

## Photorefractive properties in poly(*N*-vinylcarbazole)/CdSe nanocomposites through chemical hybridization

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This letter reports on an organic/inorganic hybridized polymer system that combines semiconductor inorganic nanoparticles, a conjugated poly(*N*-vinylcarbazole) (PVK) polymer, and 4-(4-nitrophenylazo) chromophores to manifest a photorefractive effect. PVK nanocomposites doped with cadmium selenide (CdSe) nanoparticles were prepared through chemical hybridization and their optical properties were characterized. The photorefractive effects in the prepared PVK/CdSe nanocomposite systems were directly compared with those of a similar PVK/CdSe nanoblend system. Significant enhancement of the gain coefficient was observed in the PVK/CdSe nanocomposite system relative to the PVK/CdSe nanoblend system. © 2006 American Institute of Physics. [DOI: 10.1063/1.2374804]

The realization of advanced information and image processing technology depends on the development of multifunctional materials that are able to simultaneously satisfy several requirements.<sup>1</sup> The photorefractive effect is defined as the spatial modulation of the index of refraction in an electro-optically active material due to the redistribution of charge carriers photogenerated under nonuniform illumination. For the buildup of the refractive effect, the following processes are necessary: (i) photogeneration of charge carriers, (ii) diffusion or drift of the mobile carriers, (iii) trapping of these charge carriers in regions of low light intensity, and (iv) change of the index of refraction due to the buildup of an internal space-charge field.

Semiconductor nanoparticles, which exhibit properties that are different from those of bulk materials, are attractive materials that hold considerable promise for numerous applications in the fields of electronics and photonics.<sup>1</sup> With the advent of nanocrystal technology, several means by which to photosensitize polymer composites have been realized, establishing a class of inorganic-organic hybrid photoconductive materials.<sup>2</sup> Semiconductor particles are a potentially useful class of polymer photosensitizers for many applications that require materials with photoconductive and photorefractive properties. Since only a small amount of nanoparticles are required to photosensitize the matrix, the nanoparticles are isolated from each other and are responsible for the charge generation, while the polymer is responsible for hole transport.<sup>3,4</sup> Thus far, the reported photorefractive polymer systems have been prepared by simply mixing synthesized nanoparticles and polymers. Conventionally synthesized semiconductor nanoparticles have a tendency to aggregate into larger clusters, and thus attaining a fine dispersion of the nanoparticles in the polymer has proved challenging. Although organically capped nanoparticles have been synthesized, the effect of capping molecules of the synthesized semiconductor nanoparticles is not yet clear. Recently, chemically hybridized poly(*N*-vinylcarbazole) (PVK)/cadmium sulfide (CdS) nanocomposites were obtained, and

large photoconductivity enhancement was observed in comparison with PVK/CdS nanoblends.<sup>5</sup> The enhanced photoconductivity of CdS nanoparticles, which results more efficient charge generation, is attributed to improved interface quality between the CdS particles and PVK in the nanocomposites.<sup>5,6</sup>

In this work, we synthesized chemically hybridized PVK/cadmium selenide (CdSe) nanocomposites for application to a 633 nm (wavelength) photorefractive system. The optical and electrical properties of the nanocomposites, along with their photorefractive characteristics, have been investigated. It is shown that the composite has a significantly enhanced photorefractive gain value compared with that of a PVK/CdSe nanoblend system.

Chemically hybridized PVK/CdSe nanocomposites were prepared by (1) sulfonation of PVK, (2) preparation of the precursor PVK(SO<sub>3</sub>)<sub>2</sub>Cd, and (3) formation of the PVK/CdSe nanocomposite. The detailed procedure of the synthesis in steps (1) and (2) can be found in a previous report.<sup>5</sup> Cd-exchanged sulfonated PVK (80 mg) was dissolved in 80 ml of tetrahydrofuran, and an alkaline Se aqueous solution was prepared as follows: 0.25 mol sodium hydroxide, 0.001 mol sodium sulfide, and 0.001 mol Se were added to 30 ml of distilled water. Two solutions were combined slowly with vigorous stirring. Immediately, the originally colorless solution turned bright red. By controlling the partial sulfonation of the PVK, we can vary the molar ratio of CdSe to PVK. In this study, two samples, PVK/CdSe 15 and PVK/CdSe30, were prepared: the molar ratios of CdSe to PVK were 1:34 and 1:17. The theoretical weight ratio of CdSe in the nanocomposites is 2.9% and 5.8%, respectively. For a comparative study, CdSe nanoparticles were synthesized by the aqueous method and the surface of the CdSe nanoparticles was treated so as to become organophilic using 4-methylbenzene thiol as an organic modifier.<sup>7</sup>

