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Photorefractive Polymers with Superior Performance

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We report on development of photorefractive materials with superior performance. High-voltage (5-10 kV) poling necessary for the operation of photorefractive polymeric devices has been a drawback of these materials. We have now developed devices that can be poled at order of magnitude lower voltages by carefully engineering the material composition using high performance nonlinear chromophores for thinner devices. For a thickness of 20 μm, the device showed more than 90% diffraction efficiency with a dominant fast response time of 27 ms at about an applied voltage of 1 kV. A useful diffraction efficiency of about 10% can be observed even at a voltage as little as 450 V, which demonstrates a major step forward in the possible applications of photorefractive devices.

We have also been able to extend the operating wavelength to near IR. By employing a new sensitizer dye, we have demonstrated a first-time proof of photorefractivity at 975 nm in an all-organic composite with 90% diffraction efficiency and video rate response time using a low power cw laser. This is a significant advance in the development of all-organic PR device for near-infrared imaging and optical communication. Furthermore, devices were made to operate at 1550 nm wavelength, suitable for fiber optics applications. Using two-photon absorption (TPA) processes, we demonstrated more than 40% diffraction efficiency maintaining near video-rate response time. This approach provides the inherent advantage of non-destructive read-out using cw laser light. As an application of these devices, we demonstrated beam cleanup and aberration correction in a free space communication application. An oil-filled phase plate, which generates atmospheric-like wavefront aberrations, was employed and demonstrated high quality aberration corrections.

INTRODUCTION

Photorefractive polymers offer several advantages over their inorganic counterparts because of their flexibility, large area, wavelength tenability, ease of fabrication and low cost. [1–3] Photorefractive effect refers to the modulation of refractive index due to the spatial distribution of charges and the electro-optic effect. Optical information can be recorded, erased and rewritten using a low power laser beam. Currently, photorefractive materials are potential candidates to explore applications in beam clean-up and amplification, real time image processing, optical phase conjugation, pattern recognition, 3D display and novelty filters.

LOW-POLING VOLTAGE OPERATION

The composites we have developed employ a highly efficient hole transport matrix poly(acrylic tetraphenyldiaminobiphenyl) (PATPD) polymer, nonlinear optical (NLO) chromophores with a high hyperpolarizability and dipole moment, 4-homopiperidino benzylidine-malonitrile (7-DCST) and/3-(N,N-di-*n*-butylaniline-4-yl)-1-dicyanomethylidene-2-cyclohexene (DBDC), for orientational nonlinearity, and a plasticizer, N-ethylcarbazole (ECZ), to reduce the glass transition temperature (T_g). For 1550 nm PR operation, sensitization was done by the use of a TPA dye, 2-[2-{5-[4-(di-*n*-butylamino) phenyl]-2, 4-pentadienylidene}-1, 1-dioxido-1-benzothien-3 (2*H*)-ylidene] malononitrile (DBM).

In photorefractive polymers with low Tg, the orientational non-linearity (birefringence) is the dominant effect for the recording of holographic gratings. The non-linear chromophore aligns with the net electric field in the medium, resulting in very large index modulations. Ellipsometric measurements of photorefractive polymers provide valuable information on the strength of the index modulation due to birefringence. We have performed ellipsometric measurements on our polymer composites in order to determine the optimum ratio of various functional components. The recipes for the composites were varied to obtain similar T_g around room temperature. The index change obtained at the highest applied fields for the composite PATPD/7-DCST/ECZ/DBM (49:40:10:1 wt. %) (C1) was 9×10^{-3} (Figure 1). For this composite, the refractive index modulation is more than an order of magnitude larger than the previously developed IR operating polymer composite; PATPD/7-DCST/ECZ/DBM (50:25:15:10 wt. %) (C2). The composite C2 showed an index modulation of 4.5×10^{-4} at the same applied field. The increased non-linear chromophore loading is usually the main reason for the improved index change in polymer composites with similar components and T_g. Interestingly, however, the index change in a composite, PATPD/7-DCST/ECZ/DBM (50:25:20:5 wt. %) (C3), which

