Investigation on the panchromaticity of silver-doped poly(vinyl alcohol)/acrylamide photopolymer

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An investigation on the panchromaticity of a silver-doped poly(vinyl alcohol)/acrylamide photopolymer system is presented in this paper. Frequency-doubled Nd:YAG (532 nm) and Ar^+ (488 nm) lasers were used for the characterization of the films. Previous studies using an He–Ne laser (632.8 nm) showed that plane-wave transmission grating with a high diffraction efficiency of 75% could be stored in the optimized film. From the present study, it was noted that transmission gratings with 70% diffraction efficiency could be recorded using Ar^+ and Nd:YAG lasers, thereby elucidating the possibility of using the developed photopolymer system as a competent panchromatic recording medium.

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1. Introduction

High-quality panchromatic holographic recording material with high diffraction efficiency, high photosensitivity, high spatial resolution, and high signal-to-noise ratio is one of the key factors for the successful recording of true-color holograms. Traditionally, the materials used for recording color holograms have been silver halide emulsions, dichromated gelatin and panchromatic photopolymers [1–10]. Commercial silver halide materials like the Russian Sphere-S material and noncommercial materials such as the SilverCross emulsion are suitable for color holography. Although the silver halide materials outperform the photopolymers in sensitivity in the visible and in the dynamic range, they have lower diffraction efficiency than the photopolymers and suffer from low signal-to-noise ratio due to increased light scattering in the blue spectral region. The panchromatic photopolymer material from DuPont is an alternative recording material for color holograms [7,9,10]. The DuPont materials are less sensitive than the ultrafine-grain silver halide emulsions, but they have advantages of easy handling and dry processing. However, DuPont polymer materials are mainly used for DuPont's own production of holograms, and only approved customers working in the field of optical security are able to obtain these materials. The photopolymer materials are in particular suitable for mass production of color holograms. The future of color holography is highly dependent on the availability of better panchromatic recording materials based on photopolymers. All these factors have resulted in an augmented interest for developing new panchromatic photopolymer materials.

The self-processing acrylamide-based photopolymer systems sensitized by suitable dyes have attracted great deal of attention because of their high diffraction efficiency (DE) and low cost. Acrylamide-based panchromatic photopolymers for transmission

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holographic recording have been developed by several research groups. Fimia *et al.* have developed a liquid photopolymer system containing a 1 : 1 mixture of 4, 5-diiodosuccinylfluorescein, Methylene Blue (MB), three monomers [acrylamide (AA); N, N′-methylene bisacrylamide (BMA); and zinc acrylate], and sodium *p*-toluenesulphinate (*p*TS-Na) (coinitiator), which showed 15–20% for 15–60 mJ/cm^2 for transmission gratings recorded with He–Ne (633 nm) and Ar$^+$ (514 nm) lasers [11]. Another AA-based photopolymer comprising poly(vinyl alcohol) (PVA) as binder and an ion pair isolated from Rose Bengal (RB) and MB as photoinitiator system with response at 514 and 633 nm was developed by Mallavia *et al.* [12]. This photopolymer system showed diffraction efficiencies of 65% at 30 mJ/cm^2 with an He–Ne laser (633 nm) and 35% at 100 mJ/cm^2 with an Ar$^+$ laser (514 nm), with a spatial resolution of 1000 lines/mm. The efficiency of the PVA/AA film containing an RB–MB photoinitiator system has been improved by the incorporation of BMA [13]. The efficiency obtained was nearly 80% for gratings recorded using an He–Ne laser (632.8 nm), 60% for an Ar$^+$ laser (514 nm), and 40% for gratings recorded using an Ar$^+$ laser (488 nm). The exposure energy was nearly 120 mJ/cm^2 in all cases.

