Resisting shrinkage properties of volume holograms recorded in TiO_2 nanoparticle-dispersed acrylamide-based photopolymer*

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A novel organic–inorganic nanoparticle–photopolymer composite system is developed, and its fundamental holographic recording characteristics are studied. In this hydrophilic TiO_2-nanoparticle-dispersed acrylamide photopolymer composite system, the counter-diffusion of monomers and nanoparticles plays a fundamental and key role in hologram grating formation. The experimental results indicate that the volume shrinkage of the nanoparticle–photopolymer film during the holographic recording can be drastically reduced compared with the undoped photopolymer film. It is also found that the diffraction efficiency of the grating recorded in the nanoparticle–photopolymer film depends strongly on the concentration of the TiO_2-nanoparticles, and there exists an optimal TiO_2-nanoparticle-doping concentration to make the diffraction efficiency and the refractive index modulation reach their maxima. Additionally, the digital data page is stored and reconstructed in the nanoparticle–photopolymer film.

Keywords: holographic proprieties, TiO_2-nanoparticle, diffraction efficiency, Bragg-mismatch

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1. Introduction

In the past 20 years, photopolymers have attracted much attention since they have many advantages as holographic recording materials, such as high sensitivities, high spatial resolutions, wide frequency response ranges, easy optimization, and relatively low cost.[1,2] Due to these advantages, photopolymers have been applied to various holographic optical elements and security/surveillance holograms; meanwhile, they will also be used as digital holographic data storage media, three-dimensional images, and high speed photoelectric parts in the near future.[3] In spite of these merits, photopolymers still have the fundamental problem that the original images are distorted because of volume shrinkage during the polymerization process of the monomers. This volume shrinkage takes place chiefly in the direction perpendicular to the film surface, i.e., it is thickness shrinkage. In the process of the hologram reconstruction, the volume shrinkage causes aberrations and wavelength shift and/or angular rotation for maximum diffraction-efficiency compared with the origin condition of recording, which restricts the use of the photopolymer as a holographic data storage medium.[4] In order to overcome the shrinkage of photopolymers, Vaia *et al.*[5] introduced the idea of incorporation of inorganic nanoparticles such as SiO_2, ZrO_2, TiO_2, etc., into a photopolymer composite system as a movable nonreactive component. Later this idea was widely adopted by other groups.[6–8] Their experimental results show that nanoparticles doped in methacrylate photopolymer system can not only substantially suppress shrinkage but also obtain much larger refractive index modulation[8–10] compared with conventional all-organic photopolymers.

The water-soluble photopolymer system based on polyvinyl alcohol/acrylamide (PVA/AA) has the advantages of simplifying operation, having little toxicity and high diffraction efficiency, etc. Therefore, it is one of the most commonly used photopolymer systems.[11–15] In recent years, the doped inorganic nanoparticles in the methacrylate oil-soluble system have been studied by several groups, e.g., Vaia *et al.*,[5] Sanchez *et al.*,[6] Kim *et al.*,[7] Suzuki *et al.*,[8] Suzuki and Tomita,[9] Suzuki *et al.*,[10] but the study on the doped nanoparticles in the AA/PVA water-soluble system has still been rarely reported.

In the present work, we develop a novel TiO_2-nanoparticle-dispersed PVA/AA-based photopolymer composite system, and study its holographic recording characteristics. The experimental results show that the volume shrinkage during the holographic exposure process can be noticeably suppressed by doping the TiO_2-nanoparticles into the PVA/AA-based photopolymer composite system. The diffraction efficiency and other performance parameters can also be improved in the hydrophilic TiO_2-nanoparticles-dispersed pho-

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topolymer composite system compared with those in traditional undoped samples. Additionally, the digital data page is stored in this medium, and transmittance and reconstructed holograms each have a good fidelity. All of these experimental results demonstrate that doping TiO_2-nanoparticles in acrylamide photopolymer composite system is a good way of improving the holographic performance.

2. Experiments

2.1. Preparation of nanoparticle

The TiO_2 nanoparticles in the experiment are prepared by the liquid phase deposition method, and are subjected to surface modification *in situ* with citric acid. A TEM photograph of the TiO_2 nanoparticle is given in Fig. 1. From Fig. 1, it can be seen that the average particle size of the TiO_2-nanoparticles is about 10 nm.

