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Effect of lanthanoid organometallic compounds on holographic storage characteristics of doped PQ/poly(hydroxyethyl methacrylate-co-methyl methacrylate) hybrids

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Abstract
In this research, we fabricate and characterize lanthanide organometallic compounds and 9,10-phenanthrenequinone (PQ) co-doped poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) photopolymers for holographic recording. Five different lanthanoid (Ce³⁺, Nd³⁺, Er³⁺, Yb³⁺ and Lu³⁺) organometallic compounds, one at a time, is co-doped with PQ in a poly(HEMA-co-MMA) matrix, respectively. Holographic experiments demonstrate that lutetium organometallic compounds and a PQ co-doped poly(HEMA-co-MMA) photopolymer can greatly enhance the volume holographic characteristics. The degree of improvement in hologram diffraction efficiency and the recording dynamic range for these co-doped photopolymers follows the order: Lu³⁺ > Yb³⁺ > Er³⁺ > Nd³⁺ > Ce³⁺.

Keywords: organometallic compounds, photopolymer, diffraction efficiency, exposure energy, volume holographic data storage, phenanthrenequinone

1. Introduction
Recoding media have been a key issue in realizing holographic data storage. Among different materials [1–5], the photopolymer has been considered as a promising medium due to several advantages, such as it being easy to modify the compositions, cheap, simple fabrication and large refractive index change. Several techniques have been developed for fabricating high quality photopolymers for holographic recording. Aromatic monomers that contain heavy atoms [6, 7], or mixing monomers [8, 9] with different functionalities, have been used to enhance the refractive index change. Photosensitizers with different kinds of additives, N-methyldiethanolamine [10, 11] and diphenyliodonium salt [12–14], have been used to improve the holographic recording sensitivity. Different matrices such as epoxy [15–18] and sol–gel [19–21], or photopolymer components mixed with a cross-linking monomer [8, 14], have...
been utilized to reduce the shrinkage effect in the recording process. In addition, to improve the sensitivity, radical and cationic photopolymerization with different additives and photosensitizers has been applied to speed up the photoinitiation process, such as sol–gel [19, 20] and two-step thermo-polymerization [22–25]. Neutral components such as bromonaphthalene [3], liquid crystals [4, 5, 26, 27] or nanoparticles [28–31] are introduced into the photopolymer to enhance the diffraction efficiency. This research is aimed at developing a material with large refractive index change, high sensitivity and good dimensional stability.

Recently, doping organometallic compounds [23, 32, 33] has been an attractive method for improving the holographic recording characteristics of photopolymers. Through the photocatalytic reaction between metal ions and ligands [34, 35], organometalic compounds have been applied widely for chemical reaction catalysts [36, 37], nanoparticle syntheses [38–40] and organic syntheses [41–44]. In our previous research, the holographic recording characteristics of the PQ/PMMA photopolymer have been enhanced by co-doping organometallic compounds, zinc methacrylate [23], through the reaction between the metal ion and carbonyl functional groups in PQ molecules [25].

In the PQ/PMMA photopolymer, the PQ molecules react with the residual MMA monomers to form a one-to-one oligomer in the light illuminated region. As a result, the refractive index in the bright region is different from that of the dark region, so the phase grating can be formed in the material. The recording mechanism is that, under light exposure, the PQ molecules absorb photon energy to form a photo-excited triplet state. The excited PQ molecules further form radicals by receiving a hydrogen atom from the residual MMA monomers to form the one-to-one photoproduct of the phase grating. This process is achieved through the electron and the following proton transfers.

Research on the photoreaction between PQ and metal ions indicate that the metal ions, acting as Lewis acids in co-doped organometallics, can be used to accelerate the electron transfer reaction processes [25]. Organometallic compounds with high Lewis acidities can easily react with imine or carbonyl functionalities in organic compounds. In other words, co-doping organometallic components into quinone-based dye-doped photopolymers will provide a means to enhance the photoreaction rate upon light exposure.

In this research, we improve the holographic characteristics of the PQ/HEMA-co-MMA) photopolymer through co-doping of the lanthanoid compounds. Five different lanthanoid (Ce³⁺, Nd³⁺, Er³⁺, Yb³⁺ and Lu³⁺) organometallic compounds have been co-doped with PQ with five different photopolymers. Holographic characteristics, including the recording sensitivity and dynamic range, are experimentally characterized.

