Riboflavin Sensitized Photopolymer Materials for Holographic Storage *

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Riboflavin is employed as the photosensitizer of a novel photopolymer material for holographic recording. This material has a broad absorption spectrum range (more than 200 nm) due to the addition of this dye. The experimental results show that our material has high diffraction efficiency and large refractive index modulation. The maximum diffraction efficiency of the photopolymer is about 56%. The digital data pages are stored in this medium and the reconstructed data page has a good fidelity, with the bit-error-ratio of about 1.8×10^{-4}*. It is found that the photopolymer material is suitable for high-density volume holographic digital storage.*

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In recent years, interests in optical holographic technology have dramatically increased owing to its potential applications in many fields such as optical interconnection,[1] design and manufacturing of optical holographic elements,[2,3] displays holography,[4,5] especially in the holographic data storage.[6,7] However recording materials is a key problem of holographic storage technology systems. Researchers have taken great efforts to researching various light sensitive materials for holographic optical information storage.[8−10] Photopolymer materials[8] are one kind of recording materials with many advantages: high diffraction efficiency, large dynamic rage, relatively low cost and no requirement of wet chemical processing.

Typically, a photopolymer system consists of one monomer or a mixture of monomers, a sensitizer, and a polymeric film-forming binder. Many dyes (methylene blue,[11,12] bengal rose,[12,13] Eosin Y,[14,15], and Erythrosin B[16,17]) were employed as sensitizers in the polymer mixtures. However a photosensitized dye, i.e. riboflavin, has not been reported in the literature. In this Letter, we report a photopolymeriable system sensitized by using riboflavin based on PVA-acrylamide.

Riboflavin (i.e. vitamin B_2, VB_2) is a sensitizer with a broad spectral range (is about 250 nm). It has a high quantum yield of intersystem crossing ($\Phi_{ISC} = 0.67$).[18] Thus the molecules of riboflavin can absorb photons and are stimulated to an excited triple state easily. At the same time, it also has important applications in photobiology, such as phototaxis, phototropism and photo-dynamic therapy, etc. The molecule structure and absorption are shown in Figs. 1 and 2, respectively. We can see from Fig. 2 that the absorption spectral range is from UV to visible light (200–500 nm), so the photopolymer can be illuminated by using an Ar^+ laser at 488 nm.

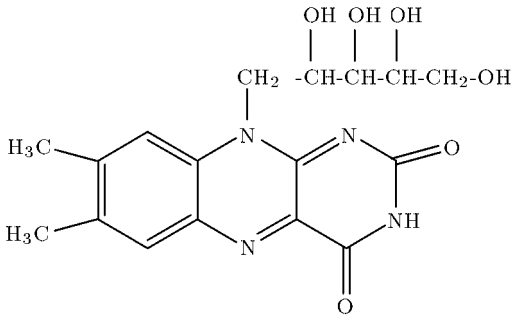


Fig. 1. The molecule structure of riboflavin.

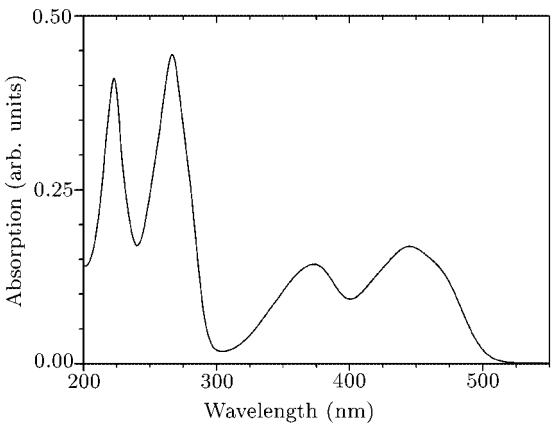


Fig. 2. Absorption spectra of riboflavin.

When the material is exposed to certain wavelength light, the dye molecules absorb photons and are stimulated to excited states, then the exited molecules

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initiate free radicals (or ions). As a result, the free radicals initiate a spatially nonuniform polymerization of the free monomers. There are more free monomers polymerized in bright regions than those in dark regions. This nonuniform distribution sets up the monomer concentration gradients corresponding to the interference fringe pattern, and results in the diffusion of monomers from dark regions to the bright regions. Therefore, a polymer density spatial distribution is formed to result in a refractive index modulation distribution in a similar form, and the phase grating is recorded in the medium. If we assume that all reactions occur in the PVA matrix and the PVA is not reacted, the processes can be depicted by[19]

$$\mathrm{RF} \xrightarrow{h\nu} \mathrm{RF}^*,$$
$$\mathrm{RF}^* + \mathrm{Am} \xrightarrow{k} \mathrm{Am}^{*+} + \mathrm{LRF},$$
$$\mathrm{Am}^{*+} + \mathrm{M} \xrightarrow{k'} \mathrm{P},$$

where RF denotes photosensitizer riboflavin; RF^* denotes the excited photosensitizer; LRF denotes leuco dye; Am^{*+} denotes the action radical of amine; M denotes monomers; P denotes the polymer; $h\nu$ represents the energy quantum of photon; k and k' are the reaction constants.

