

Enhanced photorefractive performance in CdSe quantum-dot-dispersed poly(styrene-co-acrylonitrile) polymers

Xiangping Li,¹ Joel van Embden,¹ James W. M. Chon,¹ Richard A. Evans,² and Min Gu^{1,a)}

¹Centre for Micro-Photonics, Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, Hawthorn, Victoria 3122, Australia

²CSIRO Molecular and Health Technologies, Bag 10, Clayton South, Victoria 3169, Australia

(Received 22 March 2010; accepted 26 May 2010; published online 21 June 2010)

This paper reports on the enhanced photorefractive behavior of a CdSe quantum-dot-dispersed less expensive polymer of poly(styrene-co-acrylonitrile). The capability of CdSe quantum dots used as photosensitizers and the associated photorefractive performance are characterized through a photocurrent experiment and a two-beam coupling experiment, respectively. An enhanced two-beam coupling gain coefficient of 12.2 cm^{-1} at $46 \text{ V}/\mu\text{m}$ was observed owing to the reduced potential barrier. The photorefractive performance per CdSe quantum dot is three orders of magnitude higher than that in the sample sensitized by trinitrofluorenone in poly(styrene-co-acrylonitrile), and almost ten times higher than that in the CdSe quantum-dot-sensitized poly(N-vinylcarbazole) polymers.

© 2010 American Institute of Physics. [doi:10.1063/1.3454780]

Owing to the easy preparation procedure, the flexibility in compositions, and the reversible refractive-index modulation, photorefractive polymers have attracted considerable interest in the past two decades.^{1,2} Photorefractive polymers typically consist of four necessary components including photosensitizers, nonlinear dyes, photoconductive polymers, and plasticizers.² Since the observation of photorefractivity in polymers³ tremendous efforts have been spent to improve their performance. A key solution for the improvement of the photorefractive performance is to replace the organic sensitizers with photosensitizers of higher charge generation efficiency and higher photostability. Due to their attractive optical properties such as the tunability of spectral response with size, large photocharge generation efficiency, and the high photostability, semiconductor quantum dots (QDs) (Ref. 4) are appealing materials for application in photorefractive polymers as a replacement of organic sensitizers. A variety of QDs with different sizes and compositions has been dispersed into poly(9-vinylcarbazole) (PVK) based photorefractive polymers to induce the photorefractivity.⁵⁻⁸

PVK has been one of the popular photorefractive polymers but may not be necessarily the best for QD-sensitized systems since most QDs have a poor solubility in PVK matrices. The reported photorefractive performance was conducted with a layer of organic molecules capped on the surface of QDs to avoid aggregation and increase the solubility and the stability in polymer matrix.⁹⁻¹¹ As a result of the potential barrier constructed by the capping molecules, the photocharge generation, and the charge transfer efficiency are significantly degraded.^{6,9,11,12} Therefore, the photorefractive performance of QD-sensitized polymers generally remains low. At the more general field of $42 \text{ V}/\mu\text{m}$ the two-beam coupling gain coefficient was approximately 5 cm^{-1} (Ref. 13) or even less.^{6,11} It has been shown that QDs have a good solubility in polystyrene^{14,15} and poly(lauryl methacrylate);¹⁶ however no photorefractive performance has been reported yet in such polymers. It is mainly attrib-

uted to the lack of photoconductivity in such polymers and their derivatives, which is required for the photorefractive effect. In this letter, we report on an optimized photorefractive formula consisting of poly(styrene-co-acrylonitrile) (PSCA) (average molecule weight $\sim 165\,000$, consisting of 25 wt % of acrylonitrile) sensitized by CdSe QDs. The photorefractive performance of CdSe QDs was characterized through the comparison with the control sample sensitized by trinitrofluorenone (TNF).

CdSe QDs were synthesized following a well established method.¹⁷ Varying the amount of oleic acid used in the preparation procedure, CdSe QDs of size 6.2 nm with first transition peak at 630 nm were synthesized. The as-prepared QDs were washed and precipitated till nearly unpassivated using chloroform and methanol. The well washed QDs were redispersed into chloroform. The absorption spectrum is shown in Fig. 1. A photorefractive polymer formula consisting of PSCA (Sigma Aldrich), ethyl carbazole (ECZ), and nonlinear dye 4-diethylaminobenzylidene-malononitrile (DABM) (Ref. 18) was prepared. Here ECZ is responsible for charge transportation along the polymer matrix.² Both PSCA and ECZ were recrystallized six times before usage. The mixture of 50 mg of PSCA, 20 mg of ECZ, 30 mg of DABM, and 0.5 nmol CdSe QDs were dissolved in chloroform. The solution was dried in a vacuumed oven at $70 \text{ }^\circ\text{C}$ for overnight. To characterize the photocurrent and photorefractive performance the dried sample was heated to $150 \text{ }^\circ\text{C}$ and subsequently sandwiched between two indium tin oxide-coated glass slides with a spacer. The measured sample thickness is $120 \pm 10 \mu\text{m}$.

