Safranine T Sensitized Photopolymer Materials for Holographic Storage

XIAO Yong, TANG Dao-guang, SUN Cai-xia, LI Ruo-ping, HUANG Ming-ju†

(*a. Institute of Photon & Optoelectronics Technique, b. College of Physics and Electronics, Henan University, Kaifeng, Henan* 475001, *China*)

Abstract: Safranine T was employed as one of photo-sensitizers of a novel photopolymer material for holographic recording. The experimental results show that the material has high diffraction efficiency and large refractive index modulation. The maximum diffraction efficiency of the photopolymer is about 38.5%, and the refractive index modulation is about 0.547×10^{-3}. The analog holograms are stored in the medium and the reconstructed picture has a good fidelity. It shows that the photopolymer material has the potential for high-density volume holographic storage.

Key words: Holography; Volume holographic storage; Diffraction efficiency; Refractive index modulation

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0 Introduction

Volume holographic recording of information holds promise for the next generation digital mass storage systems with high capacity density and fast transfer rate[1]. For holographic storage to become a practical system, a stable recording medium with nearly ideal properties is required. The desirable properties include high diffraction efficiency, rapid in - place development, no wet processing, no grating shrinkage, long shelf life, temperature and moisture stability, high exposure sensitivity and good resolution, etc[2]. Therefore, researchers have taken great efforts to research various light sensitive materials or other optical holographic elements for holographic optical information storage. Photopolymer materials are one kind of recording materials with many advantages mentioned above.

Typically, a photopolymer system consists of one monomer or a mixture of monomers, a sensitizer, an initiator, and a polymeric film-forming binder. Due to addition of various sensitizers, the photopolymer can be sensitized to various wavelength, many organic dyes were employed as photo-sensitizers. Such as Fluorescein, Eosin Y[3-4], Erythrosin B[5-7], Methylene blue[8-10], Bengal rose[11-12], Riboflavin[13] and so on. However, Safranine T as a kind of photo-sensitizer, has not been reported in the literature. In this paper, we report the holographic characteristic of the photopolymer that sensitized by safranine T.

1 Proporties of Safranine

Safranine T is a sensitizer with a broad spectral range (is more than 100 nm), and a broad spectral range is propitious to multi-wavelength holographic storage to improve the recording density and capacity. The molecules of safranine T can absorb photons and are stimulated to an exited triple state easily. And it has important application in photobiology, too. Such as phototaxis, phototropism and Photo-dynamic therapy, etc[14-16]. The molecule structure and absorption are shown in Fig. 1 and Fig. 2 respectively. We can

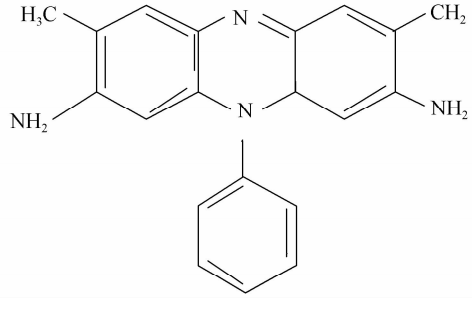

Fig. 1 The molecule structure of safranine T

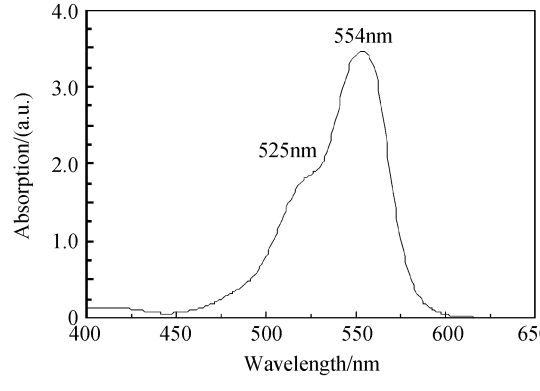

Fig. 2 Absorption spectra of safranine T

* Supported by the Natural Science Foundation of Henan University(06ZDZR002)

† Tel: 0378-3881602 Email: hmingju@163.com

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see from Fig. 2 that the absorption spectral range is from 460 nm to 590 nm, so we can use 488 nm, 514.5 nm or 532 nm etc. wavelengths of laser to write and read the holograms in this photopolymer. And the spectral range belongs to the short wavelength range. This is favor to improve the holographic storage density and capacity.

