Photorefractive polymers sensitized by two-photon absorption


Optical Sciences Center, The University of Arizona, Tucson, Arizona 85721

S. R. Marder

Optical Sciences Center and Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

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We demonstrate the recording of holograms and their nondestructive readout in a photorefractive polymer, using two-photon absorption. Sensitivity is provided by the excitation of the electroactive chromophore with femtosecond pulses, followed by charge injection into the photoconducting poly(N-vinylcarbazole) matrix. The holograms can be fully erased with a pulsed laser source but are insensitive to cw laser beams with the same wavelength. Studies of the field and intensity dependence of the diffraction efficiency indicate that the holograms are formed through the photorefractive effect. © 2002 Optical Society of America


Photorefractive materials are being widely studied for use as real-time recording media for holographic applications. In contrast to many physical processes that can be used to change the refractive index permanently, the photorefractive effect is fully reversible, as the recorded holograms can be erased with a spatially uniform light beam. This reversibility makes photorefractive materials suitable for real-time optical applications but at the same time constitutes an intrinsic problem, as the reconstruction of the stored information is done by illumination of the material with a spatially homogeneous light beam at the same wavelength that gets diffracted by the reversible index modulation and at the same time erases the hologram. Solutions to this problem, referred to as destructive readout, have been proposed in inorganic photorefractive crystals and involve two-photon absorption 1 (TPA) or two-step resonant excitation. 2 Recently, photorefractive polymers emerged 3 as a low-cost alternative to their inorganic counterparts. Polymer composites with high diffraction efficiency, 4 two-beam coupling gain coefficients, 4 and millisecond response times 5 have been demonstrated. However, except for the observation of quasi-nondestructive readout in a photorefractive polymer under low reading intensity, 6 to our knowledge no nondestructive readout could be demonstrated to date in these new materials.

Here, we extend the multiphoton photorefractive process as proposed by von der Linde et al. 1,2 to polymers. We demonstrate the recording of volume holograms with femtosecond pulses by use of TPA and their nondestructive readout by use of cw lasers with the same wavelength. In our experiments, we used 105-μm-thick samples of the photorefractive polymer composite FTCN:PVK-BBP:ECZ (25:55:10:10 wt. %) sandwiched between two indium tin oxide-coated transparent electrodes. The composite contained the electroactive fluorinated cyano-tolane chromophore [(FTCN) see Fig. 1], the photoconducting polymer matrix poly(N-vinylcarbazole) (PVK), and the plasticizers N-ethylcarbazole (ECZ), and benzyl butyl phthalate (BBP). The glass-transition temperature of the composite was measured by use of differential scanning calorimetry to be Tg = 3°C. This low value ensures that orientational photorefractivity can take place in the sample. Sensitization in this case was achieved through TPA in the electroactive dopant molecule FTCN. Holographic recording was achieved through four-wave mixing experiments with 130-fs pulses at a wavelength of 650 nm, produced at a repetition rate of 1 kHz by an optical parametric amplifier pumped by the amplified output of a Ti:sapphire laser system.

The two writing beams were s polarized, formed an angle of 40° in air, had an equal average power of 0.25 mW each, and were focused to a spot size of 300 μm. The sample surface normal was rotated by 40° with respect to the bisector of these beams. The grating period in the sample was 1.2 μm, given a refractive index of 1.7. Reading was achieved by diffraction of a delayed weak p-polarized beam with average power of 0.25 μW.

TPA is a third-order nonlinear optical process that leads to an intensity-dependent absorption coefficient, αNL = α2I, when the linear part of the absorption is ignored. For observation of photorefractivity under two-photon excitation, the polymer composite should exhibit a nonlinear absorption coefficient αNL of a few inverse centimeters at optical intensities that are below the damage threshold of the sample. On a molecular level, the nonlinear response is characterized by the TPA cross section γ, in Göppert–Mayer (GM) units, where 1 GM = 10–50 cm4 photon s–1. α2 and γ are related through