Transmission electron microscope images (TEM) reveal spherical shaped CdSe nanoparticles (Fig. 1). The size of the CdSe nanoparticles was in a range of 5–20 nm, based on estimates from the TEM images. Thus, it is implied that nanosized CdSe particles were made via chemical hybridization. Figure 2(a) shows the UV-vis absorption spectra of

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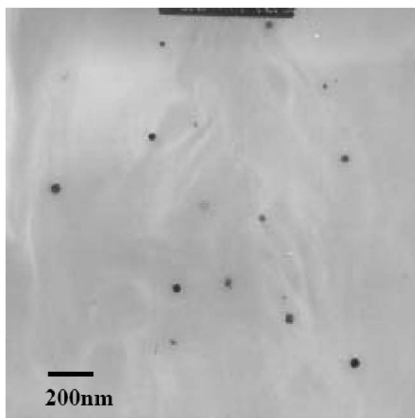


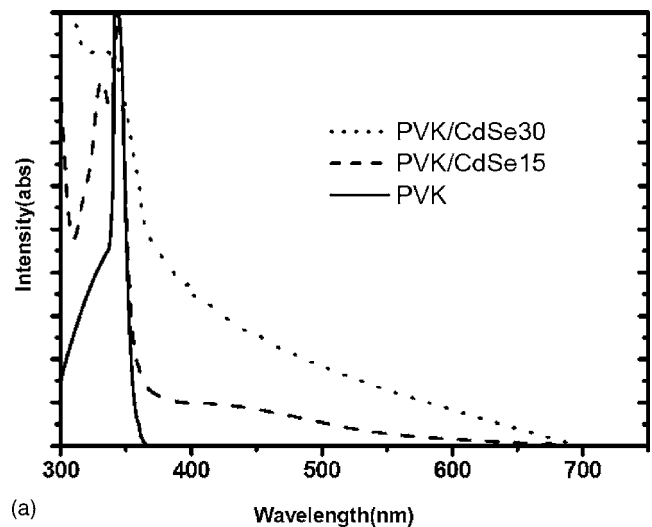
FIG. 1. TEM images of the CdSe nanoparticles in the chemically derivatized nanocomposites (PVK/CdSe30).

PVK, PVK/CdSe15, and PVK/CdSe30. It is clear that there is a significant difference between the UV-vis spectra of PVK and the chemically derivatized nanocomposite PVK/CdSe; furthermore, a broad absorption tail appears above 400 nm in the latter. This is attributed to the band-gap absorption of the CdSe nanoparticles.<sup>8</sup> By increasing the molar ratio of CdSe in the nanocomposites, the range of absorption is redshifted. It is worth noting that a distinct absorption of 633 nm has been observed in the absorption spectra of the PVK/CdSe nanocomposites, indicating that they can be applicable to a photorefractive system using a 633 nm laser.

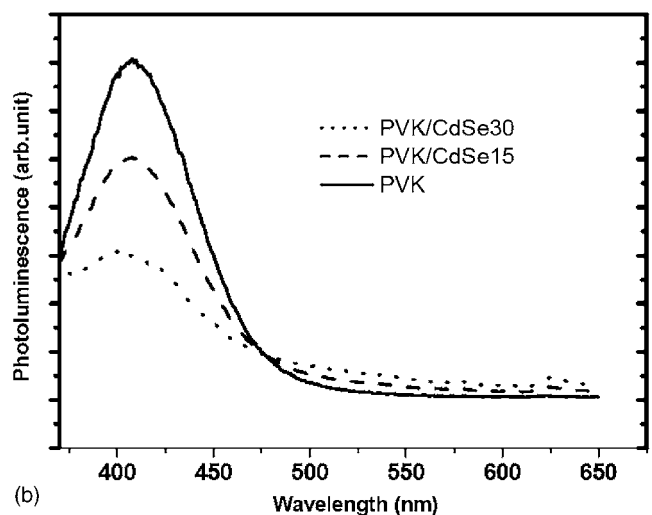
When the as-prepared chemically derivatized nanocomposite was excited with a laser at a wavelength of 360 nm, the intensity of the photoluminescence was lower than that of the pure PVK film with the same concentration [Fig. 2(b)]. As can be seen from Fig. 2(b), as the CdSe molar ratio is increased the photoluminescence (PL) intensity is lowered. The reduced PL can be attributed to the quenching by interfacial charge transfer due to the close contact between the polymer and the CdSe nanocomposite.<sup>6</sup> This interfacial charge transfer lowers the transition probability from lowest unoccupied molecular orbital to highest occupied molecular orbital, and thus reduces the PVK PL.<sup>9</sup>