A panchromatic AA-based photopolymer for multicolor reflection holography has been recently developed by Meka *et al.* [14]. This photopolymer system consisted of AA (monomer), BMA (cross-linking monomer), PVA (binder), and triethanolamine (electron donor or coinitiator). The photopolymer was sensitized using MB, Erythrosine B, and Acriflavine dyes to record at red–green–blue wavelengths, respectively. The maximum DE for the reflection gratings recorded using 633 nm, 532 nm, and 473 nm wavelengths were 11.5% (144 mJ/cm^2), 6% (216 mJ/cm^2), and 1.6% (180 mJ/cm^2), respectively.

Beena *et al.* have studied the possibility of using an AA-based photopolymer system with PVA binder, MB dye, and triethanolamine (TEA) coinitiator as a panchromatic recording media [15]. This photopolymer film showed a DE of 70% for transmission gratings recorded using 632.8 nm He–Ne (120 mJ/cm^2) and 532 nm Nd:YAG (250 mJ/cm^2) lasers, while the efficiency for grating recorded with a 488 nm Ar$^+$ laser was ~50% (900 mJ/cm^2). In this case, high exposure energy was required for attaining maximum efficiency, and the material had limited storage and shelf life due to the lack of a crosslinker in the system. Silver-doped photopolymer films developed by incorporating silver ions into the MB-sensitized PVA/AA (MBPVA/AA) films exhibited high DE and good energetic sensitivity [16]. Transmission grating recorded in the optimized film using an He–Ne laser (632.8 nm) exhibited a DE of 75% for 80 mJ/cm^2 exposure energy. The silver-doped MBPVA/AA film exhibited good storage and shelf life as well. This paper presents the holographic characterization of silver-doped MBPVA/AA films using Ar$^+$ (488 nm) and frequency-doubled Nd:YAG (532 nm) lasers.

2. Experimental

The photopolymer material used in the present study comprises PVA as the binder matrix, AA as the monomer, MB and TEA as the photoinitiation system, and silver nitrate as the crosslinker. The films were fabricated by the gravity settling method. The films had a thickness of 130 ± 2 μm (measured using Dektak 6 m stylus profiler). Spectral and energetic sensitivity of the films were determined by optical absorption and real-time transmittance studies. A UV–visible–near-IR spectrophotometer (JASCO V-570) was used for recording the optical absorption spectra of the films. An Ar$^+$ laser (488 nm, 543 series, Melles Griot, 180 mW, CW) and a frequency-doubled Nd:YAG laser (532 nm, Compass 215 M-20, Coherent, 20 mW, CW) were used for real-time transmittance studies, for recording of transmission gratings, for recording of holograms, and for DE measurements.

3. Results and Discussions

A. Optical Absorption and Real-Time Transmittance Studies

Optical absorption studies were carried out to determine the spectral response of the silver-doped MBPVA/AA photopolymer film prepared with composition as given in Table 1. The optical absorption spectra of silver-doped and undoped MBPVA/AA films are shown in Fig. 1. From the graph, it can be seen that, even though the maximum absorption is in the red region (peak at 665 nm) for both undoped and silver-doped MBPVA/AA films, silver-doped films showed another absorption peak in the blue region (425 nm) as well. Even for 532 nm, there is a small absorption. The broad spectral sensitivity of the silver-doped film indicates the possibility of using it as a panchromatic recording material.

Real-time transmittance on laser exposure was monitored by exposing the film to a laser beam of irradiance 1 mW/cm^2 for 4 min, and the transmitted power at regular intervals was monitored using an optical power meter. The relative transmittance T/T_0 was also determined, where T is the real-time transmittance of silver-doped films and T_0 is the transmittance of the PVA/AA films without dye and silver nitrate. The variation of relative transmittance with exposure energy is shown in Fig. 2. As the material sensitivity, i.e., the response of the material to laser exposure, increases, the transmittance increases at low exposures. This is because even at low exposure, the dye molecules (MB) were getting excited and got

Table 1. Optimum Film Composition

Constituent	Concentration
PVA	10% w/v
AA	0.4 M
TEA	0.05 M
MB	0.014 mM
$AgNO_3$	0.05 mM