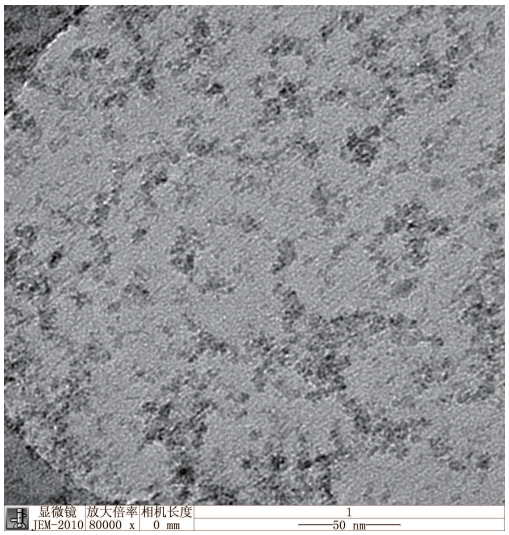


Fig. 1. TEM image of TiO_2.

2.2. Preparation of photopolymer

Our photopolymer film consists of acrylamide-polyvinylalcohol (PVA, with a refractive index of 1.51) as the binder, acryl amide (AA, with a relatively high refractive index of 1.469) as a monomer, N, N'-methylene-bis-acrylamide (BAA, with a refractive index of 1.473) as a cross-linking agent, Eosin Y (EY) as a dye photosensitizer. The popular initiator for PVA photopolymer composite system is triethanolamine (TEA), which has slow initiating speed, so an activator is required to maintain proper polymerization speed. Hydrophilic TiO_2 nanoparticles (with a refractive index of 2.51) are used as an inorganic guest to introduce the PVA photopolymer composite system.

According to our previous investigations,[14,16] six kinds of photopolymer samples doped with different TiO_2-nanoparticle are prepared. Each of composition concentrations in these samples is the same as that in Ref. [17]. The thickness values of the dry samples are measured with a micrometer caliper and they are in a range of 88 μm–92 μm.

2.3. Optical setup

Diffraction efficiency is one of the most important parameters for the hologram recording material. The system configuration for measuring diffraction efficiency of the hologram is schematically illustrated in Fig. 2. The holographic recording beams, i.e., the object beam and the reference beam come from a CW Ar-ion laser operating at wavelength 514.5 nm. Two beams are symmetrically incident on the sample, whose intersection angle is $\theta = 45^\circ$. The intensities of the two recording beams are set to be equal. A Kr-ion laser with wavelength 647 nm is used as a reading beam to monitor the growth of the holographic grating. The incident direction of the reading beam is positioned at the Bragg angle to compensate for the Bragg mismatch, and the diffraction intensity is probed by a power meter.

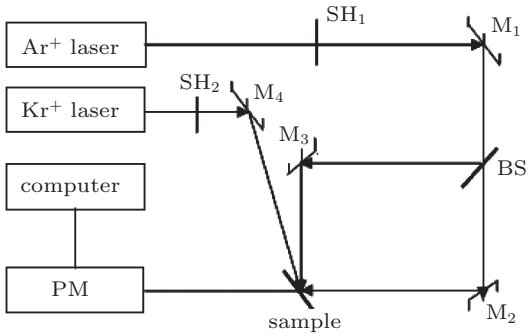


Fig. 2. Experimental setup of diffraction efficiency testing. SH: Shutter, M: mirrors, BS: beam splitter, PM: power meter.

3. Results and discussion

3.1. Sample absorption

Figure 3 shows the absorption spectra of two photopolymer samples (S1 and S4). From Fig. 3, it can be seen that the absorption spectra of the doped and undoped TiO_2-nanoparticle photopolymer samples are almost the same, except that the absorption intensity of S4 is slightly higher than that of S1 in the whole region. There is no new absorption peak occurring in the absorption spectra, which indicates no new material is produced after adding nanoparticles. The absorption peaks of the samples are both at 528 nm, showing that the absorption of the photopolymer film is determined only by the sensitizing dye and the photopolymer is suited for the holographic recording by using an Ar-ion laser at 514 nm.