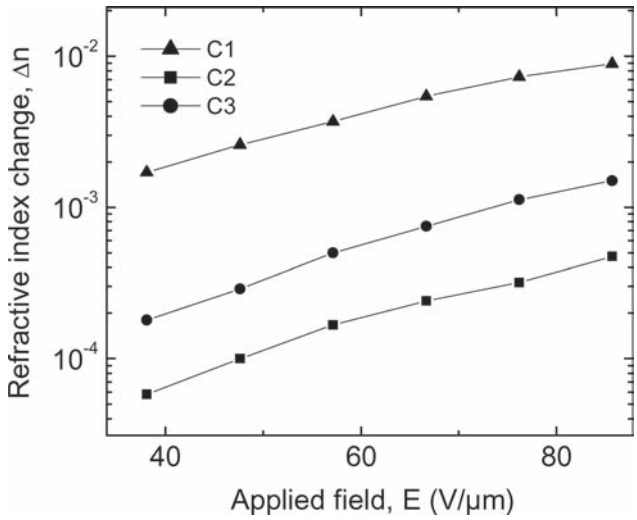

FIGURE 1
Refractive index change as a function of the applied electric field for composites C1, C2 and C3 measured by steady state ellipsometry at 1550 nm. PATPD/7-DCST/ECZ/DBM (49:40:10:1 wt. %) (C1); PATPD/7-DCST/ECZ/DBM (50:25:15:10 wt. %) (C2); PATPD/7-DCST/ECZ/DBM (50:25:20:5 wt. %) (C3).

contained same amount of chromophore (25 wt. %) as C2 but a smaller amount of sensitizer showed an index change of 9×10^{-4} at the same applied field. The reduction of the DBM sensitizer dye loading from 10 wt. % to 5 wt. % has increased the index modulation significantly. Considering that the T_g for these materials are similar, this result indicates that the room temperature orientation of the non-linear chromophore is adversely affected from such a high loading of the sensitizer. This conclusion was further verified by finely tuning the concentration of various components in these composites. As a result of the ellipsometry measurements, an optimized sensitizer concentration of 1 wt. % was used in C1 which provided a maximum index change with fastest response.

We have also developed composites which overmodulates the diffraction efficiency at low applied voltages ($\sim$1 kV) without sacrificing the video rate response time (see Figure 2). This is accomplished by carefully engineering the material composition and exploiting our highly performing nonlinear chromophores, DBDC and 7-DCST and reducing the device thickness. These devices can provide both low-voltage operation and an enhanced external efficiency due to their increased overall transparency. The measurements were done at 633 nm using standard single-photon sensitization. The sample compositions are PATPD: DBDC: 7DCST: ECZ: C60 (39.3:40:10:10:0.7) (C4) and PATPD: DBDC: 7DCST: ECZ: C60 (39.5:25:25:10:0.5) (C5). The sample thickness is reduced from 105 μm to 20 μm, the Q value in the

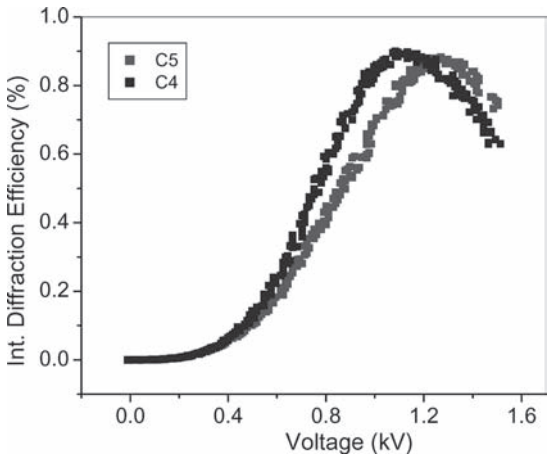

FIGURE 2
Diffraction efficiency as a function of applied voltage of 20μm thick devices operating at 633 nm; PATPD: DBDC: 7DCST: ECZ: C60 (39.3:40:10:10:0.7) (C4) and PATPD: DBDC: 7DCST: ECZ: C60 (39.5:25:25:10:0.5) (C5).

following equation (1) was down to 2.3 which is still above the thin-film regime (Q < 1). The Q value which differentiate the thick regime from the thin regime is given by

$$Q = \pi \lambda d / n \Lambda^2 \tag{1}$$

where λ – wavelength used; d – thickness of the device; n – refractive index; Λ – grating spacing.