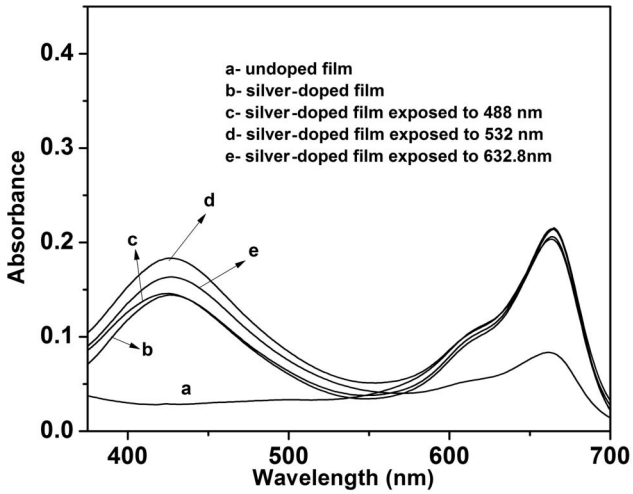

Fig. 1. Optical absorption spectra.

converted to the leucoform. It could be seen that the transmittance increases for low exposure energies, which indicates the good energetic sensitivity of the films. The threshold energy requirement was $\sim 0.5\,\mathrm{mJ/cm^2}$ for both wavelengths. From Fig. 3, it can be seen that, on irradiation using a longer wavelength (632.8 nm He–Ne laser), transmittance was found to be increasing with the increase in exposure time and reached a final saturation value when all the dye molecules are bleached. This may be due to less scattering in the sample at a longer wavelength. For higher exposure energies, the relative transmittance decreases in the case of irradiation with 488 nm Ar^+ and 532 nm Nd:YAG lasers. This may be due to scattering, since the shorter the exposure wavelength, the greater the scattering power, consistent with the classical scattering theory [13].

B. Recording of Grating and DE Measurements

Plane-wave transmission gratings were recorded in the films by double beam holographic recording

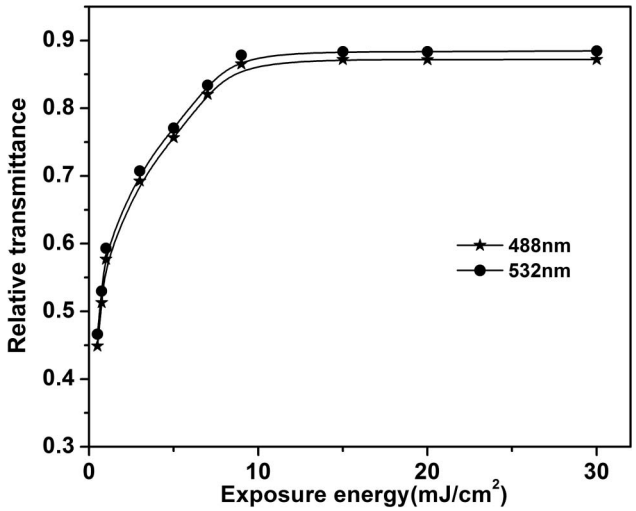

Fig. 2. Variation of relative transmittance on irradiation with Ar^+ and Nd:YAG lasers.

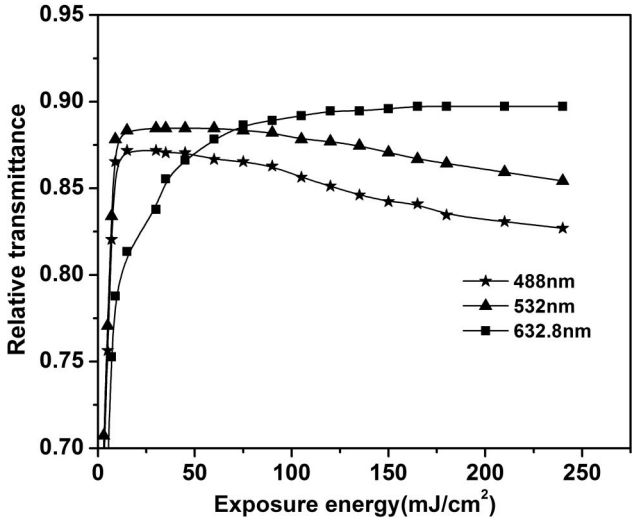

Fig. 3. Variation of relative transmittance on irradiation with Ar^+, Nd:YAG, and He–Ne lasers.