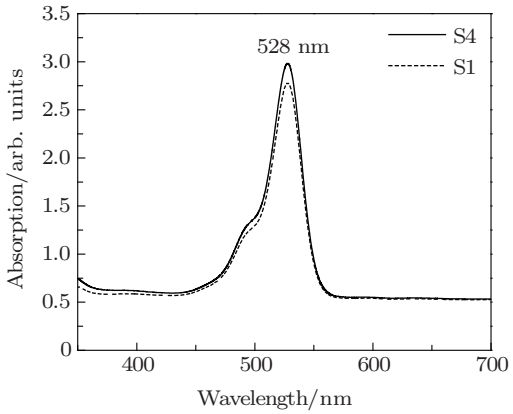


Fig. 3. Absorption spectra of photopolymers.

3.2. Diffraction efficiency

In the holographic data storage, diffraction efficiency is normally considered one of the most important parameters to determine the optical properties of the photopolymer material. We use the experimental arrangement shown in Fig. 2 to write an unslanted transmission hologram. The intensities of two coherent writing beams are each set to be 100 mW/cm^2.

The diffraction efficiency (η) is defined as $I_{+1}/(I_{+1}+I_t)$ in which I_t and I_{+1} are the intensities of the transmitted beam and the first order diffraction beam, respectively.[8–10] The loss factors such as linear absorption and light scattering are excluded. Figure 4(a) shows the diffraction efficiency kinetic curves of six kinds of samples. Figure 4(b) shows the corresponding refractive index modulation (Δn) kinetic curves of samples 1 and 4.

From Fig. 4(a), we can see that the trend of the diffraction efficiency curve of each sample is consistent. At the beginning of the exposure time, the diffraction efficiency increases nearly linearly with the increase of the exposure time; with the increase of the exposure time, the diffraction efficiency becomes saturated and then attains a stable value (maximum). This phenomenon is the formation process of the photopolymer holographic grating. The maximum diffraction efficiencies of S1–S6 are 78.6%, 80.7%, 82.3%, 92.4%, 79.7%, and 68.6%, respectively. We find that at the low concentration of the doping of TiO_2, the diffraction efficiency increases with doping concentration increasing, and there exists an optimal doping concentration at which the diffraction efficiency can reach a maximum; when the doping concentration is higher than the optimal doping concentration, the diffraction efficiency decreases. The maximum diffraction efficiency of the optimal doping concentration sample S4 enhances approximately 20% compared with that of the undoped sample S1.

Figure 4(b) shows the corresponding dynamics of Δn. Δn is deduced from data of the saturated η with Kogelnik's formula.[18] From Fig. 4(b), we can see that the Δn of the undoped sample S1 is 1.764×10^{-3}, while that of TiO_2-nanoparticles-doped sample S4 reaches 2.093×10^{-3}, so Δn is improved by nearly 20%. The experimental results indicate that the maximum diffraction efficiency and the maximum Δn of the sample S4 are remarkably enhanced in comparison with those of the undoped photopolymer films. This phenomenon cannot be explained by the conventional monomer-diffusion model. We speculate that this is because the monomers and nanoparticles counter diffuse under inhomogeneous illumination and ultimately form the phase modulation grating of the nanoparticle–polymer. In the nanoparticle–photopolymer composite system, it is possible that the nanoparticles of the order of 10 nm in diameter would diffuse according to the following numerical estimation: assuming a spherical nanoparticle with diameter (d) to be in a liquid with viscosity (ν), the diffusion constant (D) of the nanoparticle is given by the Stokes–Einstein relation $D = kT/3p\nu d$. Substituting $d =$ 10 nm and $n = 50$ cP (a typical value of photopolymerizable monomers for holographic recording) into this formula, we obtain $D \approx 1\times10^{-8}$ cm^2/s at room temperature. This value is comparable to that of monomers (10^{-9} cm^2/s $\sim$ 10^{-7} cm^2/s),[19] which suggests that mutual diffusion is possible.