The absorption spectrum of the as-prepared sample was measured and normalized by the first transition peak to compare with that of QD solution, as shown in Fig. 1. The sample is optically clear. The shape of the first transition peak is almost identical to that of QDs in solution, which confirms that QDs are well separated and no aggregation occurs during the sample preparation process. However strong scattering and broadening of the first transition peak were observed in the PVK sample (not shown here), which is

^{a)}Electronic mail: mgu@swin.edu.au.

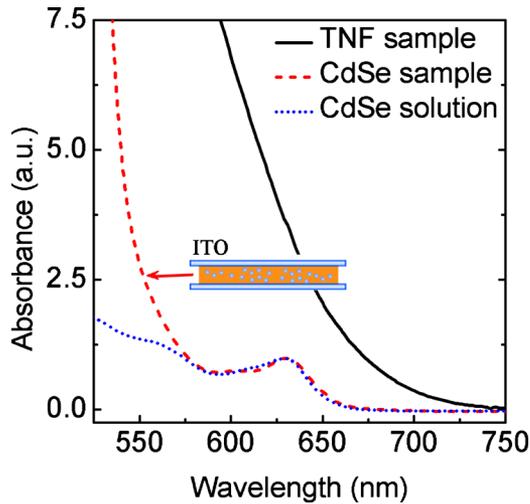


FIG. 1. (Color online) Absorption spectra of CdSe QDs redispersed in chloroform solution (dotted line) and the CdSe QD-dispersed photorefractive sample (dashed line) after normalized by the first transition peak. The solid line is the absorption spectrum of the TNF sensitized PSCA photorefractive thin film.

due to the aggregation of QDs without surface passivation, even at one fifth doping concentration of the PSCA sample. From the absorbance of the first transition peak we calculated the concentration of QDs inside the polymer film is $5.2 \mu\text{M}$.¹⁹ For a comparison, a sample dispersed with 1 wt % of TNF, a concentration of 31.7 mM, was prepared following the same procedure. Its absorption spectrum is shown in Fig. 1 as well.

The photosensitivity of the sample sensitized by CdSe QDs and TNF, respectively, was compared on the per sensitizer basis in Fig. 2. The photosensitivity is defined as²⁰

$$S_{\text{ph}} = J_{\text{ph}} / (EI), \quad (1)$$

where J_{ph} is the photocurrent density, E is the external electric field applied, and I is the illumination intensity of the beam. To characterize the photocurrent generation at the wavelength of 632.8 nm, a He-Ne laser expanded to a beam size of 5 mm was employed as the excitation source. The photocurrent signal was amplified by a lock-in amplifier and a beam chopper was inserted in the beam pass to synchronize the amplifier with the photocurrent signal. In the reference sample consisting of no sensitizers, there is no measurable

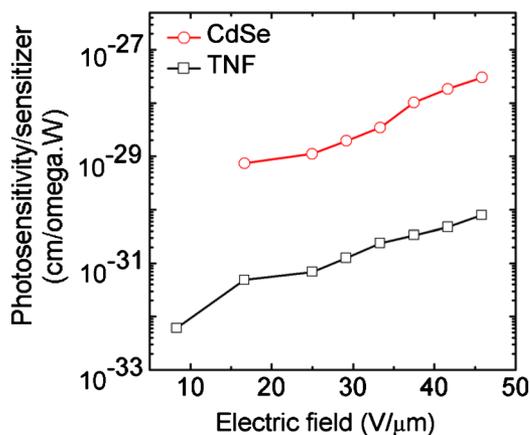


FIG. 2. (Color online) Comparison of photosensitivity of CdSe QD (circles) and TNF (squares) sensitized samples on the per sensitizer basis.

