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Observation of photorefractivity in a fullerene-doped polymer composite

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A photorefractive effect was observed in a fullerene (C_{60}) -doped organic composite containing polyvinylcarbazole and a second-order molecule, diethyl-amino-nitrostyrene (DEANST). Electro-optic modulation and degenerate four-wave mixing experiments were conducted. The material shows relatively high electro-optic coefficient, photocharge generation quantum efficiency, and photorefractive diffraction efficiency.

The potential applications of photorefractive (PR) materials in optical information storage and processing have drawn great interest to the search for new materials.[1] The photorefractive effect has been observed in a variety of inorganic crystals such as $LiNbO_3$, $KNbO_3$, and $LiTaO_3$. Organic and polymeric materials are potential candidates for nonlinear optical applications because of their large optical nonlinearity, high optical-damage threshold, and ease of processing.[2] The requirements for the photorefractive effect can be fulfilled simultaneously in an organic composite which contains both photoconductive and electro-optic components. A large number of polymers, such as polyvinylcarbazole, show high photoconductivity.[3] Photorefractivity has been reported in both an organic crystal[4] and doped polymers[5,6] which show both photoconductivity and linear electro-optic effect. There have also been theoretical studies of the photorefractive effect in organic materials.[7–9]

There has been an increasing number of studies on the unusual properties of carbon clusters such as C_{60} and C_{70} since the discovery of the techniques of preparation of these fullerenes in macroscopic quantity.[10] Interesting photophysical[11] and nonlinear optical[12] properties of fullerenes and their charge-transfer complexes have been reported. Pure fullerene films obtained by vacuum vapor deposition have been shown to be photoconductive[13] and the temperature dependence of the photoconductivity has been reported.[14] Fullerene-doped polyvinylcarbazole[15] was found to be comparable to the best available organic photoconductors.

We report in this paper the observation of photorefractivity in a fullerene-doped organic composite. C_{60} and a second-order nonlinear optical (NLO) molecule, diethyl-amino-nitrostyrene (DEANST) [with a first hyperpolarizability of $\beta = 2.2 \times 10^{-28}$ esu (Ref. 16)] were doped into a charge-transporting polymer, polyvinylcarbazole. The electro-optic effect and the electric-field dependence of both the photocharge generation quantum efficiency and the four-wave mixing diffraction efficiency have been studied.

Fullerene C_{60} (from Aldrich) was dissolved in spectral grade toluene with a concentration of 4 mg/ml. Poly-(9-vinylcarbazole) (560 mg) and diethyl-amino-nitrostyrene (DEANST) (265 mg) were added to 4 ml of a filtered fullerene solution while stirred. For electro-optic coefficient and photoconductivity measurements, the solution was spin coated onto indium-tin-oxiide (ITO) -covered soda lime glass substrates. The film thickness ranged from 1 to 5 μm under various spin speeds. For the four-wave mixing experiment, thick films with thickness of around 100 μm were cast onto ITO glass substrates. All films were soft baked for at least 24 h to ensure the evaporation of any residual solvent. The material is optically clear and shows an optical density of 0.89 at 633 nm at which our experiments were performed.

The electro-optic coefficient of the film was determined using the method as given by Zhang *et al.*[17] A set of thin silver films was vacuum deposited on the top of the C_{60}-PVK-DEANST films. The films were heated to a temperature of 70 °C, followed by the application of a dc voltage to the silver electrodes while the ITO layer was grounded. After poling at this temperature for 10 min, the films were cooled gradually to room temperature while the poling field was maintained. The film shows a similar behavior as reported for guest-host polymer composites; i.e., the electro-optic coefficient shows some decay after the poling field is removed. We can still maintain about 70% of the electro-optic coefficient three days after poling and a stable electro-optic coefficient of 4 pm/V was obtained.