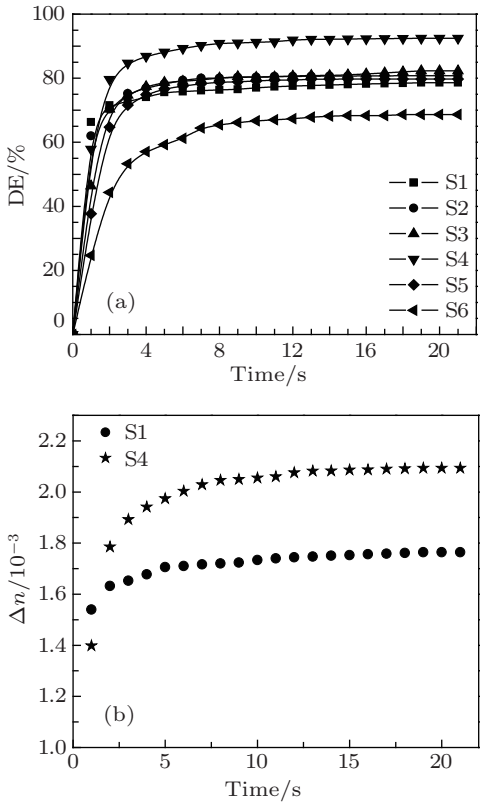


Fig. 4. Recording dynamic behaviors of (a) the diffraction efficiency and (b) corresponding n at a writing intensity of 100 mW/cm^2 and spatial frequency of 2751 l/mm for samples with different TiO_2 nanoparticles concentrations.

In our nanoparticle–photopolymer composite system, both monomers and nanoparticles are considered to transport during photopolymerization. According to the theory reported by Karpov *et al.*,[20] the consumption of monomers due to photopolymerization breaks the thermo-dynamical equilibrium balance between monomers and nanoparticles, which requires that their volume fraction ratio between these two components should be constant at any position. Such an imbalance leads to the diffusion of the monomers in the dark regions to the bright regions, while photo-insensitive inorganic nanoparticles counter diffuse from the bright regions to the dark regions. This counter-diffusion process takes place in a very short period repeatedly until the termination of polymerization. In this way, a permanent refractive index grating is formed, owing to the spatial redistribution of the effective refractive index with periodically distributed nanoparticles and polymerized monomers (polymer). A large amount of experimental evidence shows that such a redistribution indeed occurs in the photopolymerization of the nanoparticle–photopolymer composite system.[21,22]

We use a square-wave particle distribution function to explain the reasons for Δn increasing. It is assumed that as a result of the holographic recording of a grating, the simplest hologram used to characterize the material properties, a square-wave particle distribution, is introduced, then the refractive index modulation amplitude can be expressed by[5]

$$\Delta n = \frac{2 f_{\text{nano}}}{\pi} (n_{\text{nano}} - n_{\text{host}}) \sin(\alpha\pi), \tag{1}$$

where f_{nano} is the volume fraction of nanoparticles in the nanoparticle-rich region, n_{nano} is the refractive index of the nanodopants, n_{host} is the refractive index of the host organic matrix, and α is the fraction of the period spacing with a rich content of nanoparticles. In our experiments, the refractive indices of AA, PVA, and TiO_2 nanoparticles are 1.47, 1.51, and 2.51, respectively. According to formula (1), it is easily obtained that

$$(n_{\text{TiO}_2} - n_{\text{AA}}) > (n_{\text{PVA}} - n_{\text{AA}}). \tag{2}$$

In other words, the photopolymer composite system doped with the TiO_2-nanoparticles can effectively increase Δn of the hologram grating. So the "counter-diffusion" results in the final formation which causes Δn to increase, and also induces the diffraction efficiency and other parameters to increase.

In our photopolymer system we can find that there exists an optimal TiO_2-nanoparticles doping concentration to make the diffraction efficiency reach a maximum. From Fig. 4(a), we can find the reasons for the decline of the diffraction efficiency of the sample with higher nanoparticle doping concentration. We speculate that, on the one hand, with the increase of doped nanoparticle concentration, the reunion phenomenon of nanoparticles is intensified, which inhibits the diffusion of monomers, for the larger the nanoparticle, the more difficult it is to diffuse and block the photopolymerization process. On the other hand, adding more nanoparticles will exacerbate Rayleigh scattering of light, and reduce the transmitted light and the diffracted light, thereby reducing the diffraction efficiency.