2 Experimental mechanism and design

When the material is exposed to interference light field under certain wavelength, the dye molecules absorb photons and are excited to the excited state, the exited molecules initiate the free radicals. As a result, the free radicals initiate a spatially nonuniform polymerization of the free monomers. There are more free monomers being polymerized in bright regions than those in dark regions. This nonuniform distribution sets up the monomers concentration gradients corresponding to the interference fringe pattern, and results in the diffusion of monomers from dark regions to the bright regions. At last, a polymer density spatial distribution is formed which results in a refractive index modulation distribution as a similar form, and the phase grating is recorded in the medium. If we assume all reactions are occurred in PVA matrix and the PVA is not reacted . The processes can be depicted by:

$$\mathrm{DYE} \xrightarrow{h\upsilon} \mathrm{DYE}^{*}$$

$$\mathrm{DYE}^{*} + \mathrm{Am} \xrightarrow{k} \mathrm{Am}^{*} + \mathrm{LDYE}$$

$$\mathrm{Am}^{*+} + \mathrm{M} \xrightarrow{k'} \mathrm{P}$$

Where DYE denotes photo-sensitizer (safranine T); DYE^{*} the excited photo-sensitizer; LDYE, leuco dye ; Am^{*+}, action radical of amine; M , monomers; P, polymer; $h\nu$ represents energy quantum of photon; k and k' are the reaction constants.

Our photopolymer consists of monomers acrylamide (AA) and N, N′-mehylenebisacrylaminde (BAA), photo-sensitizer safranine T (ST), photoinitiator triethanolamine (TEA), and the binder polyvinylacohol (PVA). The samples were fabricated in dark room under the normal laboratory condition (20 ~ 25 ℃ temperture and 35%~55% relative humidity). 2 g polyvinyl-alcohol (PVA, $Mr \approx 1\ 750$) was dissolved in distilled water and heated to 80 ℃, and a PVA aqueous solution with 10wt% of PVA was obtained. 3ml triethanolamine (TEA) was poured into the PVA solution, crystals of safranine T were dissolved in distilled water to obtain 9.0×10^{-3} M solution and 1ml was added to the PVA solution. 0.75 g acrylaminde (AA) and 0.25 g N, N′-mehylenebisacrylaminde (BAA) were dissolved in distilled water and heat to 30 ℃, then added into the PVA solution and approximately 30 mL mixture solution was obtained. 7 mL mixture solution was dropped onto a 60 mm×60 mm×1.1 mm glass plate and dried for a period of 36-72 hours in dark room, a dry layer recording medium with the thickness about 200 μm was obtained. The components of the photopolymerizable mixture are listed in table. 1.

Table1 Components of photopolymerizable mixture

Reagents	PVA	TEA	AA	BAA	ST
Conc.	10wt%	0.27M	0.34M	0.052M	3.0×10^{-4}M

The experimental setup is shown in Fig. 3 . We measured the exposure characteristic curves (e. g. diffraction efficiency versus exposure energy or exposure time). The ratio reference intensity to object intensity was one to one, and recorded power was 4 mW, the same as reading power. The two incident beams recombined in the sample with angle 45°. The holographic grating was recorded with Ar^{+} laser tuned at 514.5 nm wavelength. The He-Ne laser with wavelength 632.8 nm, where the holographic did not absorb, was used as the beam to probe the growth of the holographic grating and the incident direction of the reference beam was positioned at the Bragg angle.

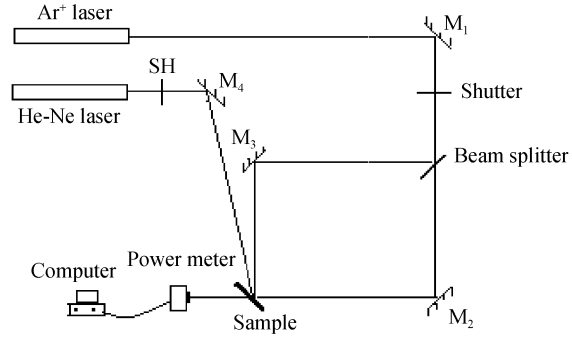


Fig. 3 The experimental setup

3 Results and discussion

3.1 Diffraction efficiency and exposure sensitivity

Diffraction efficiency (DE) is one of the most important parameters for the recording material. DE is defined as

$$\eta = I_{\mathrm{d}}/(I_{\mathrm{i}} - I_{\mathrm{r}}) \tag{1}$$

Where I_{d} is the diffraction light intensity; I_{i} is the incident light intensity; I_{r} is the reflection light intensity.