OPERATION AT IR WAVELENGTHS [4–5]

For 1550 nm operation we used sample C1 and performed four-wave mixing (FWM) experiments using a pulsed (130 fs) laser at 1550 nm. The s-polarized output from a Ti-sapphire pumped optical parametric amplifier tuned to 1550 nm operating at a repetition rate of 1000 Hz was used for writing beams in a traditional FWM geometry with the addition of a delay line to ensure temporal overlap of the pulses in the polymer sample. The reading was achieved at the same wavelength using a counter propagating p-polarized CW beam from a laser diode. Both the transmitted and diffracted beams were monitored using photodiodes and a lock-in amplifier. The writing beams were focused to a spot size of 180 μm (diameter) at the sample position and the reading beam diameter was 60 μm. A smaller than usual reading beam diameter was used to ensure the overlap of the reading beam and the photorefractive grating, which is confined to a small volume due to TPA writing. The pulse energy used for writing the holograms

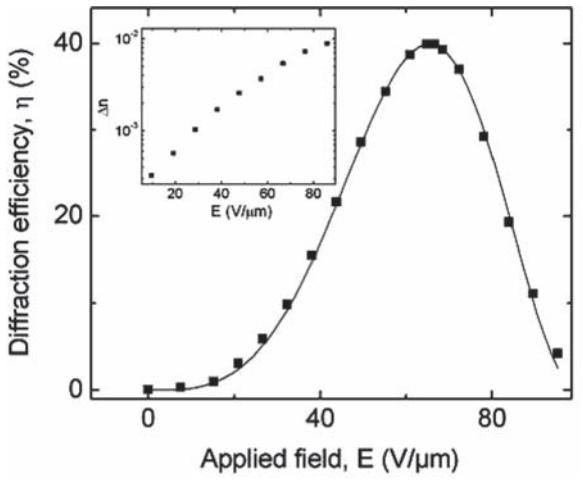

FIGURE 3
Internal diffraction efficiency at 1550 nm as a function of the applied electric field. The solid line is the theoretical fit. The inset shows the modulation of refractive index as a function of applied field.

for these experiments was around 4.5 μJ. Figure 3 shows the internal diffraction efficiency as a function of applied electric field for C1 measured in the FWM setup described above. In this experiment we observed 40% internal diffraction efficiency at an applied electric field of 65 V/μm at 1550 nm. It is clearly seen that the diffraction efficiency overmodulates at fields exceeding 65 V/μm. The strong diffraction of IR light from this photorefractive thin-film device shows that the nonlinear writing scheme has important potential in holographic applications. Since the absorption of CW light was negligible at this wavelength, the use of the powerful CW reading beams (up to 20 mW) had no effect on the holographic writing/reading/erasure processes in this polymer. In these experiments the grating decay time was independent of the CW reading beam power, in contrast to the case where pulsed reading beams were used. The ease of the restriction in reading beam intensities and non-destructive readout are important advantages in imaging and laser communication applications of photorefractive materials.

The response time of the photorefractive grating recording is an important parameter in practical applications such as real-time beam clean-up. To determine the temporal characteristics of our polymer composites, transient FWM experiments were performed using a fast photo-detector and computer interfaced data acquisition system. Figure 4 shows the diffraction efficiency as a function of time for C1 measured using the experimental setup described above. At time zero, the writing beams were unblocked and the photorefractive grating build-up was observed at an applied electric field of

93 V/μm and a pulse energy of 11.4 μJ focused to a spot with a diameter of 180 μm. The data fitted to the bi-exponential function

$$\eta = A \sin^2\{B[1 - m\exp(-t/t1) - (1 - m)\exp(-t/t2)]\} \qquad (2)$$

provided a fast response time of 35 ms with a weighing factor of m = 0.45. The response time is found to be a strong function of the writing beam peak power compared to linearly sensitized photorefractive polymers, showing longer writing times as the writing irradiance was reduced. This suggests that with the incorporation of a sensitizer with larger TPA cross section, the irradiance required to observe near video-rate response times can be brought to smaller writing powers without difficulty.

With the present polymer composite we have also performed two-beam coupling (TBC) measurements using the same pulsed laser at 1550 nm (Figure 4 inset). The TBC gain, the increase in the energy of one of the writing beams at the expense of the other, is the fingerprint of the photorefractive effect. In these measurements we observed a net gain of 20 cm^{-1} at an applied electric field of 95 V/μm using *p*-polarized irradiation (pulse energy$\sim$6 μJ, beam diameter$\sim$180 μm). The demonstration of a net TBC gain at 1550 nm proves that the holographic gratings written in these composites are due to the photorefractive effect.

