True-color reflection holograms recorded in a single-layer panchromatic dichromated gelatin material

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ABSTRACT

By employing new types of multi-color photosensitizers and photochemical promoters to photo-crosslinking gelatin system, a high-quality single-layer panchromatic dichromated gelatin material is achieved for color holography. Some preliminary results of spectral response, photosensitivity, and spectral selectivity are reported in this paper. Using red, green and blue lasers, namely three primary colors, the bright volume transmission and reflection holograms can be recorded successfully on the panchromatic material at the exposure level of 30 mJ/cm^2. It can be expected to have practical applications in the fields of true-color display holography, wavelength multiplexing holographic storage, and holographic optical elements.

Keywords: color holography, reflection hologram, holographic recording material, panchromatic dichromated gelatin

1. INTRODUCTION

Three-dimensional true-color holographic images have important applications in visual representation of artworks, industrial products, museum items, medical images, etc. High-quality panchromatic holographic recording material is the prerequisite factor for the successful recording of true-color hologram and has been a long and diligent research goal all along of display holographers and researchers. An ideal holographic recording material is required to have high diffraction efficiency, high photosensitivity, high spatial resolution and signal-to-noise ratio, etc. After many years of practical research, much progress has been made and Slavich single-layer fine-grain silver-halide emulsion [1,2,3] and Du Pont photopolymers [4,5] have been successfully developed for color hologram recording. However, the research outcomes of color holography based on dichromated gelatin material are still infrequent and very limited. In 1986, Toshihiro Kubota produced sandwich color holograms by using dichromated gelatin plate for the recording of green (514.5nm) and blue (488nm) components [6], and Agfa 8E75 plate for the red (632.8nm) component of the image, but the dichromated gelatin material itself is not a panchromatic recording material. Recently, by controlling the concentrations of sensitizers and the moisture and PH value of photosensitive layer, Kazumasa Kurokawa prepared a methylene-blue-sensitized dichromated gelatin for recording full-color holograms [7], but the finally red photosensitivity is only 600 mJ/cm2 for 647.1nm. Besides, the compatibility of red sensitizer methylene-blue (MB) and green-blue sensitizer ammonium dichromate (ADC) is not so good, MB is liable to separate out from the solution in an acidic state, and ADC will have low sensitivity in an alkaline state.

In this paper, based on the further study on the imaging mechanism of dye-sensitized dichromated gelatin, we develop a new single-layer panchromatic gelatin material by introducing efficient photosensitive dyes and photochemical promotors to the photo-crosslinking gelatin system. It has high diffraction efficiency, high spatial resolution, and high photosensitivity for three-primary-color laser lines and high-quality true-color reflection holograms are successfully recorded in our laboratory.

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2. PREPARATION OF PANCHROMATIC GELATIN HOLOGRAPHIC MATERIAL

Basically the photosensitive layer of our single-layer panchromatic gelatin consists of French inert gelatin as polymer binder and active reactant, methylene-blue as red sensitizer, Rhodamine 6G (R6G) as green and blue sensitizer, potassium chromate as cross-linker, 1,1,3,3-tetramethylguanidine (TMG) as electron donor, and other chemical additives. The primary procedures for preparing the photosensitive film are outlined in Table 1. MB and R6G dyes distribute well in photosensitive solution in an alkaline state, and the dried photosensitive layer shows a uniform color of light purple. The postprocessing procedure is given in Table 2 for fixing the latent image after holographic exposure.

Table 1. Procedure for making the photosensitive layer of panchromatic gelatin material

Step	Description	Temperature (°C)	Time
(1)	Sock 2g of French inert gelatin in 40ml deionized water	25	12 hours
(2)	Heat the suspension in a thermostatic water bath to about 45 °C, then keep the temperature and stir the mixed solution slowly	45	15 minutes
(3)	Add 2.5ml of 0.5% potassium chromate solution while stirring	45	2 minutes
(4)	Add 0.6ml of 25% TMG solution while stirring	45	2 minutes
(5)	Adjust the PH value to 9.18 with TMG or acetic acid solution	45	2 minutes
(6)	Add 0.3ml of 0.4% MB solution to the suspension while stirring	45	5 minutes
	Add 0.3ml of 0.2% R6G solution to the suspension while stirring	45	5 minutes
(7)	Pipette out 8 ml of the mixed solution and spread it over $8\times24cm^2$		
(8)	leveled optical glass, keep it in dark and dry in horizontal position	25	24 hours