3.3. Material stability

Holographic storage is based on the principle of the interference record and the diffraction readout to write and read information. In information recording process, the object beam carrying the information about the object and the reference beam simultaneously irradiate a sample, their interference pattern is formed inside the sample. When the photopolymer material is exposed to an interference fringe pattern, there are more monomers being polymerized in the bright region than in the dark region. This nonuniform illumination distribution sets up monomer concentration gradients, driving the monomers to diffuse from the dark regions to the neighboring bright regions. The polymerization of monomers in the bright region easily leads to the sample shrinkage and distortion, which induces Bragg-mismatch. Bragg-mismatch is the angle displacement of the reading reference beam from the recording reference beam. Bragg mismatch may significantly reduce the diffraction efficiency, and lead to the degradation of the signal-to-noise ratio.[4]

Figure 5 shows the curves of diffraction efficiency versus the incidence angle of reading beam. In Fig. 5, the curve with solid squares corresponds to the theoretical result obtained from the Kogelnik coupled-wave theory,[18] the others are for the experimental results.

From Fig. 5, we can see that the angular selectivity in the experiment is slightly wider than the theoretical calculation by using Kogelnik's model. We speculate that the inconsistence between experimental result and theoretical calculation originates from the plane wave assumption, i.e., the assumption of the incident light in recording and reconstruction being infinite plane-wave, in the theoretical model. However, in our experiment, the beam is a fundamental Gaussian wave with a finite curvature-radius of the wavefront and also with a finite beam radius. According to diffraction theory, the finite beam size is bound to broaden. The measured Bragg-mismatch of sample S4 is smaller than that of sample S1, and is closer to the the-

oretical value. Moreover, the measured diffraction efficiency of sample S1 in the original angle (i.e. the curve of 0°) is only 60% of the maximum diffraction efficiency in the Bragg-mismatch angle (i.e., the curve of 0.16°), while for sample S4, the measured diffraction efficiency in the original angle (i.e., the curve of 0°) is only 95% of the maximum diffraction efficiency in the Bragg-mismatch angle (i.e., the curve of 0.04°). So the Bragg-mismatch and shrinkage of sample S4 are smaller than those of sample S1, which is just of benefit to the doping of the nanoparticles in the samples.

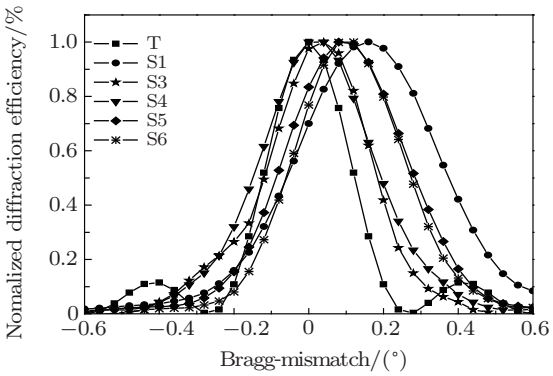


Fig. 5. Normalized diffraction efficiencies versus incident angle of the read beam with respect to the recording reference beam.

Additionally, according to the shrinkage model,[23] the shrinkage rate of material can be easily calculated. For instance, the shrinkage fractions of S1 and S4 are calculated to be 3.22% and 0.80%, respectively.

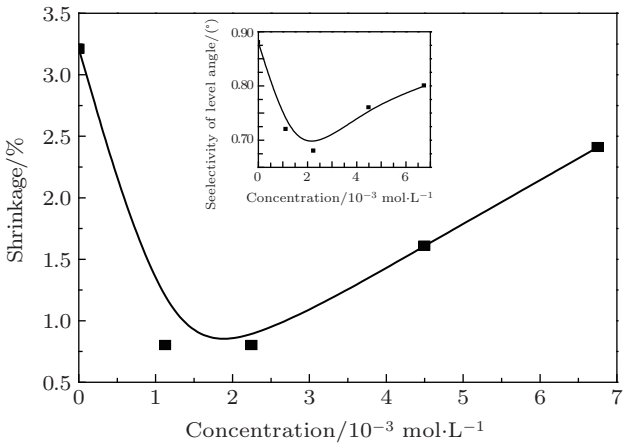


Fig. 6. Plot of σ against TiO_2-nanoparticles doping concentration, with the inset showing the variation of corresponding selectivity of the level angle with nanoparticles doping concentration.

