PQ:DMNA/PMMA photopolymer having amazing volume holographic recording at wavelength of insignificant absorption

Yu-Fang Chen,[1] June-Hua Lin,[3] Shiuan Huei Lin,[2,*] Ken Y. Hsu,[3] and Wha-Tzong Whang[1,4]

[1]Department of Materials Science and Engineering, National Chiao Tung Univeristy, Hsinchu 30010, Taiwan

[2]Department of Electrophysics, National Chiao Tung Univeristy, Hsinchu 30010, Taiwan

[3]Department of Photonics, National Chiao Tung University, Hsinchu 30050, Taiwan

[4]e-mail: wtahang@mail.nctu.edu.tw

*Corresponding author: lin@mail.nctu.edu.tw

N, N-dimethyl-4-nitroaniline doping enables red-light holographic recording that was originally insensitive in thick phenanthrenequinone/poly(methyl methacrylate) photopolymer to have reasonable sensitivity. A volume hologram was recorded by a 647 nm laser with maximum diffraction efficiency of about 43% in a 2-mm-thick sample. A Bragg selectivity curve and an image hologram reconstruction are also demonstrated. These experimental results support recording material for volume holographic applications in an extended red spectral range.   © 2013 Optical Society of America

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With the Bragg selectivity property, volume holography has been considered an important technology in many photonic applications, such as holographic data storage, holographic filters, holographic interferometry, and holographic optical elements [1,2]. Such applications need recording materials with large thickness and good optical quality. For a long time, inorganic crystals-like $LiNbO_3$ and $LiTaO_3$ were used almost exclusively [3,4]. More recently, organic materials have been moved into the focus of research because their fabrication is less complicated and costly and because organic materials provide more possibilities for material engineering, i.e., the adjustment of desired (optical) properties by modifying the chemical composition of the material.

Doped photopolymers are part of this organic material group and demonstrate exemplary advantages of material engineering since they can be tailored by adding appropriate dopants to match different needs [5,6]. Polymers also have the flexibility to be set down in a thin layer or in bulk, spread over large surfaces, and formed in complex shapes. Phenanthrenequinone (PQ)-doped poly (methyl metharcylate) (PMMA) photopolymer, encoded as PQ/PMMA, is one of the particularly successful examples [7–9]. In this material, the refractive index change for holographic recording is induced by the molecular structure change of the doping elements, PQ. The polymer host, PMMA, is not affected by the light during holographic recording such that PQ/PMMA can avoid the light-induced shrinkage problem, which is the most severe problem of thick conventional photopolymerizable photopolymer [10]. This unique feature makes PQ/PMMA a promising candidate for developing millimeter-scale holographic material with high optical quality and negligible photoinduced shrinkage. Furthermore, many experiments have demonstrated that by either adding another dopant or changing the doping elements similar to PQ, material performances, including the stability of the recorded

hologram, dynamic range, and sensitivity can be improved [11–14]. Until recently, the PQ/PMMA material was optimized for green and blue wavelengths due to the limited absorption band of PQ, as shown by the solid curve with open triangle symbol in Fig. 1. In this Letter, we demonstrate experimentally that the addition of the nonlinear optical (NLO) organic molecule can enable PQ/PMMA photopolymer to record the volume hologram in the red spectral range, which is away from the absorption spectral range of both PQ and codoped NLO molecules. We show a 10^5-fold increase in the diffraction efficiency at 647 nm. A maximum diffraction efficiency of ~43% was obtained for a 2-mm-thick sample. To the best of our knowledge it is the first demonstration of red-sensitive PQ/PMMA photopolymer, which may provide the possibility to utilize cheap diode lasers in the development of volume holographic devices. The capacity for image reconstruction is also demonstrated, supporting the
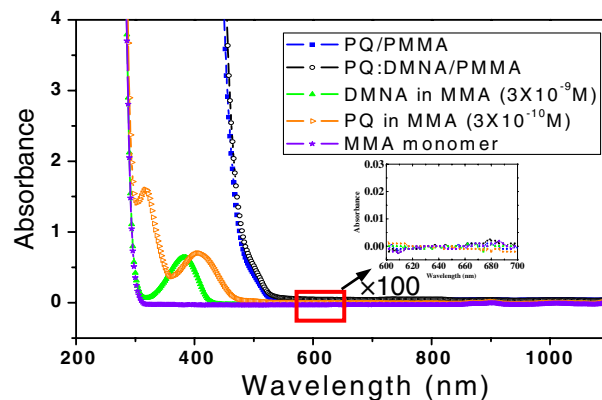

Fig. 1.   Optical absorption spectra of PQ, DMNA in MMA solution, PQ/PMMA, and PQ:DMNA/PMMA photopolymers. All curves were taken before the samples were exposed to red light.

possibility for further applications in information processing and storage.