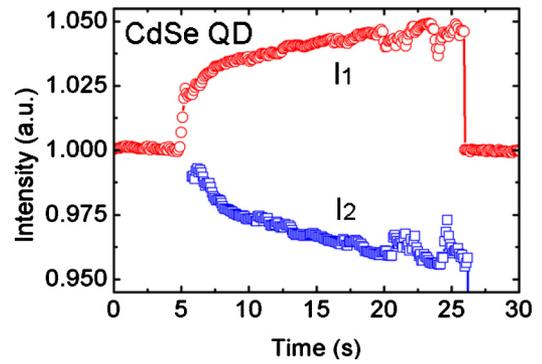


FIG. 3. (Color online) The transmitted intensity of the two beams intersected in the CdSe QD-sensitized photorefractive thin film. The circles are data for I_1 and the squares are data for I_2 .

photocurrent at the experimental condition of intensity of $3.6 \text{ mW}/\text{cm}^2$. Figure 2 depicts clearly that in the whole external electric field range, the photosensitivity per CdSe QD is three orders of magnitude higher than that of TNF owing to the significantly enhanced absorption cross section per sensitizer. The photosensitivity of TNF sensitized sample is comparable with previous results of the PVK/ECZ/TNF system.²¹ There is 20% of enhancement in the photosensitivity per nanoparticle in PSCA polymers compared to the reported results of CdSe QDs with a similar size in the PVK/ECZ system.¹⁰ This enhancement in the CdSe QD-sensitized PSCA polymers is mainly attributed to the reduced potential barrier of charge generation and transfer as nearly no capping ligands are present on the surface of QDs, which is highly desirable since a larger photosensitivity can lead to a stronger photorefractive performance.² Based on the photosensitivity in Fig. 2, one can calculate the photocharge generation efficiency of the samples as follows:²⁰

$$\phi = J_{\text{ph}} \frac{hc}{I\lambda e\alpha d}, \quad (2)$$

where h is the Planck's constant, c is the speed of the light, and e is the fundamental unit of charges. α and d are the absorption coefficient and the thickness of the samples, respectively.

The enhanced photosensitivity can lead to an enhanced photorefractive performance. To compare the photorefractive performance, we carried out a two-beam coupling experiment. A characteristic feature of photorefractivity is the phase shift in constructed refractive-index gratings compared to the illumination patterns.² As a result; asymmetric energy transfer occurs between the two incident beams intersecting inside the photorefractive polymers. Figure 3 shows the data of the transmitted intensity of the two beams as a function of time in CdSe QD-sensitized sample excited at the wavelength of 632.8 nm. For this experiment, an external electric field of $46 \text{ V}/\mu\text{m}$ was applied across the sample and the intensity of the two writing beams, I_1 and I_2 , was $400 \text{ mW}/\text{cm}^2$ and $200 \text{ mW}/\text{cm}^2$, respectively. The two p-polarized beams intersected in the sample with incident angles of 30° and 60° in air, respectively. The beam I_2 was turned on at $t=5 \text{ s}$ and turned off at $t=26 \text{ s}$. Figure 3 reveals clearly that strong asymmetric energy transfer was observed as I_1 gained energy while I_2 lost an equivalent amount of energy, with corresponding energy transfer by 5%. The two-beam coupling gain coefficient of CdSe QD-sensitized

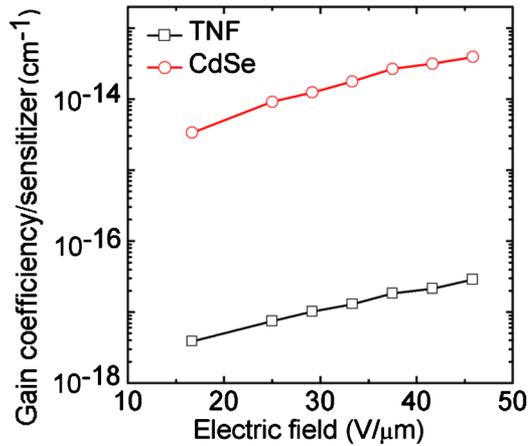


FIG. 4. (Color online) The two-beam coupling gain coefficient per sensitizer of CdSe QD (circles) and TNF (squares) sensitized samples as a function of the external electric field.

sample is calculated to be 12.2 cm^{-1} , which is already doubled compared to the reported results in the PVK system at a similar condition.^{6,11,13} Figure 4 depicts the comparison of the two-beam coupling gain coefficient per sensitizer as a function of the external electric field. This result is consistent with the photosensitivity and photocharge generation experiment, which confirms that the photorefractive performance per CdSe QD is three orders of magnitude better than that of TNF. For a comparison, the two-beam coupling gain coefficient per nanoparticle is almost ten times larger than that of CdSe QD-sensitized PVK polymers.^{10,13} It should be noted that the concentration of ECZ is crucial in PSCA samples, as it is mainly responsible for charge transportation. No two-beam coupling phenomenon was observed in a sample without ECZ doping due to the lack of photoconductivity of PSCA. Once the ECZ doping is over 20%, the dielectric breakdown threshold drops off quickly.