Two photorefractive systems, PVK/CdSe nanocomposite-ECZ (9-ethylcarbazole)-DO3 ((4-(4-nitrophenylazo)aniline)) and the nanoblend system, PVK/CdSe nanoblend-ECZ-DO3, were dissolved in chlorobenzene for 1 day while being stirred by a magnetic bar. The composition of the samples was PVK/CdSe/ECZ/DO3 in a 44.8/0.2/45/10 weight ratio. Because the weight fraction of CdSe in the photorefractive system is only 0.2% (by weight) we could not prepare a photorefractive system using the PVK/CdSe15 nanocomposite material only. Hence, we prepared the photorefractive system with 0.2 wt. % CdSe by blending the PVK/CdSe15 nanocomposite (2.9 wt. % CdSe in PVK/CdSe) with pure PVK. Because PVK/CdSe30 is not soluble in chlorobenzene, a nanocomposite based photorefractive system using PVK/CdSe15 was prepared. The mixtures were cast on indium tin oxide-coated glass substrates at room temperature and left to dry overnight. The plates were finally hot pressed for 10 min at 120 °C.

The photorefractive properties were studied using a two-beam coupling (TBC) experimental setup. A laser wavelength of *p*-polarized 633 nm was used, and the two beams intersected in the sample with incident angles at 30° and 60°,



(a)



(b)

FIG. 2. UV-vis spectra (a) and PL spectra (b) of the pure PVK, PVK/CdSe15, and PVK/CdSe30.

respectively, to the normal angle of the sample.

Figure 3(a) shows the energy transfer in TBC experiments using the PVK-based photorefractive systems. The nonlocal nature of the photorefractive grating is the key feature for the photorefractive effect, distinguishing itself from other mechanisms that may result in refractive index gratings. This is demonstrated by asymmetric energy transfer between the two coupling beams. Therefore, the TBC experiment is typically used for direct adjudication of the photorefractive property. From the TBC experiments, an important parameter, namely, the optical gain ( $\Gamma$ ), could be deduced. The TBC gain coefficient  $\Gamma$  was calculated from the following equation:

$$\Gamma = (1/L) \ln[\gamma\beta/(\beta + 1 - \gamma)],$$

where  $L$  is the optical path,  $\beta$  is the intensity ratio of the two incident beams, and  $\gamma$  is the beam couple ratio. The TBC gain coefficients (inset of Fig. 3) were measured by the TBC experiment under various external electric fields for the PVK/CdSe nanocomposites and PVK/CdSe blend systems. At a wavelength of 633 nm, the absorption coefficient was  $10 \text{ cm}^{-1}$ . The photorefractive system containing PVK/CdSe nanocomposites shows better properties than that containing the PVK/CdSe blend system. It is thought that photoconductivity plays a major role in the enhancement of the photore-

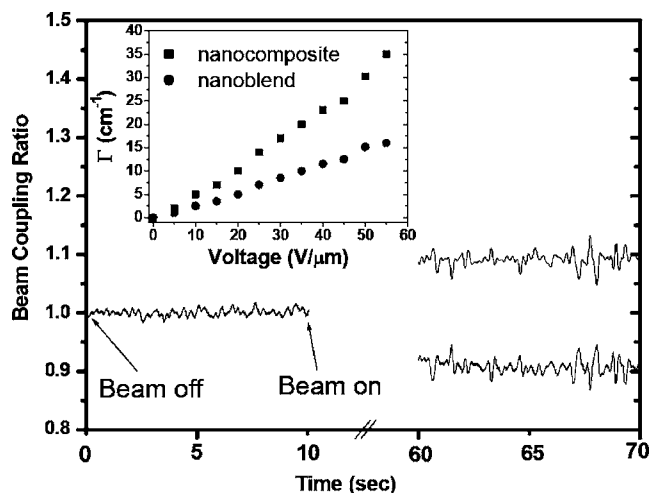


FIG. 3. (a) Energy transfer in a TBC experiment of the PVK/CdSe nanocomposite-ECZ-DO3 system. Asymmetric energy transfer observed for the PR system in a TBC experiment: dc external electric field of  $30 \text{ V}/\mu\text{m}$  was applied at 10 s. For steady-state conditions, the data were collected after a period of 50 s and averaged. The inset figure shows steady-state gain coefficients of the PVK/CdSe nanocomposite-ECZ-DO3 system and PVK/CdSe nanoblend-ECZ-DO3 system at various applied electric fields.

