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Third-order optical nonlinearity and figure of merit of CdS nanocrystals chemically stabilized in spin-processable polymeric films

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We report figure of merit for sub-picosecond nonlinearity at 815 nm for nanocrystals of CdS dispersed in poly(methyl methacrylate) (PMMA). CdS nanocrystals were successfully transferred from the aqueous to the organic phase and stabilized in PMMA films using a new chemical route. We report a nonlinear Kerr coefficient n_2 of $-(8.4 \pm 0.4) \times 10^{-14}$ cm^2/W, and a one-photon figure of merit $W = 1.2$ for 3 wt% CdS-doped PMMA film. The results suggest the combined processibility and promising optical properties of such materials for use in transmission-mode optical switching and limiting devices based on ultrafast nonlinearity. *© 2004 Kluwer Academic Publishers*

1. Introduction

Semiconductor nanocrystals provide tunable optical properties arising from the quantum size effect [1–8]. Quantum confinement plays a role in applications such as saturable absorbers, electroluminescent displays, optical switching, optical limiting, lasers, and optical data storage. For realization of practical solid-state devices, nanocrystals are typically integrated into a processable matrix such as a glass or a polymer [7]. The matrix must meet mechanical, electrical, and optical criteria determined by the application for which the resulting hybrid material is required.

Hybrid films of inorganic semiconductor nanocrystals dispersed in a polymer matrix can combine the electroluminescent and nonlinear optical advantages of each component [5–13]. Polymers provide a highly processible matrix compatible with various conducting and insulating substrates without lattice-matching required in semiconductor epitaxy [13]. Semiconductor nanocrystals provide a sharp density of states, with sudden onset of excitonic transitions and concentration of oscillator strength into a narrow spectral range; tuning of spectral features through the quantum size effect; and electron/hole confinement/anticonfinement through heterostructure engineering.

Nonlinear optical materials provide building blocks for optical switching, modulation, and limiting in future-generation *all-optical* networks. We focus in the present work on the optical properties of these promising nanocrystal-polymer composites in nonlinear optical switching and limiting. To be useful in transmissive devices exploiting nonlinear phase change such as nonlinear directional couplers [14] and optical limiters [15], the material must provide a π phase change before the optical power exciting the phase change is substantially absorbed. The Stegeman figures of merit W and T quantify this requirement [16]. The Stegeman figure of merit relating to linear absorption, T, has a substantial technological component inside inhomogeneous (hence scattering) materials. Cotter *et al.* [10] have shown that three-dimensional quantum confinement can alter radically the nonlinear optical properties of semiconductors in the transparency region. The discovery that introducing the quantum confinement can enhance W opens new opportunities for practical exploitation of the quantum-size effect in devices.

In this paper we report the results of our new chemical route to transfer CdS nanocrystals from the aqueous to the organic phase, mix them with poly(methyl methacrylate) (PMMA), and make thin solid films. Optical absorption and photoluminescence measurements demonstrate that the CdS nanocrystals were successfully doped into and stabilized in the PMMA films with high optical quality. Kerr coefficient and Stegeman figure of merit T were obtained for PMMA film with high doping but stabilized CdS nanocrystals.

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2. Experimental details

The incorporation of inorganic nanocrystals with high surface energy into a polymeric matrix is a major challenge that must be overcome to fabricate high optical quality nanostructured films. CdS nanocrystals were synthesized with thiols as stabilizer using a modified method of Weller *et al.* [17–20]. CdS nanocrystal solution was purified from a large amount of salt by dialysis against water using molecular porous membrane tubing (Spectrum Laboratories Inc. MWCO 6,000–8,000) against water. After 3 days, the system gelated without volume shrinkage and became opaque—unusual since generally only alkoxides such as SiO_2 and TiO_2 form gels during hydrolysis. Following 7-day dialysis, the gel precipitated. The yellow precipitate was washed with the purified water to remove the traces of salts, then repeatedly rinsed with methanol to dehydrate CdS crystals, and finally re-dispersed in pyridine under gentle agitation. It is known that coordination complexation occurs between pyridine and some transition metals [21, 22]. During this process, the hydrophobicity of the nanoparticles increased and they could be dispersed in nonpolar solvents. The CdS-PMMA pyridine solution was concentrated in a rotary evaporator to remove most of the solvent, transferred into a Teflon mold, and dried at 70°C overnight. The last stage in sample fabrication included press-molding of the nanocomposite films in a die between two polished stainless steal slides at 150°C and under 2.5 Psi pressure. The concentration of CdS in the composite films, was 0.1, 1, 3 and 10 wt%. Film thickness was in the range of 0.14–0.18 mm.