Figure 6 shows the dependences of the thickness shrinkage rate (σ) on TiO_2-nanoparticle concentration for the six samples. It can be clearly seen that with the increase of the doped concentration of TiO_2 nanoparticles, σ first declines and then increases. It is obvious that there exists the optimal concentration of TiO_2-nanoparticles to make the σ reach the maximum. We speculate that under the action of an external force, the nanoparticles and the photopolymer form the homogenous three-dimensional networks which play a role in stress concentration and cause the photopolymer to absorb the impulse, thus inducing σ to decline. With the increase of doped nanoparticle concentration, the reunion of nanoparticles is intensified, and thus the size of nanoparticles increases, which not only damages the photopolymerization process but also causes the system performance to degrade. So σ increases. This is consistent with the result reported by Hata and Tomita.[24] From Fig. 5, we can see that the shrinkage of nanoparticles-doped sample is smaller than that of the undoped one. We speculate that such a decrease in shrinkage may be attributed to the increase in rigidity of the sample material resulting from the dispersion of the nanoparticles.[25] The results show that the incorporation of TiO_2 nanoparticles into the photopolymer leads to the substantive suppression of the volume shrinkage during holographic exposure.

The above analysis shows that TiO_2-nanoparticle doping improves the mechanical and thermal stabilities of a polymer film because it effectively suppresses the mechanical stress caused by heating and/or polymerization shrinkage. So in this system inorganic nanoparticle doping can improve the performance of the photopolymer for holographic storage.

3.4. Digital holographic storage experiment

Recording the images in the material using holographic technology and retrieving the images by a reconstruction beam are based on the principle of holographic information storage. In the digital holographic storage experiments, the information which is encoded as two-dimensional data page is shown by the spatial light modulator (SLM). Bright and dark spots of the SLM pixel array correspond to black and white modules of the two-dimensional matrix barcode, resulting in SLM forming a binary image. The beam through the SLM is modulated, and then interferes with the reference beam to form a hologram in the material.

The experimental arrangement used for digital hologram storage is shown in Fig. 7, which is a typical Fourier holographic storage setup. A continuous wave (CW) Ar-ion laser operating at a wavelength of 514.5 nm is used for hologram recording and reconstruction. An SLM with 1024×768 pixels and pixel size 26 μm×24 μm is located in the front focal plane of the Fourier lens (L_3).

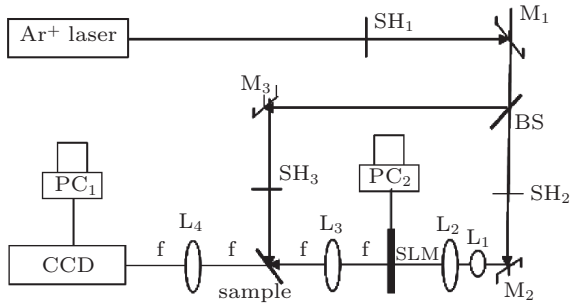


Fig. 7. Setup of digital data holographic storage. L_1 and L_2: lenses; L_3 and L_4: Fourier lenses; f: lenses focus; SLM: spatial light modulator; CCD: charge couple pickup camera.

The experimental results are shown in Fig. 8. Figure 8(a) shows the MATLAB encoded origin object that is loaded into the SLM. Figure 8(b) shows the CCD recorded object image. Figure 8(c) exhibits a reconstruction image. It can be seen that the reconstructed image has a good contrast between bright and dark pixels. Figures 8(d) and 8(e) show the grey-scale distributions along the horizontal and vertical directions of an arbitrary point of Fig. 8(b). Figures 8(f) and 8(g) display the grey-scale distributions along the horizontal and vertical directions of the point of Fig. 8(c), corresponding to the said point in Fig. 8(b). From these images, we can see that the pixel intensity distributions of the reconstructed image and the original image have good correspondence; comparing with our previous work,[26,27] we can see clearly the reconstructed image of the TiO_2-nanoparticles-dispersed photopolymer composite system, therefore, the reconstructed data page has a good fidelity.