setup [16]. The exposure energy required for achieving maximum DE was determined by recording gratings for different exposure times, keeping the total recording power as 4 mW. The interbeam angle was 40° and beam intensity ratio was 1:1. The spatial frequency of the grating recorded using the Ar^+ laser was ~1400 lines/mm, while that with the Nd:YAG laser was ~1285 lines/mm. The gratings were reconstructed using the recording laser, and the DE was calculated as the ratio of the power of the first-order diffracted beam to the reading beam power. The exposure characteristic curves are shown in Fig. 4. For both recording wavelengths, the DE increased with the increase of the exposure time at first, reached its maximum value, and then gradually decreased. This is because, with the increase in exposure time, more monomers will get polymerized, which increases the refractive index (RI) modulation, and hence the DE increases with exposure

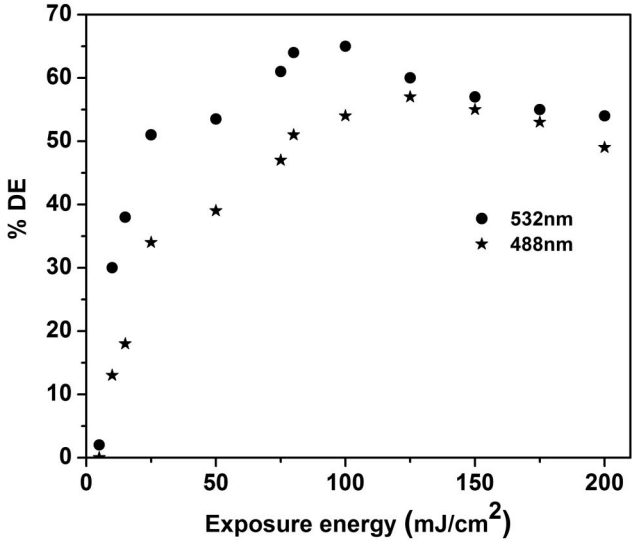

Fig. 4. Change in DE with exposure energy.

time [17]. But when the exposure time is further increased, the scattering light induced in the photopolymer (due to optical imperfection of the film) increases, which results in the polymerization of the residual monomers in the dark region thereby decreasing the RI modulation, and consequently the DE decreases [17]. Efficiency reaches its saturation value when all the monomers are polymerized. Maximum efficiency achieved with 488 nm was 57% for 125 mJ/cm^2, while with 532 nm, the peak efficiency was 65% for exposure of 100 mJ/cm^2.

In order to study the effect of total recording power on the DE, gratings were recorded by varying the power at the recording position. The exposure energy was maintained at the optimum value (125 mJ/cm^2 for 488 nm and 100 mJ/cm^2 for 532 nm) throughout the recording process. Figure 5 shows the variation of DE with the recording power. For recording power in the 2.5–5 mW range, efficiency above 60% could be obtained with 532 nm, while the efficiency was above 55% for gratings recorded using the 488 nm Ar^+ laser. There was not much variation in efficiencies while the recording power was in the range of 2.5 to 4 mW. For both recording wavelengths, the maximum DE was achieved when the recording power was 3 mW. For this recording power, the peak DE was 60% for 488 nm and 67% for 532 nm. The variation of DE with exposure energy for gratings recorded using 3 mW/cm^2 is shown in Fig. 6. It was observed that, even for an exposure of 25 mJ/cm^2, the DE was nearly 40% for a grating recorded with an 488 nm Ar^+ laser and a DE above 50% could be obtained with 532 nm.