The CdS/PMMA composites were characterized for linear optical loss using a Cary 500 UV-VIS-NIR spectrophotometer. The photoluminescence (PL) was measured using the PTI spectrofluorometer at room temperature under 442 nm He-Cd laser line excitation. The nonlinear properties of the films were measured using amplified pulses from a Coherent MIRA 900 femtosecond Ti:Sapphire laser at 815 nm. Autocorrelation results indicated a pulse width of 120 fs. In order to ensure that fast electronic nonlinear optical effects were observed rather than slow thermal effects, a MEDOX Pockels cell was used to provide an output pulse repetition rate of 5 kHz. The laser beam was focused onto the sample using a lens of focal length $f = 100$ mm. The beam profiles at the sample surface were measured to have $1/e^2$ diameter of 39–49 μm. An aperture with linear beam transmittance $S = 0.1$ was used for all closed-aperture measurements.

3. Results and discussion

We show in Fig. 1 the spectra of linear absorption spectra for 0.25 wt% CdS nanocrystals in water; pure PMMA film and 0.1, 1, 3, 10 wt% CdS/PMMA hybrid films. The onset of absorption for CdS nanocrystals in solution occurs at 477 nm, consistent with nanocrystal sized around 4 nm [23]. PMMA is tranparent from 900 to 400 nm. The CdS/PMMA blends absorb below ~480 nm and absorption grows with CdS doping level, attesting to successful incorporation of CdS nanocrystals into PMMA. Above 500 nm, scattering is the dominant source of loss out of the tranmsmitted mode.

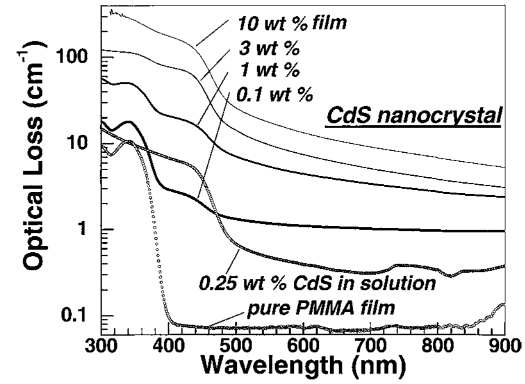

Figure 1 Optical loss measured for samples of CdS nanocrystal in PMMA films with concentrations of 0.1, 1, 3, and 10 wt%, together with samples of CdS nanocrystals in solution and pure PMMA film.

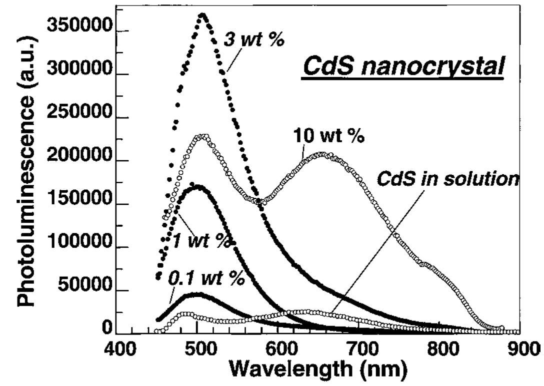

Figure 2 Photoluminescence for CdS nanocrystal in PMMA films with concentrations of 0.1, 1, 3, and 10 wt%, together with sample of CdS nanocrystals in solution.

PL was measured for various CdS nanocrystals in solution and in films and shown in Fig. 2. The PL properties of nanocrystals depend typically on conditions not revealed by absorption experiments alone: surface structure, chemical environment, migration of carriers, and some guest-host effects. The PL of nanocrystals in solution reveals a peak near 480 nm due to emission associated with band-to-band transitions, as well as a broad peak around 640 nm associated with emission from surface trap states [24–26]. For CdS nanocrystal doped in PMMA with 0.1, 1 and 3 wt%, the PL shows only one peak around 490 nm: the nanocrystals have successfully been stabilized in the PMMA polymeric environment at these low and moderate doping levels. With 10 wt% doping, the broad peak appears again, together with lower PL efficiency for band-to-band emission. Earlier report [27] identified the emergence of CdS cluster network for doping levels higher than 4 wt%.