Fig. 1. Structure of the electroactive molecule FTCN used as two-photon sensitizer.
\[
\alpha_2 = N \delta / \hbar \omega ,
\]
where \( N \) is the density of molecules and \( \hbar \omega \) is the photon energy. At a 25-wt.% loading level of the sensitizer with a molecular weight of \( M = 355 \) g, and assuming a density of \( \rho = 1 \) g/cm\(^3\), we obtain a density of sensitizers of \( N = 4.2 \times 10^{20} \) cm\(^{-3}\). With \( \delta = 60 \) GM measured by nonlinear transmission measurements, 1 GW/cm\(^2\) of optical intensity with 1.9-eV photon energy leads to a nonlinear absorption coefficient of 0.8 cm\(^{-1}\). Since PVK is a hole transport material, photoconductivity can be initiated efficiently if the excitation of the sensitizer by TPA leads to hole injection into PVK. This injection is possible if the ionization potential of the sensitizer is higher than that of PVK, which is 5.9 eV. The ionization potential of FTCN was evaluated by cyclic voltammetry experiments performed on the molecule in 0.005-M solutions of acetonitrile, with the ferrocene-ferrocenium as a reference. A value of 6.35 eV could be deduced from the relative oxidation potential. Hence, we believe that photoconduction in PVK is activated by electron transfer from the highest occupied molecular orbital level of neutral PVK into the FTCN molecules excited by TPA, followed by field-induced dissociation to prevent geminate recombination.

Figure 2 shows the linear absorption spectrum of the our sample. At the optical recording wavelength of 650 nm, the sample is transparent. The lowest excited state of FTCN in the polymer composite has an absorption maximum at 340 nm with several vibronic bands. As shown in the inset of Fig. 2, the energy of two photons is resonant with the high-energy edge of this transition.

To demonstrate the recording of photorefractive gratings in our polymers, we performed four-wave mixing experiments with three femtosecond pulse trains. Figure 3 shows the diffraction efficiency, \( \eta \), defined as the ratio between the intensities of the diffracted and the incident beams, as a function of the delay between the two writing beams. In this experiment, for each data point, the value of the delay between the writing beams was preset and the diffraction efficiency was allowed to reach a steady-state value. This takes a few seconds for each new value of the delay. The diffraction efficiency increased as the temporal overlap of the beams was increased and reached a maximum for zero delay when the visibility of the fringes of the two interfering beams was the highest. This behavior shows the dynamic nature of the grating, as expected for a photorefractive grating using pulsed writing beams. To investigate the photorefractive nature of the grating, we measured the field dependence of the diffraction efficiency. According to the Kukhtarev model of a saturated space-charge field and the model describing orientation photorefractivity in polymers,\(^7\) the diffraction efficiency is expected to vary as the fourth power of the applied field. Such a fit is shown as a solid curve in Fig. 4. For a field value of 65 V/\( \mu \)m, a maximum diffraction efficiency of \( \eta = 0.03% \) is measured. This corresponds to an index change of \( \Delta n = 1.6 \times 10^{-7} \) for \( d = 105 \) \( \mu \)m. The buildup time to reach steady-state conditions was of the order of a few seconds. This slow response time can be attributed to a small photogeneration efficiency that in turn is caused by a strong geminate recombination, as seen in the fluorescence of the sensitizer that could be observed during optical recording. We also studied the dependence of the steady-state diffraction efficiency on the intensity of the writing beams and found a superlinear dependence (see Fig. 5).

To demonstrate nondestructive readout, we changed the wavelength of the pulsed laser source experiments to 700 nm and replaced the pulsed reading beam with a cw laser diode emitting at the same wavelength. No changes in diffraction efficiency could be detected for several minutes with a reading power as high as 5 mW, that is, an order of magnitude higher than the average power of the pulsed writing beams. However, when one of the pulsed writing beams was blocked, the grating could be erased completely within a few seconds by the remaining spatially uniform writing beam. No evidence of any grating was found when wave-mixing experiments were performed entirely
Fig. 4. Diffraction efficiency as a function of applied field. The squares are experimental points. The curve is the function $\eta = a E^4$ with $a = 2.225 \times 10^{-9}$, where $E$ is the applied field. The sum of the intensities of the two writing pulses was 5 GW/cm$^2$. Diffraction efficiency was measured at the maximum temporal overlap of the writing beams.

Fig. 5. Diffraction efficiency as a function of the sum of the intensities of the two writing pulses measured at an applied field of 50 V/μm. The squares are experimental points. The curve is the function $\eta = b I^{1.86}$, with $b = 0.001$, where $I$ is the total intensity. Diffraction efficiency was measured at the maximum temporal overlap of the writing beams.

In conclusion, we have demonstrated, for the first time to our knowledge, the recording of holograms in a photorefractive polymer through TPA and their non-destructive readout with a cw beam. Future studies of two-photon photorefractivity will address some of the current limitations by capitalizing on the progress made in developing organic molecules with large TPA cross sections.

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*Permanent address, Department of Chemistry, University of Leuven, Celestijnenlaan 200 D, Leuven, B-3001, Belgium.

References