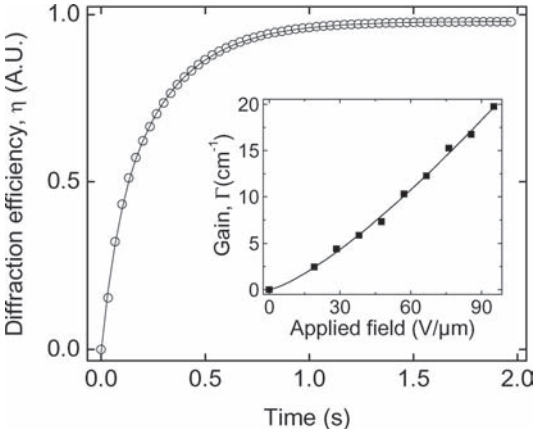

FIGURE 4
Diffraction efficiency as a function of time for composite C1 showing grating build-up. At time zero the writing beams were turned on. The data fits to the bi-exponential function (Equation 2) with a fast time constant (m = 0.45) of 35 ms (solid line). Inset: TBC gain as a function of the applied electric field for p-polarized irradiation at 1550 nm. The solid line is a guide to the eye.

ALL-OPTICAL DYNAMIC CORRECTION OF ATMOSPHERIC-LIKE WAVEFRONT ABERRATIONS [6]

Laser communication systems are attractive since they possess higher information bandwidth and security than radio-frequency systems. However, atmospheric turbulence perturbs phase and cause intensity scintillation on the detectors. The scintillation reduces the information capacity and increases the bit error rate. Adaptive optics technology can dynamically correct the spatial aberrations in the transmitted beam and significantly improve the performance. A typical adaptive optics system includes a wavefront sensor for measurement of the aberrations, an actuator for wavefront correction, and associated control electronics. Implementation of such a system is expensive and complex. Considerable research efforts have been devoted to real-time, low-cost adaptive optical systems. A simplified system that combines the actuator and the blind optimization algorithm has been proposed. The other approach uses nonlinear optical effects such as phase conjugation and multiple waves mixing. Photorefractive (PR) dynamic holographic techniques are of interest for laser communication since fast, low-cost, and all-optical compensation of wavefront distortion can be achieved without expensive actuators, intensive computation, and complex subsystems. PR materials consist of mainly two classes: inorganic crystals and organic polymers. Phase conjugation in various PR crystals has been investigated intensively. However, most of the crystals are sensitive only in the visible region and are difficult to grow and polish. In contrast, PR polymers have advantages such as response times in the millisecond range, near 100% diffraction efficiency and wavelength tunability.

We use a typical system that employs a modulated phase conjugate mirror as a remote sensor for free-space communication. As shown in Figure 5(a), consider two communication stations with the objective being to communicate from Station 2 to Station 1. Station 1 has a light source and a receiver, whereas Station 2 has a modulator and a phase conjugate mirror. The communication link can be completed in the following steps: Station 1 sends a laser beacon beam to the vicinity of Station 2; when receiving the light from Station 1, Station 2 encodes the signal to be communicated onto the modulator; the encoded beam is redirected to Station 1 using phase conjugation and detected by the receiver. Although the turbulent atmosphere adds distortion to the beam, Station 1 can always receive the correct signal from Station 2. In addition, because of the real-time characteristic of the dynamic phase conjugate mirror, even if both stations are mobile, the communication link can still be maintained. Correspondingly, a system shown in Figure 5(b) has been designed and implemented as a preliminary proof-of-principle experiment.