The thick codoped PMMA photopolymer in this work was prepared from raw MMA monomers by a two-step thermopolymerization method [7]. A saturated concentration (0.7% by weight) of photosensitive dye, PQ, and 2 wt. % of thermal initiator, azobisisobutyronitrile (AIBN), molecules were dissolved into the purified MMA solution. In addition, the organic NLO molecule, N, N-dimethyl-4-nitroaniline (DMNA), was added into solution with a concentration of 0.56 wt. %, which is the same molar ratio as that of PQ in the sample. The resulting solution was stirred at 35°C until the of the MMA started to be thermally polymerized and transferred to PMMA by AIBN, and the solution became homogeneously viscous. The viscous solution was poured into a glass cell with the dimensions of 10 cm × 10 cm × 2 mm, baked at 45°C for 72 h, and transferred into a self-sustained 2-mm-thick solid PMMA block for holographic and optical testing. Since there are two dopants dispersed uniformly in PMMA matrix, this material is hereafter encoded as PQ:DMNA/PMMA photopolymer. Thus, the mechanism of refractive index change for holographic recording in this new sample is the same as that in PQ/PMMA.

To identify the absorption of the NLO molecule, DMNA in our photopolymer, we have measured the UV-VIS spectrum of the DMNA dissolved MMA dilute solution (3×10^{-9} M). For comparison, the absorption spectra of 2-mm-thick PQ:DMNA/PMMA and PQ/PMMA were measured. The experimental results are shown in Fig. 1. It is seen that PQ has two absorption peaks and DMNA has one in the range from 300 to 550 nm. The PQ:DMNA/PMMA and PQ/PMMA samples have similar curves and strong absorption below 550 nm due to high concentrations of PQ and DMNA. All samples have no significant absorption when the wavelength is longer than 550 nm (as shown in the insert of Fig. 1). This indicates intuitively that PQ:DMNA/PMMA should be inactive in the red and near-infrared range. However, during holographic experiments, we found that it has reasonable sensitivity in the red spectral range, as shown in the following.

For holographic testing with red light, a krypton-ion laser operating at 647 nm (where the absorbance of the sample <0.001) was used to write gratings in a two-beam interference setup with transmission hologram geometry, as shown in the insert of Fig. 2. The intensity of each beam was 247 mW/cm², and the intersection angle of the two beams was 28° (outside the sample). During recording, the diffraction efficiency, defined as the ratio of the intensity of the diffracted beam to that of the incident beam, was monitored by blocking one beam periodically and measuring the intensity of the diffracted beam.

Figure 2 shows dynamics of the diffraction efficiency during holographic recording. For comparison, that of the PQ/PMMA sample is also included. It is seen that the material sensitivity of the holographic recording at 647 nm is dramatically enhanced with addition of the co-dopant of DMNA. The diffraction efficiency gradually increases, reaches the maximum value of ~43%, and then decreases with further exposure due to the noise grating fanning scattering. Meanwhile, the diffraction efficiency
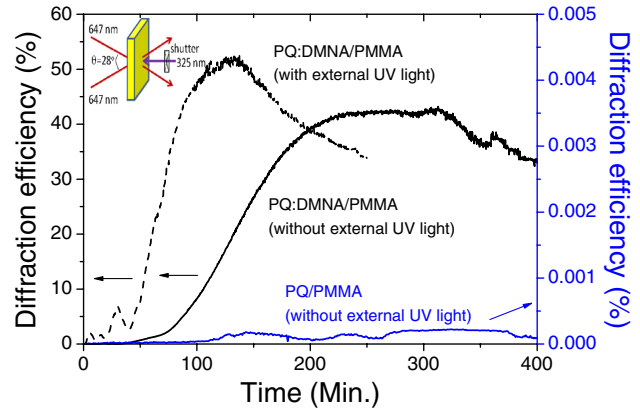

Fig. 2.   Dynamics of diffraction efficiencies of holograms in PQ/PMMA and PQ:DMNA/PMMA with 647 nm recording laser.

of PQ/PMMA is ~10^{-4}%, which is 10^{-5} times less than that of PQ:DMNA/PMMA. Thus, the PQ/PMMA material is nearly inactive at the red wavelength. The holographic experiment was also performed in the PMMA doped with only DMNA. No diffracted light was observed. These comparisons indicate that the red-sensitive recording in PQ:DMNA/PMMA material is endowed with photoreaction involved with both PQ and DMNA together.