The photoconductivity of the material was studied by measuring the photocurrent through the sample.[18] In the experiment, an Ar^+-laser-pumped cw dye laser, using DCM dye and operating at 633 nm, was used. A beam with an intensity of 1.25 W/cm^2 and a duration of 200 ms illuminated the sandwiched film (ITO glass-film-gold electrode) along the film surface normal. We obtained a photocurrent of 0.18 μA with an applied field of 500 kV/cm. The dark current is less than 6 nA. In the measurement, no trapping signal was observed. The quantum efficiency of the photoinduced charge-carrier generation was calculated from the experimentally measured photocurrent. The field dependence of the quantum efficiency is presented in Fig. 1. It is obvious that the quantum efficiency increases as the external electric field increases. This field dependence can be explained by the Onsager model.[19]

Theoretical study reveals that a space charge field can be formed even though there is no trap.[8,9] Therefore, our

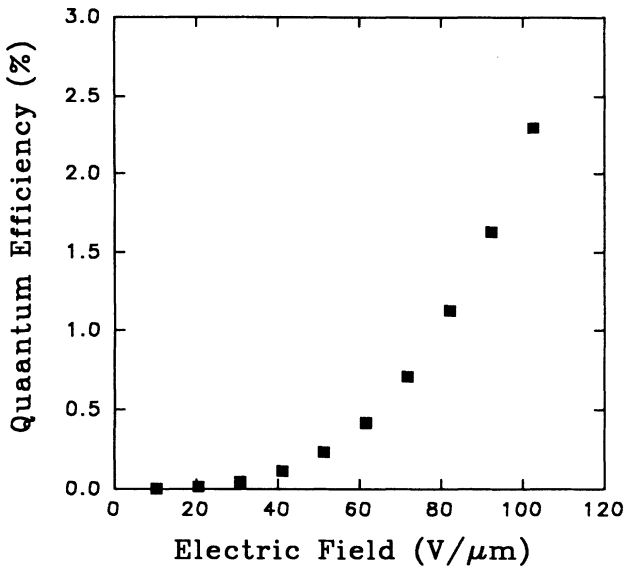

FIG. 1. Electric-field dependence of the photoinduced charge carrier generation quantum efficiency.

system satisfies three necessary characteristics for a photorefractive material (absorption, photoconduction, and electro-optic activity). Further evidence for the photorefractive effect can be obtained from a degenerate four-wave mixing study with applied external electric fields. The thick films used for the four-wave mixing experiment were sandwiched between two ITO glass substrates and have thicknesses of around 100 μm. The samples were poled at 70 °C with an applied field of 250 kV/cm. Backward degenerate four-wave mixing was employed to measure the photorefractive behavior of our material. Two *s*-polarized writing beams at wavelength of 633 nm with nearly equal intensities of 1.25 W/cm^2 were intersected in the film. The angle between the two beams is about 7.3°, corresponding to a 5-μm spacing of the interference pattern generated inside the material. The interference fringes oriented 38° with respect to the film surface normal. The *s*-polarized read beam, propagating in the direction opposite to one of the writing beams, has much weaker intensity than that of the writing beams. The diffracted signal was detected by a photomultiplier tube and processed by a boxcar averager.

Figure 2 shows a typical four-wave mixing signal from the material. In the period of $0 < t < t_1$, no electric field was applied; therefore, no diffracted signal was detected. When an external field of 500 kV/cm was applied ($t_1 < t < t_2$), a diffracted signal built up. The fluctuation of the signal is due to a random vibration of the setup. Because of the random factor and a slow response speed of the PR effect, the gratings, which are generated at different time, have a random spatial shift in the sample, and randomly cancel or enhance each other in part and therefore cause the random fluctuation of the signal. When the external field was turned off ($t > t_2$), the signal decayed to zero. The field dependence of the diffraction efficiency is shown in Fig. 3. This strong field dependence of the four-wave mixing signal proves that the observed