The RI modulation (Δn) was calculated using the measured DE (η) according to Kogelnik's theory [18,19]

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

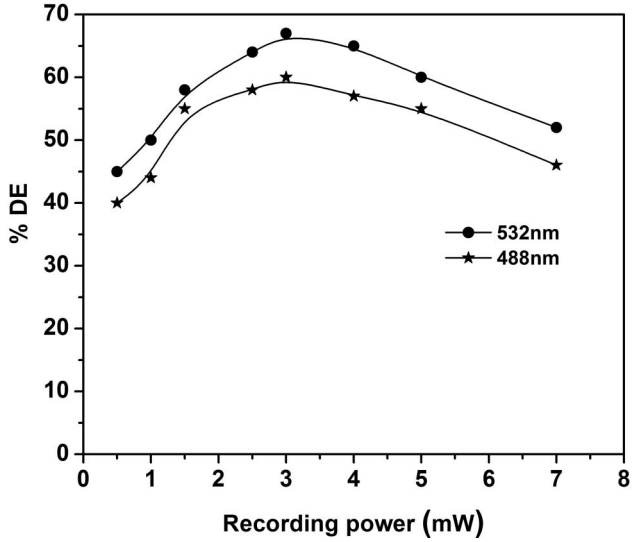

Fig. 5. Change in DE with total recording power.

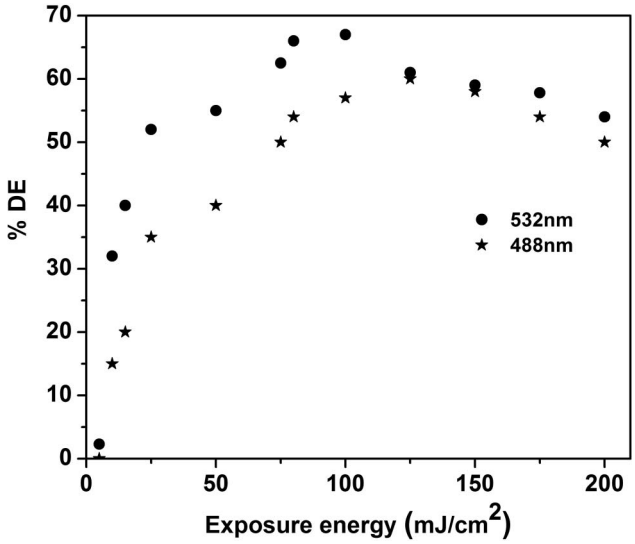

Fig. 6. DE variation with exposure energy.

where λ is the reconstruction beam wavelength, d is the sample thickness, and θ is the reading beam incidence angle. The variation of Δn with exposure energy is plotted in Fig. 7. Maximum RI modulation was nearly 1×10^{-3} for the grating recorded using the Ar^+ laser (125 mJ/cm^2), while Δn was 1.17×10^{-3} for the grating recorded using the Nd:YAG laser (100 mJ/cm^2). The RI modulation increased on exposure, reached a peak value, and decreased slightly on further increasing the exposure.

C. Optimization of Ag^+ Concentration

In order to study the variation of the DE with Ag^+ concentration, films with different Ag^+ concentrations (0.023 mM–0.38 mM) were prepared, and transmission gratings were recorded in the films using 488 nm and 532 nm lasers. The total recording power was maintained as 3 mW, and the interbeam angle was 40°. The variation of efficiency with the Ag^+ concentration for gratings recorded using 488 nm