The Fig. 4 shows the grating generating characteristic curve of diffraction efficiency versus exposure time. We can see, when the exposure energy reaches 850 mJ/cm, the highest DE (38.5%) can be obtained. However, the DE has a large drop with the increasing exposure energy, and after about 30s it rises again, at last it stables at 36%. This is the same as the result in Ref. [17]. The reason is the scatter of the monomers molecules. At first, the scattering is a secondary factor and can be ignored, so the curve of the DE rises with the time. But with the increase of exposure time, the monomer AA and BAA (about6:1) on the surface almost polymerized, the scattering become the major factor [12,17], and the curve has a large drop. After a moment, the laser light makes the monomers polymerized which under the surface. At this time the scatter of molecules again become secondary, and the DE ascends again. At last, all the monomers in the interference field are polymerized. Then the curve of DE is stables. Because the refractive index modulation is smaller, the maximum DE is smaller than the first saturation DE.

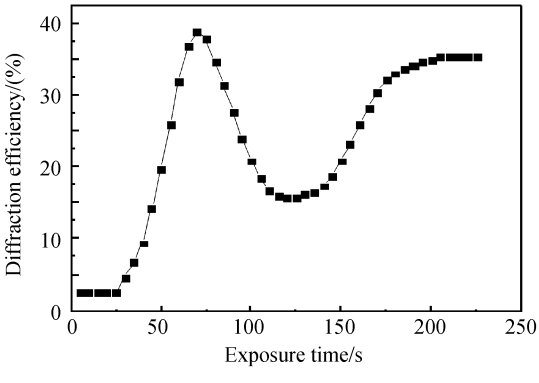


Fig. 4　Diffraction efficiency versus exposure time

Exposure sensitivity is another one important parameters for holographic storage material. It is defined as

$$S=\eta^{1/2}/(\mathrm{m}(v)E_0) \tag{2}$$

Where η is diffraction efficiency; $\mathrm{m}(v)$ is stria modulation of exposure intensity; E_0 is average exposure energy; in our experimental condition we can determined that the exposure sensitivity is 7.30×10^{-4} cm^2/mJ. We can see the exposure sensitivity is lower than other materials. It is necessary for us to think out other method to improve the exposure sensitivity.

3.2　Transmittance and refractive index modulation

When we measure the transmittance curves (transmittance versus incident time). We use the experimental setup in Fig. 3, too. But we must remove the mirror M_3, let the beam (which from M_2) incidents on the sample vertically. The transmitted light incidents in the PM, and the transmittance is defined as the ratio of the intensity of transmitted beam to incident beam. The result shows a nonlinear curve in Fig. 5. From Fig. 5 we can see that for 514.5 nm exposure wavelength the transmittance increases with the increase of the exposure time at first time. When reaches a maximum value, it decreases a little and then gets it's stable level. Why? This is just consistent with the classical scattering theory[12]. At first, with the bleaching of dye molecules, transmittance increases with the exposure time. When the time is long enough, because of the nonuniform of the material the scattering of the light in the sample is getting more and more important, more monomers in the dark area are polymerized, and the random distribution polymers act the new scattering centers and enhance the scattering, so the transmittance is getting smaller and smaller. At last, all the monomers are polymerized, so the transmittance gets it's stable level.

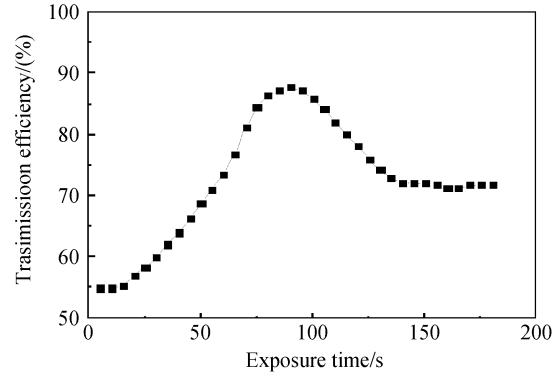


Fig. 5　Transmission efficiency versus exposure time

From Kogelnik's coupled wave theory [18-19], the refractive index modulation (Δn) of the material can be obtained by