Table 2. The postprocessing procedure of panchromatic gelatin hologram

Step	Description	Temperature (°C)	Time
(a)	Sock in F5 solution	25	1 minute
(b)	Wash holographic plate in running water	25	30 seconds
(c)	Swell holographic plate in warm water	31	1.5 minutes
(d)	Dehydrate in 60% isopropyl alcohol bath	25	1 minute
(e)	Dehydrate in 90% isopropyl alcohol bath	25	1 minute
(f)	Dehydrate in 100% isopropyl alcohol bath	25	2 minutes
(g)	Dry hologram rapidly with flowing hot air	–	–

The achievable diffraction efficiencies of transmission and reflection gelatin holograms highly linked to the volume effects of the photosensitive layer. According to Kogelnik's coupled-wave theory [8], a Q factor can be employed to evaluate the volume effect of a thick hologram. The expression is:

$$Q = 2\pi\lambda_0 t / n_0 d^2 \qquad (1)$$

Where λ_o is the playback wavelength, t the thickness of photosensitive layer, n_o the average refractive index, d the period of recorded grating. When Q factor is much bigger than 1, the grating exhibits strong volume effect, and the diffraction efficiency of a lossless transmission grating at Bragg's condition is:

$$\eta_t = \sin^2(\nu), \quad \nu = \pi\Delta nt / \lambda\cos(B) \qquad (2)$$

While the diffraction efficiency of a lossless reflection grating at Bragg's condition is:

$$\eta_r = th^2(\nu'), \quad \nu' = \pi\Delta nt / \lambda\sin(B) \qquad (3)$$

Where the parameter ν denotes the effective optical thickness of the hologram, Δn is the modulation of refractive index, t the thickness of hologram, λ the playback wavelength, *B* the angle of incidence with respect to the plane of the fringes of the hologram in the photosensitive layer. The theoretical diffraction efficiency can be as high as 100% if the parameter Δn and t are chosen properly. If we choose t as 15 μm, n_o as 1.45, d as 0.625μm, the calculated Q factors of our panchromatic gelatin layer are about 105, 85 and 81 for usually used laser lines of 633nm, 514.5nm and 488nm, respectively. They all perfectly fulfill the evaluation criterion of volume effect, and high diffraction efficiencies can be achieved on our panchromatic gelatin material.

3. IMPROVEMENT IN SPECTRAL RESPONSE AND PHOTOSENSITIVITY

In our photochemical recipe, the conventional green-blue sensitizer ADC, which is used almost in all dichromated gelatin materials, is replaced with a new water-soluble dye Rhodamine 6G to achieve the green-blue photosensitivity. Rhodamine 6G has relatively wide sensitivity within the green-blue light region, and moreover it has good compatibility with red sensitizer MB and other chemical reagents in our photosensitive layer. Fig.1 gives the spectral absorbance curves of an ordinary red-sensitive gelatin and our panchromatic gelatin, which are recorded with a high-resolution SHIMADZU UV-Vis recording spectrometer (model UV-2100). It can be seen that the spectral absorbance of red-sensitive gelatin (the dashed line in Fig. 1) is mainly located within red region, which is due to the light sensitivity of

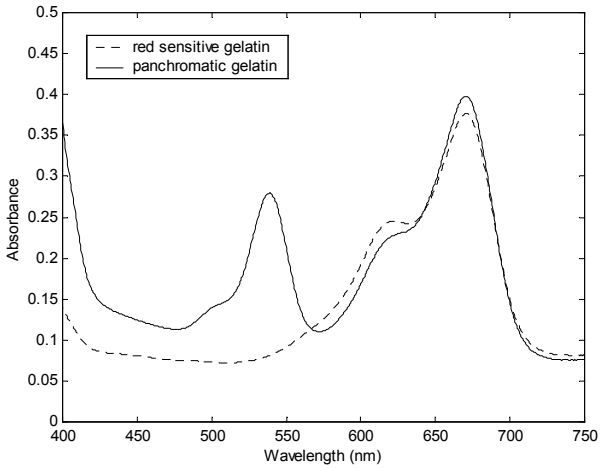

Fig. 1 The spectral absorbance of a red-sensitive gelatin and our panchromatic gelatin