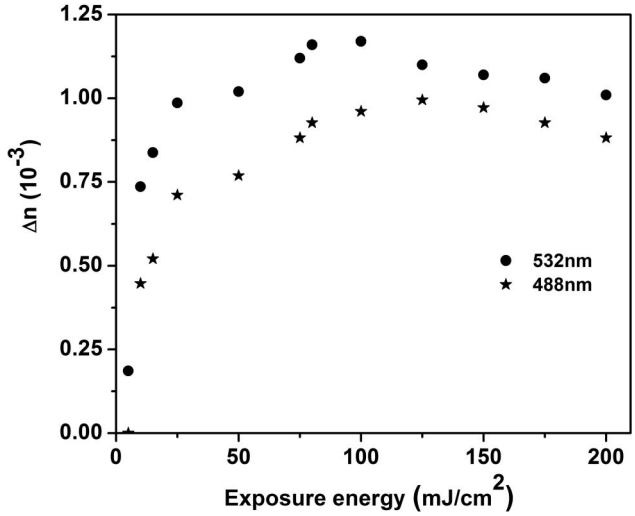

Fig. 7. Change in RI with exposure energy.

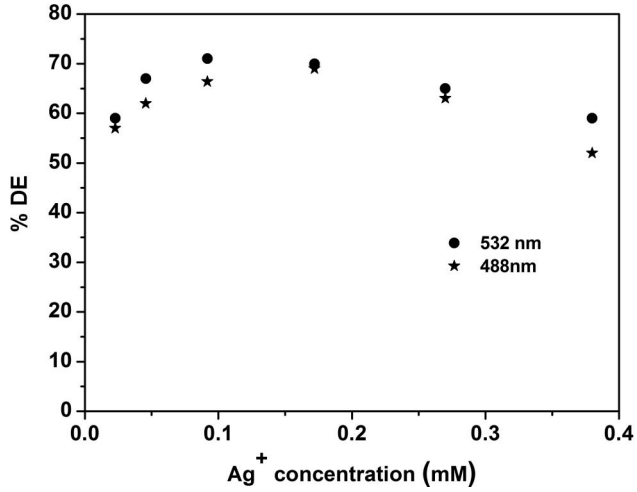

Fig. 8. Variation of efficiency with Ag^+ concentration.

(exposure energy 125 mJ/cm^2) and 532 nm (exposure energy 100 mJ/cm^2) is shown in Fig. 8. The maximum DE was 70% for the grating recorded using 488 nm in film with an Ag^+ concentration of 0.172 mM. A DE of 71% could be obtained for the grating recorded using 532 nm for film with an Ag^+ concentration of 0.092 mM. Films were prepared with these optimum Ag^+ concentrations for carrying out further studies.

D. Spatial Frequency Response

The spatial resolution of the material was determined by recording transmission gratings for various interbeam angles. The interbeam angles were varied from 15° to 100°, and spatial frequencies corresponding to each interbeam angle were calculated using Bragg's equation. The exposure energy was maintained at the optimum value (125 mJ/cm^2 for 488 nm and 100 mJ/cm^2 for 532 nm) throughout the recording. Figure 9 depicts the spatial frequency response of the material. From Fig. 9, it can be seen that recording with 488 nm Ar^+ laser had resulted in a DE above 60% for gratings with 1000–1400 lines/mm,

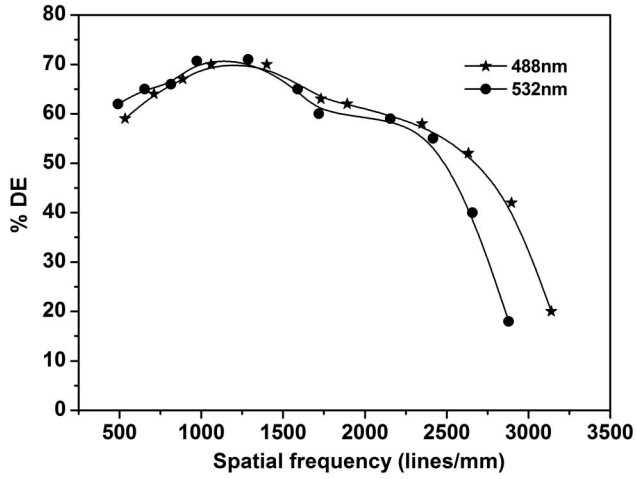

Fig. 9. Spatial frequency response.