We proceeded to measure the nonlinear optical properties of the hybrid polymeric film with high CdS doping but stabilized surfaces of 3 wt%. The nonlinear refractive index n_2 was measured by the Z-scan method [28]. The open-aperture transmittance shows absorption saturation as discussed by Sheik-Bahae *et al.* [28]. The saturation may result from state-filling in the CdS nanocrystal with increased field intensity. The closed-aperture scan was divided by the open-aperture scan and the result is shown in Fig. 3. The experimental data were fitted to the expression given by Sheik-Bahae *et al.* [28]

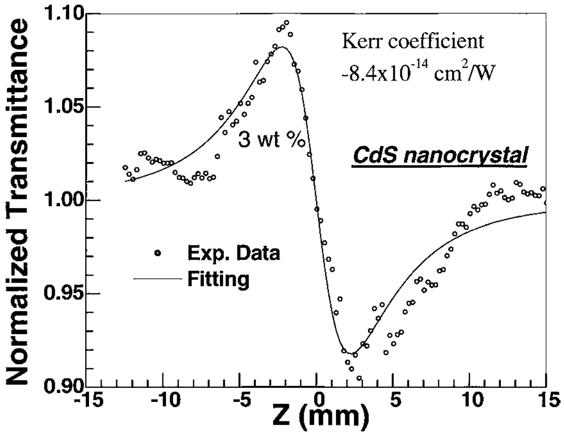

Figure 3 Closed-aperture Z-scan trace for 3 wt% CdS/PMMA hybrid film measured with pulses of 120 fs at 815 nm (5 kHz repetition rate). Circles give experimental results; the line represents a fit according to the method of Sheik-Bahae [28].

which relates the normalized transmittance $T(Z, \Delta\phi_0)$ directly to phase change $\Delta\phi_0$,

$$T(Z, \Delta\phi_0) \cong 1 + \frac{4\Delta\phi_0 x}{(1+x^2)(9+x^2)'}$$

where $x = Z/Z_0$. Nonlinear least-squares fitting with $\Delta\phi_0$ and Z_0 as parameters yields $\Delta\phi_0 = -0.404$ and $Z_0 = 0.00261$. From the relation $\Delta\phi_0 = 2\pi\,\Delta n L_{\text{eff}}/\lambda$, we obtain refractive index change at the focal point of $\Delta n = -3.6 \times 10^{-4}$ and a Kerr coefficient $n_2 = -(8.4 \pm 0.4) \times 10^{-14}$ cm^2/W. From Z_0, the beam size at the focus point is calculated to be 51 μm, in reasonable agreement with the beam profiler measurement. The negative sign in n_2 indicates that the material has a defocusing nonlinearity. This is consistent with the fact that the laser wavelength sits between the one- and two-photon absorption edges of CdS nanocrystals. The one-photon figure of merit, W, is defined as $W = \Delta n/\alpha\lambda$, where α is the absorption coefficient. For $\Delta n = 3.6 \times 10^{-4}$, $\alpha = 3.7$ cm^{-1}, and $\lambda = 815$ nm, the figure of merit $W = 1.2$. For a nonlinear optical material to be useful, it is essential the value of W be large than 1. The results suggest the combined processibility and promising optical properties of such materials for use in transmission-mode optical switching devices based on ultrafast nonlinearity. The material system is also very promising for periodic optical limiting devices [29, 30] if we combine the nonlinear optical function of nanocrystals, with electromagnetic structural resonances of photonic crystals [31].

The Kerr coefficient n_2 measured using Z-scan on a bulk CdS crystal with 100-femtosecond pulses at 610, 780 and 1270 nm has previously been reported to be on the order of 10^{-13}–10^{-14} cm^2/W [9]. Cotter and coauthors [10] reported that the dispersion of the third-order susceptibility χ^3 of nanocrystal is fundamentally different from that of bulk semiconductors. Experimentally, they found that the electronic refractive nonlinearity of 5-nm nanocrystal embedded in glass is consistently negative in sign for frequencies below the absorption edge. Our results agree with those of Cotter *et al.* There exist other experimental reports in which CdS nanocrystals were synthesized by wet chemistry and characterized in solution or in polymer film [11, 12]. Schwerzel *et al.* [12] have studied thiophenol-capped CdS nanocrystals with a size of 3.3 nm in pyridine and in polydiacetylene film using Z-scan technique at 530 nm with 5 ns pulses. The Kerr coefficient $n_2$was negative and ranged bewteen -4.0×10^{-14} and -1.4×10^{-13}cm^2/W. The explanation may lie in Cotter's and our use of ~100 fs pulses and lower repetition rates, compared to Schwerzel's multi-ns pulses: nonlocal contributions such as electrostrictive and thermal nonlinearity are expected to be negligible in the femtosecond experiments.

4. Summary and conclusions

In summary, CdS/PMMA hybrid films were synthesized with a goal of assessing and controlling their optical properties with a view to applications in nonlinear optics and switching. New chemical routes were applied to incorporate into polymeric films the CdS nanocrystal with high surface energy. The hybrid films were characterized using optical absorption and photoluminescence in order to monitor the degree of nanocrystal stabilization in the solid state films. Third-order nonlinear optical properties were measured by the single-beam Z-scan technique at 815 nm using 120 fs pulses in the ultrafast electronic nonlinear regime. The results indicate that the quantum functional films may be used to engineer nonlinearity in ultrafast transmissive nonlinear optical devices.

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