

Holographic assembly of nanoparticles in photopolymers for photonic applications

Yasuo Tomita

Manipulating nanoparticles dispersed in a photopolymer syrup proves a versatile method of fabricating high-performance holographic data storage media.

Holographic dry photopolymers have received much attention owing to their possible applications in diffractive optics, information storage and displays, and optical communications. These materials have many advantages over other conventional holographic recording media, such as self-developing capability and shape flexibility, as well as low cost and easy, large-area processability.^{1,2} Holographic dry photopolymers are practical for data storage applications if both large refractive index modulation (Δn) and high dimensional stability are obtainable.³ But simultaneously satisfying both requirements is considered difficult in conventional all-organic photopolymers owing to the limited refractive-index range of organic materials.

We have developed a method for holographic manipulation of nanoparticle assemblies in a photopolymer syrup and proposed its use in developing photonic applications.⁴⁻⁶ Because inorganic materials possess a wide variety of refractive indices, the use of inorganic nanoparticles as an optically mobile component in a photopolymer syrup offers the opportunity to obtain much larger Δn compared with conventional all-organic photopolymers. The inclusion of nanoparticles also results in substantial suppression of polymerization shrinkage, giving high dimensional stability as well.

Suppose that nanoparticles are uniformly dispersed in optically reactive liquid monomer, as shown in Figure 1(a). Spatially nonuniform illumination produces free radicals by dissociation of initiators. Subsequent reaction of free radicals with monomer molecules leads to chain polymerization of individual monomers in the bright regions. This polymerization process lowers the chemical potential of monomers in these regions, leading to their migration (diffusion) from the dark to

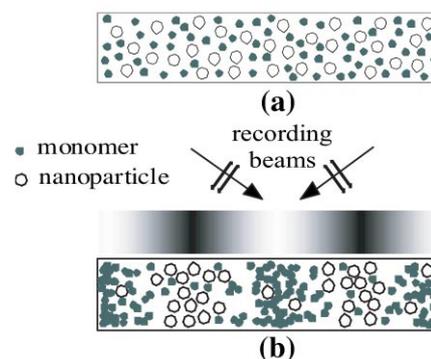


Figure 1. The distribution of constituents (monomer molecules and nanoparticles) both (a) before and (b) during holographic exposure.

the bright regions. In contrast, photo-insensitive nanoparticles, which are not consumed, undergo counter-diffusion from the bright to the dark regions, and their chemical potential increases in the bright regions due to consumption of the monomer. This polymerization-driven mutual diffusion process (i.e., phase separation) essentially continues until photopolymerization is complete. In this way, periodic assembly of nanoparticles under holographic exposure is accomplished—see Figure 1(b)—and as a result a refractive index grating is created owing to the compositional and density difference between the bright and the dark regions.

Figure 2(a) shows a transmission electron microscope (TEM) image of periodically assembled SiO₂ nanoparticles (dark portions) in a SiO₂ nanoparticle-dispersed methacrylate photopolymer hologram that was recorded at a grating spacing of 1 μ m.⁶ The similarity of the hologram's surface corrugation to the interference-fringe pattern was also observed by an atomic force microscope (AFM), but its height was only a few nanometers. Figure 2(b) shows electron probe microanalyzer (EPMA) im-

Continued on next page

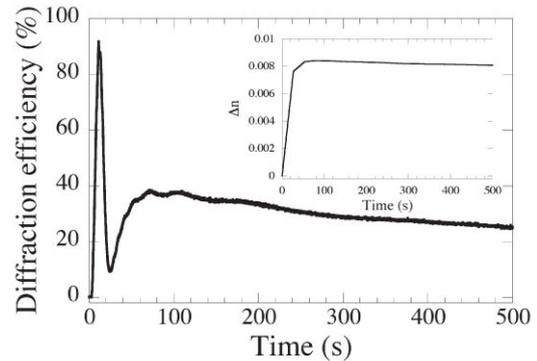
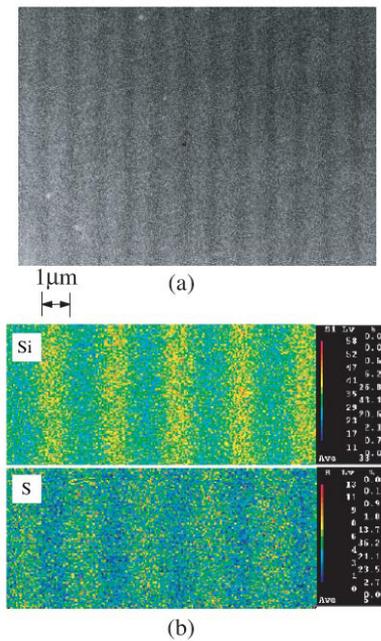


Figure 3. The graph presents recording dynamics of the diffraction efficiency for a 90 μm -thick SiO_2 nanoparticle-dispersed photopolymer film. Shown in the inset is the corresponding Δn as a function of exposure time.