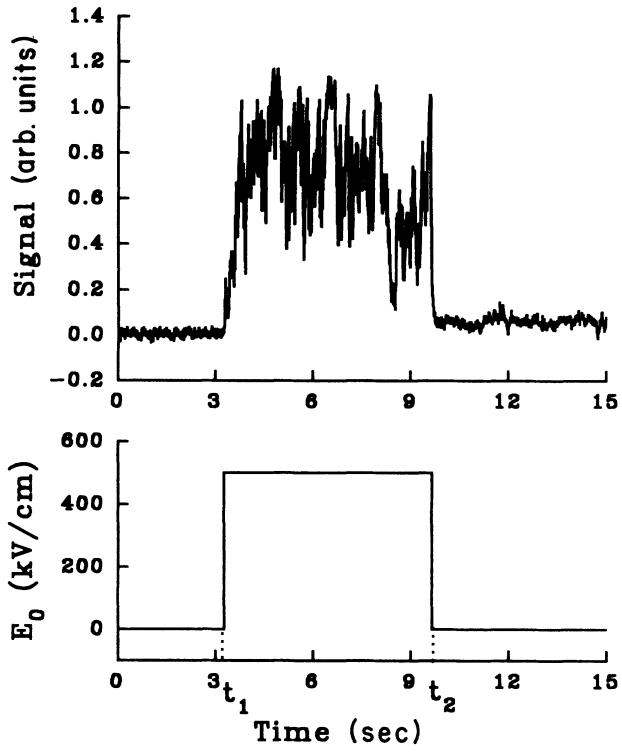

FIG. 2. A typical photorefractive four-wave mixing signal. From 0 to t_1: no electric field is applied; t_1 to t_2: electric field applied; after t_2: field turned off.

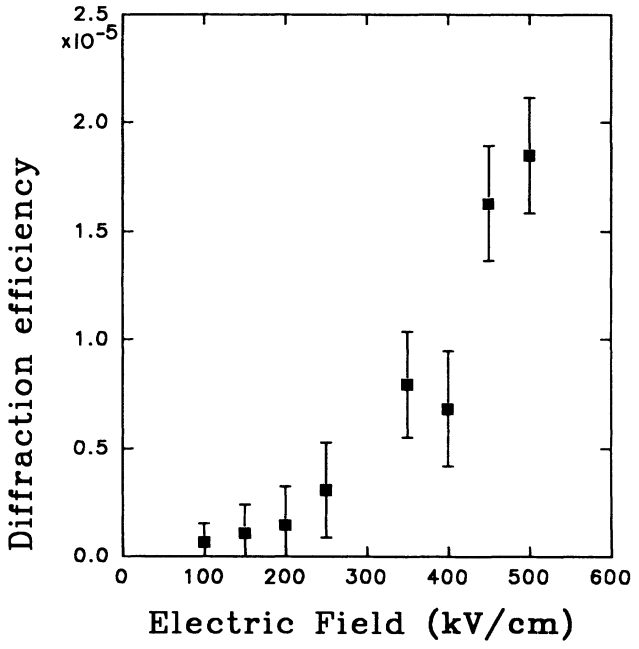

FIG. 3. Electric-field dependence of photorefractive diffraction efficiency.

grating results from the photorefractive effect. A maximum diffraction efficiency of 2×10^{-5} was obtained.

In summary, the photoconductivity, the electro-optic effect, and four-wave mixing have been demonstrated in C_{60}- and DEANST-doped polyvinylcarbazole system. The results reveal that this material composite is photorefractive. It should be pointed out that there exists great potential of this material composite. Electric-field poling was done at a rather low temperature (70 °C), resulting in a low electro-optic coefficient. The low solubility of C_{60} in the solvent used limits its concentration in the composite and thus limits the photoconductivity. By improving the poling conditions and increasing the C_{60} concentration, one can expect large increase in the photorefractivity. Furthermore, in our composite approach, the photocharge generation and the electro-optic functions are performed by two separate constituents. This provides an opportunity to optimize each separately and to tune the response of the material (by selecting appropriate photosensitizer) to the desired wavelength.

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