The samples were prepared under normal laboratory conditions (20–25°C, relative humidity, RH, 40–60%). There was 2g polyvinyl-alcohol (PVA, Mr≈ 1750) dissolved in distilled water and heated to 80°C, then a PVA aqueous solution with 8 wt.% of PVA was obtained. There was 3 ml triethanolamine (TEA) poured into the PVA solution, crystals of riboflavin were dissolved in distilled water to obtain 1.0×10^{-3} mol solution and 1 mL was added to the PVA solution. There are 0.6 g acrylaminde (AA) and 0.2 g N,N′-mehylenebisacrylaminde (BAA) dissolved in distilled water and heated to 30°C, then added into the PVA solution and approximately 30 mL mixture solution was obtained. There is 4 ml mixture solution spreading onto a 67 mm×67 mm glass plate and dried for a period of 48 h in a dark room, a dry layer recording medium with thickness 150 μm was obtained. The components of the photopolymerizable mixture are listed in Table 1.

Table 1. Components of the photopolymerizable mixture.

PVA	8 wt.%
AA	0.21 M
BAA	0.033 M
TEA	0.27 M
RF	1.0×10^{-3} M

Diffraction efficiency (DE) is one of the most important parameters for the recording materials, and DE is defined as the intensity ratio of the diffracted beam to the incident beam. The real time measurement of formation of unslanted holographic gratings was carried out using the experimental setup as shown in Fig. 3. The holographic grating were recorded with an Ar^+ laser tuned at the wavelength of 488 nm, the light beam is split into two secondary beams: object beam and reference beam with the intensity ratio 1:1 and the intensity of each beam was 1.5 mWcm^{-2}, the two incident beams recombined in the sample with the angle 45° with respect to the normal, and the spatial frequency was about 2900 lines/mm. A laser with wavelength 633 nm, where the material does not absorb, was used as the reference beam to probe the growth of the holographic grating and the incident direction of the reference beam is positioned at the Bragg angle to compensate for the Bragg mismatch, the diffraction intensity was monitored by a power meter.

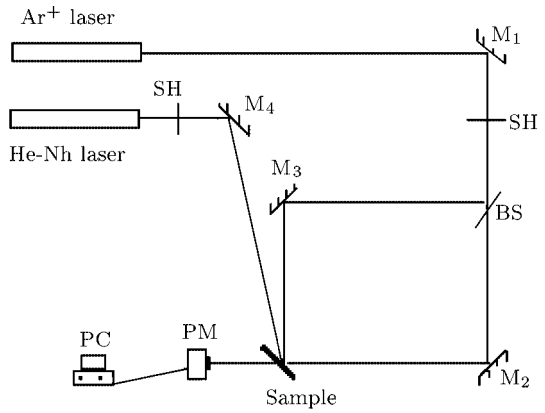


Fig. 3. The experimental setup. M_i, mirrors; BS, beam splitter; PM, power meter; PC, computer; SH, shutter.

The grating generating curve is shown in Fig. 3. We can see that at the first moment, the DE is proportional to the exposure energy. When the exposure energy reaches 210 mJcm^{-2}, the highest diffraction efficiency (∼56%) can be obtained. However the diffraction efficiency has a little drop with the increasing exposure energy. In the photopolymer, the index modulation is proportional to the concentration gradient of the monomer, so at the first seconds the index modulation increasing with the increasing of exposure energy and will be saturated when the exposure energy reaches 210 mJcm^{-2}. The reason why the DE decreases after the saturation value may be the scattering. At first, the scattering is a secondary factor and can be ignored. With the increase of exposure time, almost all monomers in bright areas are polymerized. There is more light scattered into the dark area because of the effect of the accumulation of the scattering. The scattering becomes more important and makes the polymerization of the residual monomers in the dark area. In the end, the monomers in both the bright and dark areas in the interference field are polymerized. Therefore, the maximum refractive in-

dex modulation is smaller, and the maximum diffraction efficiency is smaller.