2. Experiments

2.1. Material preparation

HEMA and MMA, used as the monomers, were purchased from the Showa Chemical Company and the Acros Company, respectively. The monomers were purified through distillation under low pressure and then stored in a refrigerator before use. 2,2-azobis-isobutynitrile(AIBN), used as the thermo-initiator and purchased from the Tokyo Chemical Industry(TCI), was purified by recrystallization. The photosensitizer, PQ, was purchased from TCI and used as received. The lanthanoid organometallic compounds, lutetium(III) acetate hydrate (99.9%) [Lu(ac)₃], ytterbium (III) acetate tetrahydrate (99%) [Yb(ac)₃], erbium (III) acetate tetrahydrate (99%) [Er(ac)₃], neodymium (III) acetate hydrate (99.9%) [Nd(ac)₃], and cerium (III) acetate hydrate (99.9%) [Ce(ac)₃] were purchased from the Sigma-Aldrich Company. All the lanthanoid organometallic compounds were used as received. Figure 1 shows the chemical structures of all compounds.

2.2. Fabrication of photopolymer samples

The monomers MMA and HEMA were first mixed with a weight ratio of 9:1. which is because the lanthanoid organometallic compounds have better solubility in HEMA than MMA monomers. We introduce HEMA monomers into our system to increase the dissolved concentration of the lanthanoid organometallic compounds. In order to study the effect of doping lanthanoid organometallic compounds, molar concentrations of the solutes were kept identical when making the samples. The lanthanoid organometallic compound of 3.6 × 10⁻³ mol% was added to the mixed co-monomer solvent.
The PQ with 0.36 mol% was dissolved in the solution. Finally, the AIBN with 0.65 mol% was added and stirred under room temperature until the solute dispersed and mixed uniformly. A filter with a hole size of 0.2 μm was used to further filter out impurities from the solution. The modified two-stage thermopolymerization was then used to fabricate the photopolymer. In the first stage, the mixed solution was stirred at 35 °C for 12 h until it became homogeneously viscous. Then, it was poured into a glass cell with the dimensions 10 cm × 10 cm × 2 mm. In the second stage, the whole set was baked at 45 °C for 3 days until most of the monomer MMA and HEMA were polymerized. All samples were prepared in a dark environment. The 2 mm photopolymer bulk with good optical properties can be prepared by this approach.

2.3. Set-up for holographic recording measurements

An optical set-up for typical non-degenerate four-wave mixing, as shown in figure 2, has been constructed to measure the holographic characteristics of the samples. A diode laser-pumped solid-state laser model Verdi-10 purchased from Coherent Company is used as the light source. The collimated light at 532 nm was split into two beams with an intensity ratio 1:1. They were incident on the sample symmetrically with an intersection angle of 30° outside the sample. By using a shutter to block one of the writing beams at constant time intervals, the intensity of the diffracted light can be measured. The diffraction efficiency is defined as the ratio of the intensity of the diffracted beam to that of the sum of the diffracted and transmitted beams. We used a peristrophic multiplexing technique to measure the thickness of the photopolymer samples was 2 mm. The intensity of each laser beam used to record a single hologram was 7 mW cm−2 and the dynamic range was 40 mW cm−2.

Figure 2. Optical set-ups for measuring volume holographic data recording characteristics. (This figure is in colour only in the electronic version)

Figure 3. UV–vis absorption spectra of lanthanoid organometallic compounds and PQ co-doped poly(HEMA-co-MMA) photopolymer with different lanthanide elements under different exposure states.

3. Characterization of photopolymer

3.1. UV–vis spectroscopy measurement

We measured the optical absorption spectrum of the lanthanoid organometallic and PQ co-doped photopolymer. The UV–vis–NIR spectrophotometer UV3600 from Shimadzu Co. was used for this purpose. Typical optical absorption spectra of our samples before and after optical exposure under green light (532 nm) are shown in figure 3. It can be seen that, before exposure, all samples with co-doped lanthanoid organometallic compounds demonstrated identical absorption to that of the PQ singly doped sample. The samples
are totally transparent for wavelengths longer than 540 nm. Adding lanthanoid organometallic compounds does not vary the absorption behaviour in this regime. The results imply that PQ acts as a single photosensitizer in the lanthanoid organometallic co-doped photopolymer and the PQ singly doped photopolymer.