In conclusion, we have developed a photorefractive formula consisting of CdSe QD-sensitized PSCA polymers. The expensive PVK is replaced by a cheap inert copolymer. The reduced potential barrier for charge generation and transfer lead to the enhanced photosensitivity and photorefractive performance. A two-beam coupling gain coefficient of

12.2 cm^{-1} was observed at an external electric field of $46 \text{ V}/\mu\text{m}$. This result shows an enhancement in the photorefractive performance per CdSe QD by three orders of magnitude compared with that of sample sensitized by TNF, and by nearly one order of magnitude compared with the reported results of the CdSe QD-sensitized PVK system.

We thank the Australian Research Council for its support (Discovery Project DP0558759).

- ¹K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen, and N. Peyghambarian, *Nature (London)* **371**, 497 (1994).
- ²W. E. Moerner, A. Grunnet-Jepsen, and C. L. Thompson, *Annu. Rev. Mater. Sci.* **27**, 585 (1997).
- ³S. Ducharme, J. C. Scott, R. J. Twieg, and W. E. Moerner, *Phys. Rev. Lett.* **66**, 1846 (1991).
- ⁴A. P. Alivisatos, *Science* **271**, 933 (1996).
- ⁵J. G. Winiarz, L. Zhang, M. Lal, C. S. Friend, and P. N. Prasad, *J. Am. Chem. Soc.* **121**, 5287 (1999).
- ⁶D. J. Binks, S. P. Bant, D. P. West, P. O'Brien, and M. A. Malik, *J. Mod. Opt.* **50**, 299 (2003).
- ⁷C. Fuentes-Hernandez, D. J. Suh, B. Kippelen, and S. R. Marder, *Appl. Phys. Lett.* **85**, 534 (2004).
- ⁸X. Li, J. W. M. Chon, and M. Gu, *Aust. J. Chem.* **61**, 317 (2008).
- ⁹D. J. Binks, D. P. West, S. Norager, and P. O'Brien, *J. Chem. Phys.* **117**, 7335 (2002).
- ¹⁰J. G. Winiarz, *J. Phys. Chem. C* **111**, 1904 (2007).
- ¹¹F. Aslam, D. J. Binks, M. D. Rahn, D. P. West, P. O'Brien, and N. Pickett, *J. Mod. Opt.* **52**, 945 (2005).
- ¹²N. C. Greenham, X. Peng, and A. P. Alivisatos, *Phys. Rev. B* **54**, 17628 (1996).
- ¹³F. Aslam, J. Stevenson-Hill, D. J. Binks, S. Daniels, N. L. Pickett, and P. O'Brien, *Chem. Phys.* **334**, 45 (2007).
- ¹⁴M. Tamborra, M. Striccoli, R. Comparelli, M. L. Curri, A. Petrella, and A. Agostiano, *Nanotechnology* **15**, S240 (2004).
- ¹⁵D. Šajinović, Z. V. Šaponjić, N. Cvjetičanin, M. Marinović-Cincović, and J. M. Nedeljković, *Chem. Phys. Lett.* **329**, 168 (2000).
- ¹⁶J. Lee, V. C. Sundar, J. R. Heine, M. G. Bawendi, and K. F. Jensen, *Adv. Mater. (Weinheim, Ger.)* **12**, 1102 (2000).
- ¹⁷J. van Embden and P. Mulvaney, *Langmuir* **21**, 10226 (2005).
- ¹⁸X. Li, C. Bullen, J. W. M. Chon, R. A. Evans, and M. Gu, *Appl. Phys. Lett.* **90**, 161116 (2007).
- ¹⁹J. Jasieniak, L. Smith, J. van Embden, P. Mulvaney, and M. Califano, *J. Phys. Chem. C* **113**, 19468 (2009).
- ²⁰E. Hendrickx, Y. Zhang, K. B. Ferrio, J. A. Herlocker, J. Anderson, N. R. Armstrong, E. A. Mash, A. P. Persoons, N. Peyghambarian, and B. Kippelen, *J. Mater. Chem.* **9**, 2251 (1999).
- ²¹G. Ramos, T. Belenguer, and D. Levy, *J. Phys. Chem. B* **110**, 24780 (2006).