Figure 2. (a) This transmission electron microscope image shows a cross-section of a hologram recorded by two mutually coherent beams at a grating spacing of 1 μm . (b) The electron probe microanalyzer images are of Si and S atom distributions in a hologram recorded at a grating spacing of 2 μm .

ages of the constituents (Si and S atoms) in a SiO_2 nanoparticle-dispersed methacrylate photopolymer hologram recorded at a grating spacing of 2 μm .⁷ Note that the methacrylate monomer contains S atoms in its chemical structure, and that the periodic distributions of Si and S atoms are out of phase. Since the concentration of the formed polymer is highest in the bright regions, the result shown in Figure 2(b) indicates that monomer molecules (SiO_2 nanoparticles) diffuse from the dark (bright) to the bright (dark) regions during holographic exposure. This 180° phase shift was also ascertained using our real-time optical technique.⁸ The results shown in Figures 2(a) and (b), together with the AFM measurement, clarify the microscopic mass transport process of monomer molecules and nanoparticles in polymerizable soft matter and suggest its application to holographic single-step fabrication of one- or multidimensional structures.

Figure 3 shows the recording dynamics of diffraction efficiency (defined as the ratio of first-order diffracted signal power to incident beam power) and Δn for a SiO_2 nanoparticle-dispersed photopolymer film of 90 μm thickness.⁵ SiO_2 nanoparticles of 34vol.% with an average diameter of 13nm were uniformly dispersed in the film before exposure. The slight deviation of the diffraction efficiency from 100% resulted from scattering loss of ~2%. The recorded hologram clearly shows over-

modulation, and the saturated value for Δn remains as large as 8×10^{-3} . Also, ~60% reduction in polymerization shrinkage was achieved by nanoparticle dispersion.

In summary, we have developed nanoparticle-dispersed photopolymers that can record high-contrast holograms with considerable suppression of polymerization shrinkage using the holographic nanoparticle assembly technique. The demonstrated capability of all-optical single-step processing can also be applied to fabricating multidimensional photonic crystal structures. Nanoparticles have unique optical and chemical properties, and our results present new possibilities for developing novel multifunctional holographic devices and sensors.

The author would like to acknowledge contributions by N. Suzuki, K. Furushima, and Y. Endoh of the University of Electro-Communications, and by K. Chikama and K. Odoi of Nissan Chemical Industries Ltd. This work was supported by the 21st Century Center of Excellence (COE) program funded by the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Author Information

Yasuo Tomita

Department of Electronics Engineering
University of Electro-Communications
Tokyo, Japan
<http://talbot.ee.uec.ac.jp/>

Yasuo Tomita is professor of electronics engineering at the University of Electro-Communications, Tokyo. He received his PhD

Continued on next page



in electrical engineering at the California Institute of Technology. His current research interests include organic, nonlinear, and nanophotonics. In addition, he has authored and presented several contributed and invited papers at SPIE conferences.

References

1. R. A. Lessard and G. Manivannan, *Holographic recording materials: an overview*, **Proc. SPIE** **2405**, pp. 2–23, 1995.
2. T. J. Trout, J. J. Schmieg, W. J. Gambogi, and A. M. Weber, *Optical photopolymers: design and applications*, **Adv. Mater.** **10** (15), pp. 1219–1224, 1998.
3. V. Barachevskii, *Photopolymerizable recording media for three-dimensional holographic optical memory*, **High Energy Chem.** **40** (3), pp. 165–176, 2006.
4. N. Suzuki, Y. Tomita, and T. Kojima, *Holographic recording in TiO₂ nanoparticle-dispersed methacrylate photopolymer films*, **Appl. Phys. Lett.** **81** (22), pp. 4121–4123, 2002.
5. N. Suzuki and Y. Tomita, *Silica-nanoparticle-dispersed methacrylate photopolymers with net diffraction efficiency near 100%*, **Appl. Opt.** **43** (10), pp. 2125–2129, 2004.
6. Y. Tomita, N. Suzuki, and K. Chikama, *Holographic manipulation of nanoparticle distribution morphology in nanoparticle-dispersed photopolymers*, **Opt. Lett.** **30** (8), pp. 839–841, 2005.
7. Y. Tomita, K. Chikama, Y. Nohara, N. Suzuki, K. Furushima, and Y. Endoh, *Two-dimensional imaging of atomic distribution morphology created by holographically induced mass transfer of monomer molecules and nanoparticles in a silica-nanoparticle-dispersed photopolymer film*, **Opt. Lett.** **31** (10), pp. 1402–1404, 2006.
8. N. Suzuki and Y. Tomita, *Real-time phase-shift measurement during formation of a volume holographic grating in nanoparticle-dispersed photopolymers*, **Appl. Phys. Lett.** **88** (1), pp. 011105–1–011105–3, 2006.