On the other hand, the absorption spectra of the after-exposure samples show much less absorption from 390 to 540 nm. These samples are totally transparent for wavelengths longer than 500 nm. Most parts of the absorption curves are overlapped, except that there is a slight difference from 400 to 475 nm. Comparing with that of a PQ singly doped photopolymer, the absorption band shows a blueshift for the lanthanoid organometallic co-doped photopolymer samples. This implies that the structures of the co-doped photoproducts are less conjugated than that of the PQ singly doped ones. This may result in a larger refractive index change induced by optical exposure. Thus, the lanthanoid organometallic co-doped photopolymers show high potentiality for recording stronger phase gratings.

3.2. Single-hologram recording characteristics

We recorded a single hologram in the photopolymer. Then, the diffraction efficiency was measured. The results are shown in figure 4. It is seen that the diffraction efficiency of all the samples first reaches a maximum, and then it drops with further exposure. It can be seen that the maximal diffraction efficiency of the lanthanoid organometallic compound co-doped photopolymer follows the order as Lu(ac)₃ > Yb(ac)₃ > Er(ac)₃ > Nd(ac)₃ > Ce(ac)₃. This trend corresponds to the decrease of the atomic number and the increase of the ionic radius according to the periodic table. Among them, it is seen that the maximal diffraction efficiencies for the co-doped samples of Lu(ac)₃, Yb(ac)₃ and Er(ac)₃ are 98.30%, 74.76% and 61.31%, respectively. Comparing this to 28.81% for the PQ singly doped sample, the diffraction efficiency of co-doped Lu(ac)₃ has been improved by more than three times. However, the maximal diffraction efficiencies of Nd(ac)₃ and Ce(ac)₃ co-doped samples are 23.12% and 22.70%, respectively, which are smaller than that of the PQ singly doped photopolymer.

Figure 4 can be used to estimate the exposure energy that is required to reach 10% diffraction efficiency. Less exposure energy means the sample is more sensitive in holographic recording. We find that the samples with co-doped Lu(ac)₃, Yb(ac)₃ and Er(ac)₃ are more sensitive than the PQ singly doped photopolymer, but the situation is reversed in the cases with co-doped Nd(ac)₃ and Ce(ac)₃. The best result is obtained for the Lu(ac)₃ co-doped photopolymer, for which the required energy is 26.7 J cm⁻², which is about less than half that of the PQ singly doped photopolymer.

3.3. Multiple-hologram recording characteristics

The characteristics of multiple-hologram recording, including dynamic range and sensitivity, can be measured by the use of the peristrophic multiplexing technique. Dynamic range, or M# [45–47], can be obtained from the saturation value of the cumulative grating strength, \( C(E) = \sum_{i=1}^{n} \eta_i \), where \( \eta_i \) is the diffraction efficiency of each hologram and \( n \) is the total number of holograms that have been recorded for a total exposure energy of \( E \) J cm⁻². Through the curve fitting, \( C(E) = C_{sat}[1 - \exp(-E/E_r)] \), the saturation value \( C_{sat} \) and \( E_r \), the exposure energy constant, respectively, can be calculated. Then, the material sensitivity \( S \), which represents an increment in cumulative grating strength with respect to the amount of exposure energy, can be approximated by \( S = C_{sat}/E_r = M#/E_r \).

In the experiment, 190 plane-wave holograms were recorded at a single location and each hologram was recorded with an exposure energy of 5.66 J cm⁻². The running curves for the cumulative grating strength of the samples are shown in figure 5. From figure 5, \( M# \) and sensitivity are calculated, as listed in table 1. We see that the \( M# \) of samples with co-doped Lu(ac)₃, Yb(ac)₃ and Er(ac)₃ are higher than that of the PQ singly doped photopolymer. The best result was obtained by co-doping Lu(ac)₃, which has been improved by around two times, from 1.87 to 3.86. Again, the magnitude of \( M# \) follows the order Lu(ac)₃ > Yb(ac)₃ > Er(ac)₃ > Nd(ac)₃ > Ce(ac)₃.

Table 1 also shows the sensitivity of the samples. It is seen that the sensitivity of the co-doped Lu(ac)₃ and Yb(ac)₃...
photopolymers are 0.0273 cm$^2$ J$^{-1}$ and 0.0296 cm$^2$ J$^{-1}$, respectively. Comparing to that of the PQ singly doped photopolymer, the sensitivity has been improved by 1.5 times. However, the sensitivity is much smaller for the photopolymer, the sensitivity has been improved by 1.5 times to 0.0296 cm$^2$ J$^{-1}$. These results suggest that adding lanthanoid organometallic molecules with large atomic number of the lanthanoid into a PQ doped P(HEMA-co-MMA) photopolymer system could be an effective way to improve the holographic recording material for volume data storage.

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