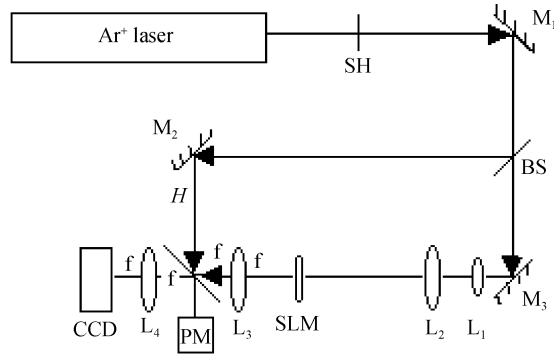
$$\eta=\sin^2\left(\frac{\Delta n\pi d}{\lambda\cos\theta}\right) \tag{3}$$

Where λ is the readout wavelength, Δn the refractive index modulation, d the thickness of the recording film, and θ the angle of the readout beam to recording film normal. So we can calculate the value of the refractive index modulation. Under our experimental condition we can determined that the refractive index modulation is about 0.547×10^{-3}.

3.3　Storage and reconstruction

In the experiment, we have recorded the images in the material, and reconstructed the images as Fig. 7. The experimental setup is used as

Fig. 6 for recording and reading. The analog hologram "全息存储" is formed with a spatial light modulator (SLM), which is connected with the computer. We put the SLM before Fourier lens. From the images we can see the reconstruction model picture is rather clear. So our material has high fidelity. However there are some disadvantages of the reconstructed images. This is because of the low contrast of the SLM and the nonuniform in the material. Otherwise because of the material shrinkage, the reconstructed image has some deformation.



CCD, charge couple pickup camera; L_1, L_2, lenses; L_3 and L_4, Fourier lenses; f, focus; SLM, spatial light modulator

Fig. 6 The experimental setup

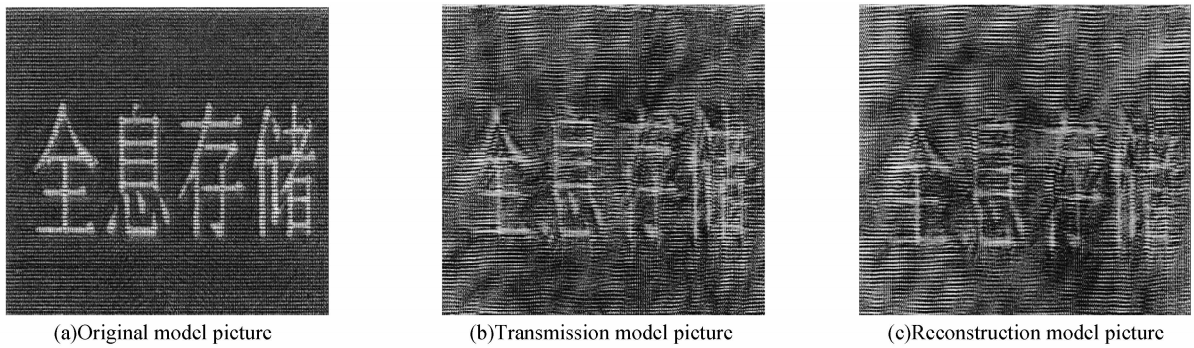


Fig. 7 The results of holographic storage

4 Conclusions

A novel photopolymer recording material for high-density data holographic storage was fabricated in this study. The material has a broad absorption spectrum range (about 150nm) due to the addition of the dye of safraine T. Experiment with 514.5nm exposure wavelength, showed that the photopolymer has a large refractive index modulation and as high as 38.5% diffraction efficiency. Two dimensional analog hologram modulated by spatial light modulator was stored in the material and the high fidelity reconstruction image was obtained. The experimental results indicate that the photopolymerizable system has the potential for the holographic storage.

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番红花红 T 敏化的新型光致聚合物全息存储材料

肖勇, 唐道广, 孙彩霞, 李若平, 黄明举

(河南大学 a. 光学与光子技术研究所, b. 物理与电子学院, 河南 开封 475001)

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摘　要: 制备了一种以番红花红 T 为光敏剂的新型全息存储材料, 实验结果表明, 该材料具有较高的衍射效率、曝光灵敏度和较大的折射率调制度等, 最大衍射效率约 38.5%, 折射率调制度为 0.547×10^{-3}, 在存储介质膜中存储了模拟全息图像, 再现图像有较好的保真度, 说明该材料适合用作高密度体全息存储介质。

关键词: 全息存储; 衍射效率; 折射率调制度; 体全息存储

XIAO Yong　was born in 1978. He graduated from Shangqiu Normal University with the B. S degree in 2005. Now he studies at Henan University for the M. S. degree, and his research focuses on high density data holographic storage.