fractive behaviors. Higher conductivity results in a larger number of photogenerated charges, and hence a stronger internal space-charge field. Consequently, a higher photorefractive response is achieved. This correlation has also been documented in previous reports on organic photorefractive materials.<sup>10–12</sup> When electron-hole pairs in the CdSe nanocrystals produced by absorbed photons electrons from the PVK migrate favorably to the CdSe to fill the holes, they create holes in the PVK or, equivalently, the holes are transferred to the PVK. Via this mechanism, contact of the polymer and nanoparticles is very important with respect to obtaining an enhanced photoinduced-charge generation and transfer process. Although organic capping of nanoparticles can serve to increase compatibility and solubility with polymers and organic solvents, charge transport across the inert passivation layer is hindered.<sup>13,14</sup> Improved interface quality between the polymer and the sensitizer in the nanocompos-

ites introduces a higher photocurrent, which results in a high space-charge field.<sup>15</sup>

In this work, organic/inorganic hybridized polymer nanocomposite photorefractive systems were introduced. PVK nanocomposites doped with CdSe nanoparticles were prepared through chemical hybridization and their optical properties were assessed. In addition, the capacity to use the PVK nanocomposite as a photosensitizer in a PVK matrix has been demonstrated. Significant enhancement of the gain coefficient was observed in the PVK/CdSe nanocomposite system compared with the PVK/CdSe nanoblend system. The experimental results demonstrate that the major contribution of the PR effect originates from the space charge field due to effective light-induced charge separation with a subsequent electro-optic refractive index change. This behavior was as attributed to improvement of the interfacial carrier transfer.

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- <sup>1</sup>J. G. Winiarz, L. Zhang, M. Lal, C. S. Friend, and P. N. Prasad, *J. Am. Chem. Soc.* **121**, 5278 (1999).
- <sup>2</sup>J. G. Winiarz, L. Zhang, J. Park, and P. N. Prasad, *J. Phys. Chem. B* **106**, 967 (2002).
- <sup>3</sup>Y. Wang and N. Herron, *Chem. Phys. Lett.* **200**, 71 (1992).
- <sup>4</sup>Y. Wang, *Pure Appl. Chem.* **68**, 1475 (1996).
- <sup>5</sup>C. L. Yang, J. N. Wang, W. K. Ge, S. H. Wang, J. X. Cheng, X. Y. Li, Y. J. Yan, and S. H. Yang, *Appl. Phys. Lett.* **78**, 760 (2001).
- <sup>6</sup>S. H. Wang, S. Yang, C. Yang, Z. Li, J. Wang, and W. K. Ge, *J. Phys. Chem. B* **104**, 11853 (2000).
- <sup>7</sup>W. Zhang, C. Wang, L. Zhang, X. Zhang, X. Liu, K. Tang, and Y. Qian, *J. Solid State Chem.* **151**, 241 (2000).
- <sup>8</sup>L. Xu, X. Huang, H. Huang, H. Chen, J. Xu, and K. Chen, *J. Appl. Phys.* **37**, 3491 (1998).
- <sup>9</sup>O. Vigil, I. Riech, M. Garcia-Rocha, and M. Zelaya-Angel, *J. Vac. Sci. Technol. A* **15**, 2282 (1997).
- <sup>10</sup>L. Yu, *J. Polym. Sci., Part A: Polym. Chem.* **39**, 2557 (2001).
- <sup>11</sup>Z. H. Peng, A. Gharavi, and L. Yu, *J. Am. Chem. Soc.* **119**, 4622 (1997).
- <sup>12</sup>L. Q. Wang, M. Wang, and L. Yu, *Adv. Mater. (Weinheim, Ger.)* **12**, 425 (2000).
- <sup>13</sup>C. I. Chao and S. A. Chen, *Appl. Phys. Lett.* **73**, 426 (1998).
- <sup>14</sup>N. C. Greenham, X. Peng, and A. P. Alivisatos, *Phys. Rev. B* **54**, 17628 (1996).
- <sup>15</sup>I. D. W. Samuel, B. Crystal, G. Rumbles, P. C. Burn, A. B. Holmes, and R. H. Friend, *Chem. Phys. Lett.* **213**, 472 (1993).