MB dye [9]. After the introduction of Rhodamine 6G dye, the spectral absorbance of panchromatic gelatin (the solid line in Fig. 1) has additionally strong absorption band in the green-blue region of the visible spectrum. The suitable laser lines for color recording are 633nm from He-Ne laser or 647.1nm from Kr-ion laser as red component, 514.5nm from Ar-ion lasser or 532nm from CW frequency-doubled Nd:YAG laser as green component, 488nm from Ar-ion laser or 442nm from He-Cd laser as blue component.

Another chemical reagent, low-concentration potassium chromate, is employed in our photosensitive layer as crosslinking reagent upon radiation. Under the radiation of related laser line (i.e., red laser for MB, green & blue lasers for R6G), the photochemical reactions of MB and R6G molecules are both photobleaching reactions, which cause a color change of the sample from blue (the color of MB) and orange (R6G) to colorless [10,11]. So the photochemical reactions of our panchromatic gelatin material can be proposed as follows [11,12]:

$$\text{dye} + h\nu \rightarrow \text{excited dye} \quad (1)$$

$$\text{excited dye} + e \rightarrow \text{leuco dye} \quad (2)$$

$$\text{leuco dye} + Cr^{6+} \rightarrow \text{dye} + Cr^{3+} \quad (3)$$

$$Cr^{3+} + \text{gelatin} \rightarrow Cr^{3+}\text{–gelatin (cross-linking complex)} \quad (4)$$

When the dye (e.g. MB) is irradiated with specific monochromatic laser line, its molecule absorbs a photon and passes to the excited state, where the dye is reduced to its leuco (colorless) form by absorbing an electron from the surrounding medium. The leuco dye acts as an active reducing agent, it reacts with Cr^{6+} in the potassium chromate, then Cr^{6+} is reduced to Cr^{3+}, while the dye returns to its unexcited state. Cr^{3+} reacts with adjacent gelatin molecules to form a cross-linking complex and increases the refractive index of the exposed gelatin, finally the volume phase hologram based on the modulation of refractive index is produced after proper postprocessing procedures.

From the photochemical reactions, we can also find that the reduction process of Cr^{6+} is dependent on the electron-capturing capacity of excited dye from neighbor reagents. In order to accelerate the photochemical reaction, a chemical reagent 1,1,3,3-tetramethylguanidine (TMG), which is firstly proposed by Jeff Blyth [13], is employed in our photosensitive layer as a photochemical promoter. TMG has four methyl groups which can donate additional electrons, and the resonating structure of guanidine allows easier electron donation than other types of electron donors [13]. The introduction of TMG as a strong electron donor can efficiently improve the photoreduction speed of chromium ion and the sensitivity of our photosensitive system.

The experimentally optimum concentrations of the photosensitive solution are 5×10-2 (w/v) gelatin, 3×10-5 (w/v) MB, 2×10-5 (w/v) R6G, 3.1×10-4 (w/v) potassium chromate, and 3.1×10-3 (v/v) TMG. The relationship curve between the diffraction efficiency of holographic transmission grating and the exposure of different recording laser line is shown in Fig. 2. The spatial frequencies of all the recorded gratings are controlled to about 1600 lines/mm for the purpose of comparison, and the diffraction efficiency is defined as the first-order light intensity divided by the incident light intensity. From Fig. 2, we can find that high diffraction efficiencies can be achieved for all the four used laser lines, and the exposure required to obtain a diffraction efficiency of 80% is about 35 mJ/cm^2 for 633nm He-Ne laser, 25 mJ/cm^2 for 488nm Ar-ion laser, 25 mJ/cm^2 for 442nm He-Cd laser, and 15 mJ/cm^2 for 514.5nm Ar-ion laser, respectively. Such a photosensitivity is significantly higher than other red-sensitive dichromated gelatin [10,12] or blue-green-sensitive dichromated gelatin [6,14].