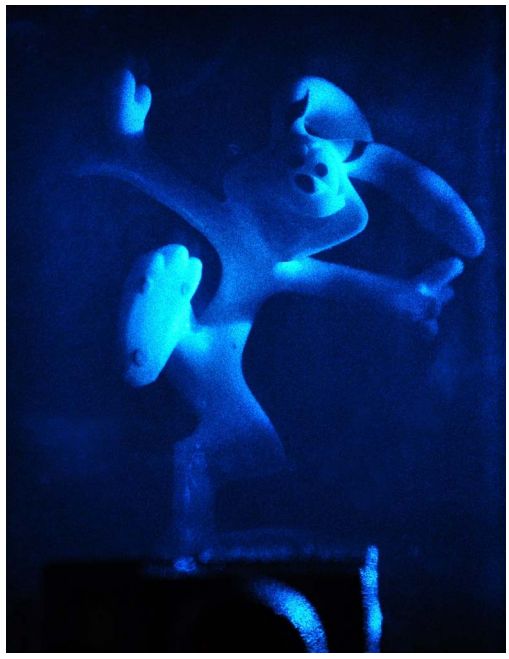

Fig. 10. (Color online) Hologram recorded using Ar^+ laser.

while the DE was nearly 70% for gratings with 970–1300 lines/mm recorded using the Nd:YAG laser.

In both cases, more than 50% efficiency could be obtained for gratings with 2000 lines/mm. For still high resolution, the DE was found to be decreased. At higher spatial frequencies, the fringe spacing is very small. This results in the diffusion of short chain polymer molecules from the exposed to the unexposed regions, thereby reducing the RI modulation and the DE [20,21]. From the present study, DE of nearly 20% could be obtained even for gratings with 3000 lines/mm. This indicates the good spatial resolution of the developed films.

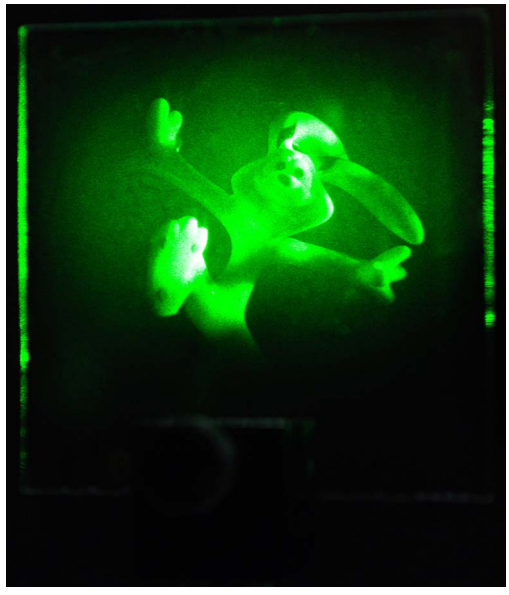

Fig. 11. (Color online) Hologram recorded using Nd:YAG laser.

E. Recording of Transmission Holograms

Transmission holograms were recorded in the optimized film using Ar^+ and Nd:YAG lasers. Standard transmission holographic recording setup was used for recording holograms. Photographs of bright transmission holograms recorded with optimum exposure energies (125 mJ/cm^2 for 488 nm and 100 mJ/cm^2 for 532 nm) are shown in Figs. 10 and 11. The developed photopolymer system has the great advantage of recording and reconstructing holograms in real time.

4. Conclusions

The feasibility of using the silver-doped photopolymer film as a panchromatic material is demonstrated. The material is capable of recording holographic transmission grating with high DE using Ar^+ (488 nm), Nd:YAG (532 nm), and He–Ne (632.8 nm) lasers. The developed panchromatic photopolymer system is excellent on account of its wide spectral sensitivity, high DE, good energy sensitivity, high resolution, cost effectiveness, ease of fabrication, and real-time imaging capabilities. The film is expected to have important applications in the fields of true-color display holography, holographic storage, and holographic optical elements.

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