cm\(^2\)/GW at 395 nm (above the band gap), which vary with the input laser energy as well as the concentration of the CdSe nanoparticles in the polymer. We believe that not only the third-order nonlinearity but also higher-order nonlinearity also exist in such CdSe/CR39 composites due to the free carrier effect. The dispersion behaviors of the nonlinear refractive indices at these two wavelengths are consistent with the bound electronic nonlinear refraction predicted by two-photon resonance. These results indicate that the CdSe/CR39 films are a new kind of promising material for optical filter applications and have favorable nonlinear optical properties.

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References

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