All of the results demonstrate that the TiO_2-nanoparticle dispersed acrylamide-based photopolymer material is suitable for digital holographic storage and the doping of nanoparticles into the photopolymers can improve the holographic performance to some extent.

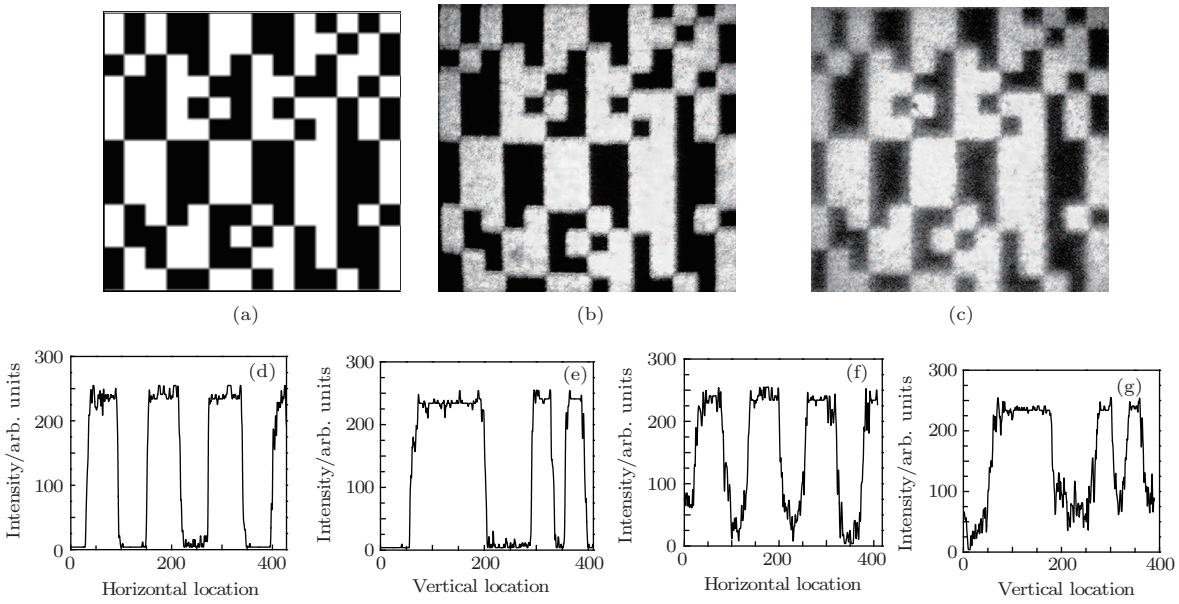


Fig. 8. Results of digital data holographic storage.

4. Conclusions

In this paper, we demonstrate permanent holographic storage with high diffraction efficiency in TiO_2-nanoparticle-dispersed PVA/AA photopolymer films. The experimental results indicate that diffraction efficiencies of the photopolymer films embedded with TiO_2-nanoparticles are remarkably enhanced in comparison with those of the traditional photopolymer films. It is found that there exists the optimum concentration of TiO_2-nanoparticles at which the diffraction efficiency can reach 92.3% and the maximum Δn can attain to 2.093×10^{-3}. We use a square-wave particle distribution function to provide the evidence that the light induces a redistribution of nanoparticles within the volume of the photopolymer layer. It is also found that the shrinkage fractions of the undoped sample and doped nanoparticles sample are 3.22% and 0.80% respectively. The results indicate that it is a good way of suppressing the polymerization shrinkage in PVA/AA photopolymer films doped with TiO_2-nanoparticles. Two-dimensional digital data pages modulated by SLM are stored in the sample S4 with a high fidelity. These results suggest that TiO_2-nanoparticles are also the promising candidates for an inorganic guest in nanoparticle-dispersed PVA/AA pho-

topolymer systems. This work implies that the dispersing of hydrophilic TiO_2-nanoparticles into the PVA/AA photopolymer system should be a simple and promising route to the enhancement of the diffraction efficiency of photopolymer and the suppression of the polymerization shrinkage as a recording medium for high-density data storage device.

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