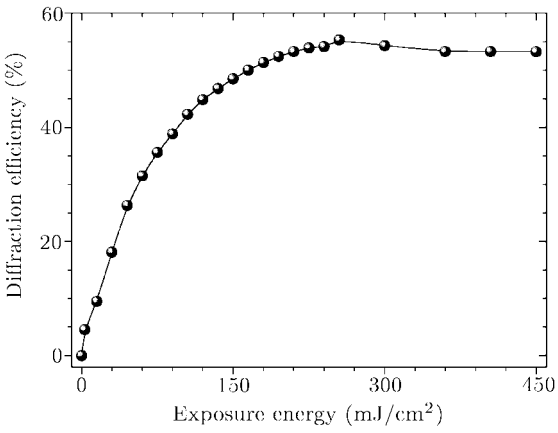


Fig. 4. Relationship of DE and exposure energy.

To evaluate the refractive index modulation (Δn) of the material, using Kogelnik's coupled wave theory,[20] the diffraction efficiency for a transmission grating without absorption in the Bragg regime under symmetric incident and diffraction angles is expressed by

$$\eta = \sin^2\left(\frac{\Delta n \pi d}{\lambda \cos\theta}\right), \qquad (1)$$

where λ is the readout wavelength, Δn is the refractive index modulation, d is the thickness of the recording film, and θ is the angle of the readout beam with respect to the recording film normal. Thus we can calculate the value of the refractive index modulation. Under our experimental condition we can determine that the refractive index modulation is about 6.2×10^{-4}.

Recording the images in the material using holographic technology and retrieving the images by a reconstruction beam employ the principle of holographic information storage. In our experiment, in order to character excellent material characteristics, the binary digital data pages generated by a spatial light modulator (SLM, 1024×768 pixels, pixel dimensions, $26\,\mu\text{m} \times 24\,\mu\text{m}$) are used as the object and are stored in the material. The experimental result is shown in Fig. 5. It can be seen that the reconstruction image has high fidelity, and the graphs at the bottom of the images show the grey-scale distribution along arbitrary horizontal and vertical directions of the reconstructed data page. It can be seen that the reconstruction image has a good contrast of ON (bright) and OFF (dark) pixels, and bit-error-ratio (BER) can also be estimated from the graphs. According to Ref. [21], we can calculate the BER value to be about 1.8×10^{-4}. The results indicate that the material we prepared is suitable for high-density volume holographic storage.

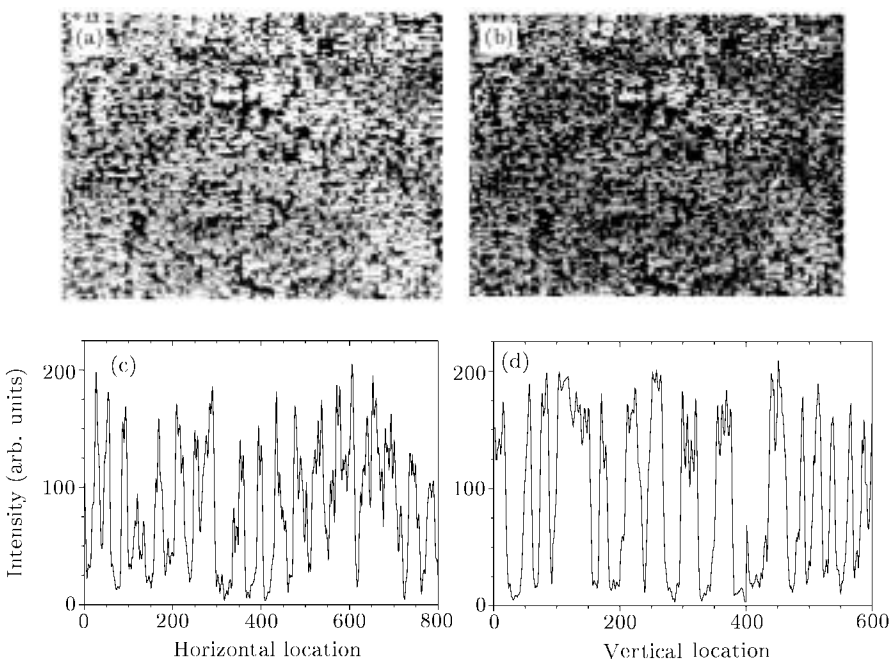


Fig. 5. The result of holographic storage: (a) original digital page, (b) reconstruction digital page, and grey-scale distributions along an arbitrary horizontal direction (c) and a vertical direction (d) on the reconstruction image.

In conclusion, we have fabricated a novel photopolymer recording material for high-density data holographic storage. The material has a broad absorption spectrum range (more than 200 nm) due to the addition of the dye of riboflavin. The experiment with 488 nm exposure wavelength shows that the photopolymer has high exposure sensitivity, large refractive index modulation, and as high as 56% diffraction

efficiency. Two dimensional digital data pages modulated by a spatial light modulator can be stored in the material with the high fidelity. The experimental results indicate that the photopolymerizable system is suitable for high-density digital holographic storage.

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