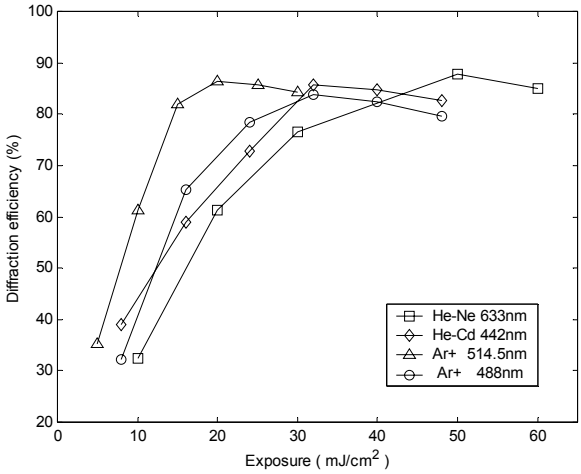

Fig. 2 Diffraction efficiency of volume holographic gratings as a function of exposure for different recording laser lines

3. RECORDING OF COLOR HOLOGRAMS

As we know, all possible colors can be obtained by appropriate mixing of the primary colors, and there are two fundamental ways of mixing colors: the additive method and the subtractive method. In color holography the additive method applies to both transmission and reflection holograms [1]. Usually red green and blue are chosen as three primary colors for the synthesis of color. When the color object is exposed to the primary laser lines, it has different reflectivity for different laser line, then the corresponding red green and blue component holograms are recorded in the panchromatic holographic recording material, respectively. When the color reflection hologram is replayed with white light, the reconstructed three component images are mixed again to represent proper color image of the original object.

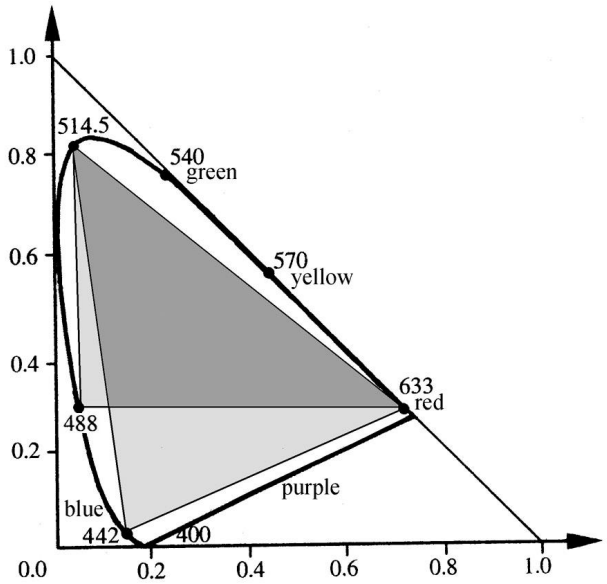

Fig. 3 The schematic chromaticity diagram

In choosing the optimal primary laser lines for color holography, the chromaticity diagram is a useful guide for predicting the colors that can be matched by additive mixing of a set of primary colors. Fig. 3 gives a schematic

illustration of 1931 CIE (Commission Internationale de l'Eclairage) chromaticity diagram. The spectral colors are fully saturated colors, which are located along the periphery of the horseshoe-shaped curve. By mixing different spectral colors, all possible colors can be synthesized, and the points situated inside the horseshoe-shaped curve can be used to represent all the visible colors. After the three primary laser lines are selected, a triangle can be drawn by connecting the three points corresponding to the primary laser wavelengths. The points within the triangle represent all the colors that can be replayed by appropriate mixing of the chosen three primary colors. So it is desirable to select the primary laser lines which can cover as large as possible an area of the chromaticity diagram. For the currently available CW laser lines, 633nm from He-Ne laser, 514.5nm Ar^+ laser and 442nm He-Cd laser can draw a much larger triangle area than 633nm He-Ne laser, 514.5 and 488nm from Ar^+ laser, then the former wavelength combination can be expected to reconstruct more practical colors.