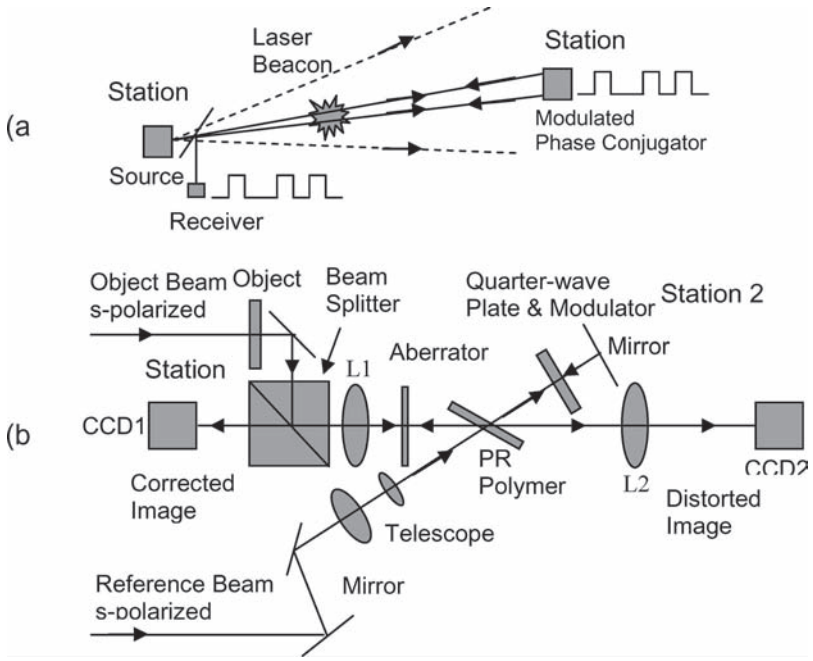

FIGURE 5
(a) Free-space remote communication link; (b) Schematic diagram of the experiment setup.

The collimated beams are split into two arms, the object arm and the reference arm. The reference beam is directed to the PR polymer film using a reducing telescope. In the object arm, a Fourier transform lens is introduced and the PR polymer film is placed in the focal plane of the lens. The spatial spectrum of the object beam is overlapped with the reference beam in the PR polymer and a volume hologram is recorded when an appropriate voltage is applied to the PR polymer. An aberrator is placed between the lens and the PR polymer to intentionally distort the beam. In order to obtain the maximum diffraction efficiency, the PR polymer film is aligned in a tilted structure and a p-polarized beam is used to read the hologram. The angle between the two writing beams is 22° and the normal to the sample and the bisector of the two writing beams form an angle of 55°. A quarter waveplate is utilized to convert the s-polarized beam to a p-polarized beam when the beam double passes it. The reading beam is counter-propagating to the reference beam, generating a phase conjugate object beam. When the phase-conjugate object beam passes through the aberrator again, a corrected image is obtained at Station 1.

We have performed a high-quality dynamic image correction experiment using an oil-filled phase plate which generates atmospheric-like wavefront aberrations. The aberrator consists of a deformed glass with a refractive

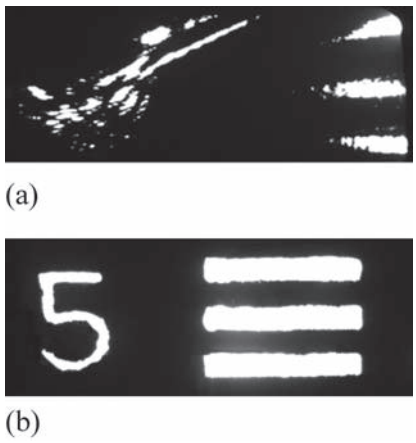

FIGURE 6
Dynamic correction of atmospheric-like phase distortion when the beam carrying the image transmits through different positions of the aberrator. (a) Distorted image; (b) Corrected image.

index n_1 filled with oil with a refractive index n_2. In order to demonstrate dynamic correction of the phase distortion, a stepper-motor is used to move the aberrator continuously in the direction perpendicular to the signal beam propagation. We have successfully performed the experiments and vidoes of dynamically corrected images. Using the oil-filled phase plate, vidoes were taken when the aberrator was moved at 0.3 mm/s. On the other hand, when the object is moved at the same speed, the corrected images can also be dynamically refreshed without distortions. Figure 6 shows distorted and corrected images when the beam carrying the image was transmitted through different positions of the aberrator.

In summary, we have successfully reduced the applied poling voltage required without sacrificing the diffraction efficiency and response time in photorefractive polymers and demonstrated beam clean-up applications. The operating wavelength was also extended from visible to 1550 nm.

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REFERENCES

[1] Peyghambarian, N., and Norwood, R. A. (2005). *Optics & Photonics News*.
[2] Peyghambarian, N., and Norwood, R. A. (2005). *Optics & Photonics News*.

[3] Thomas, J. et al., (2004). *Adv. Mater., 16,* 2032.

[4] Eralp, M. et. al., (2004). *Appl. Phys. Lett., 85,* 1095.

[5] Tay, S., Thomas, J., Eralp, M., Li, G., Kippelen, B., Marder, S. R., Meredith, G., Schülzgen, A., Peyghambarian, N. (2004). *Appl. Phys. Lett., 85,* 4561.

[6] Li, G., Eralp, M., Thomas, J., Tay, S., Schülzgen, A., Peyghambarian, N. (2005). *Appl. Phys. Lett., 86,* 161103.