A recent monograph reported by Chen *et al.* demonstrated the possibility of recording a hologram in PQ/PMMA with a 647 nm laser by using a two-wavelength method [15]. Using a 325 nm UV laser as a gating illumination during recording with a 647 nm laser, a volume hologram with diffraction efficiency of ~4% can be recorded. In addition, it is well known that DMNA contains both electron donor and electron acceptor groups in its structure, which represents a classical organic chromophore molecule possessing large molecular NLO properties [16–18]. These works suggest that the red-recordable property in our PQ:DMNA/PMMA may result from the enhancement of absorption of PQ at red wavelengths induced by the NLO effect of DMNA. When the sample is illuminated with an interference pattern produced by the 647 nm laser, in the bright region the DMNA first down-converts the red light into the evanescent UV light through the NLO effect of the molecular dipole. With UV light, the neighboring PQ molecules can be turned into radicals with 647 nm red light via two-wavelength photochemical processing [15]. The excited PQ radicals in the bright fringe attach to MMAs to form the photoproduct. Therefore, a phase hologram can be recorded although the sample has no physical absorption in the red spectral range without UV light.

To demonstrate the importance of the presence of UV light in the proposed mechanism, we performed holographic recording in PQ:DMNA/PMMA at 647 nm with simultaneous external UV illumination at 325 nm from a He–Cd laser with intensity of 368 mW/cm². The experimental result is shown with the dashed line in Fig. 2. It is seen that with a larger amount of UV photons from external light, the accumulation of intermediate-state PQ molecules in the two-wavelength recording scheme can be sped up such that a hologram can be recorded immediately with a red laser and the diffraction efficiency of the recorded hologram can be enhanced to be as high as that of a
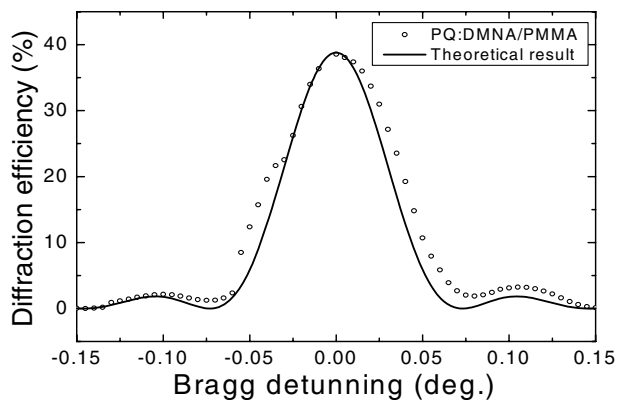
Fig. 3.   Bragg selectivity curve for a 2 mm thick sample for a hologram with diffraction efficiency ~40%. The symbols represent measured results, and the curve is theoretical calculation.

hologram recorded in PQ:DMNA/PMMA with only a 647 nm laser. However, we should note that the above-mentioned mechanism is still a hypothesis, and further investigations are necessary to confirm it. The technological significance of this research is that a hologram can be recorded with extremely low absorption of light such that uniform volume holographic grating with high diffraction efficiency can be obtained. This is crucial for photonic applications requiring precise Bragg selectivity, such as optical filters, holographic microscopy, and information storage.

The uniformity of the recorded hologram along the light propagation direction can be examined by measuring the Bragg selectivity curve of the hologram, which was monitored by rotating the sample mounted on a rotational stage. Figure 3 shows the result for a strong hologram with diffraction efficiency of ~40%. It can be seen clearly that the experimental data show a sinc-squared selectivity curve and are fitted well with the theoretical curve calculated by Kogelnik's coupled wave equation for a uniform 2-mm-thick hologram [19]. In addition, the peak of diffraction efficiency is retrieved by use of a reference beam incident at almost the same angle during writing. With the resolution of our rotational stage of 2×10^{-4} deg, the induced shrinkage coefficient in our PQ:DMNA/PMMA sample is calculated to be smaller than 10^{-4} using the formulas in [20]. These results suggest that shrinkage is not a suspect because the high-bandwidth hologram can be reconstructed completely. This is one of the most desired properties for developing volume holographic photopolymer.

With a slight modification, the experimental setup of a recording plane-wave hologram was used to test the image recording capability of the material. A small pattern of 2 mm size is used as the object. A Fresnel hologram of which the recording material was displaced slightly from the Fourier plane was recorded. The hologram was recorded with relatively low exposure (diffraction efficiency ~4%) to avoid the appearance of noise gratings. The original and reconstructed images are detected by a CCD camera with 640×480 pixels, as shown in Fig. 4. The fidelity of the reconstructed image is almost the same as the original one. This supports possibilities for further applications in optical information.

Fig. 4.   Experimental results for image reconstruction: (a) original transmitted image and (b) reconstructed image.

In summary, we have successfully performed holographic recording with a 647 nm laser beam in PQ:DMNA/PMMA, which is almost transparent in red light or the near-infrared range. The maximum diffraction efficiency can reach 43% in a 2-mm-thick sample. A sinc-squared Bragg selection curve has been obtained. We suggest that the NLO effect of DMNA endows PQ:DMNA/PMMA material with reasonable red sensitivity under such insignificant optical absorption.

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