The single-beam Denisyuk-type optical configuration is employed in our experiments for the recording of Lippmann color holograms and a multicolor image can be replayed directly with white-light illumination. The schematic optical setup is shown in Fig. 4. The expanded beam is incident perpendicular to the holographic plate as reference beam, the transmitted beam is reflected back by the object as object beam. The two beams reach the holographic layer from opposite directions and interfere with each other, then the interferograms throughout the volume of the holographic recording layer are recorded to form the reflection hologram. In making the single-line reflection holographic grating, the object is replaced with a plane mirror, and the diverged beam from the spatial filter is collimated with a collimating lens.

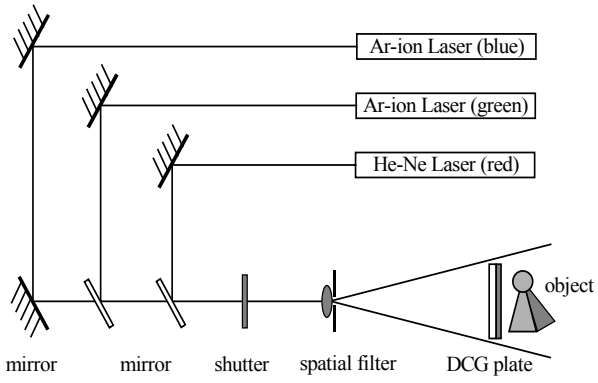

Fig. 4 The optical setup for the recording of color Lippmann holograms

The spectral response curves of reflection gratings can be deduced from transmission spectra recorded with a common UV-visible spectrophotometer. As the transmission spectrum and spectral selectivity curve (diffraction spectrum) are complementary despite the Fresnel reflection at the plate surfaces and the absorption of holographic recording layer, so the spectral selectivity curve can be calculated according to the formula:

$$\eta(\lambda)=100\%-T(\lambda)-R(\lambda)-A(\lambda) \qquad (5)$$

Where $\eta(\lambda)$ is the diffraction efficiency, $T(\lambda)$ the transmittance, $R(\lambda)$ the Fresnel reflection ratio at the plate surfaces, and $A(\lambda)$ the absorption ratio. The typical spectral selectivity curves of reflection gratings recorded in the panchromatic gelatin are given in Fig. 5. The depth of photosensitive layer is about 18μm, the required exposure of single laser beam is 60 mJ/cm^2 for 633nm, 30 mJ/cm^2 for 514.5nm, and 40 mJ/cm^2 for 442nm. For all the three reflection holographic

gratings, the central playback wavelength is very close to the original recording laser wavelength, which shows that our panchromatic gelatin material can replay the natural colors of the objects. The 7×7cm^2 Lippmann color hologram of three-dimensional color ceramic mask is also recorded using the recording scheme in Fig. 4. The 633nm 514.5nm and 488nm from He-Ne and argon-ion lasers are chosen as red, green, and blue recording light sources, and the exposure is performed sequentially, starting from red component, followed by green and blue components. Fig. 6 shows the photograph replayed with white light illumination, high color saturation, low noise, and high diffraction efficiency can be readily achieved in our experiments.

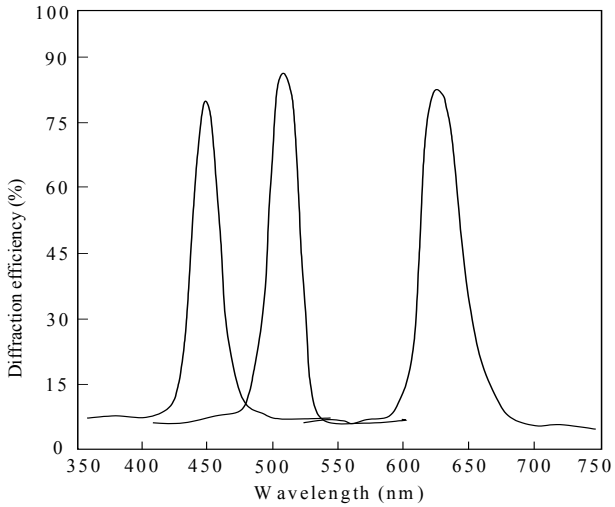

Fig. 5 The spectral selectivity curves of single-line Lippmann holographic gratings

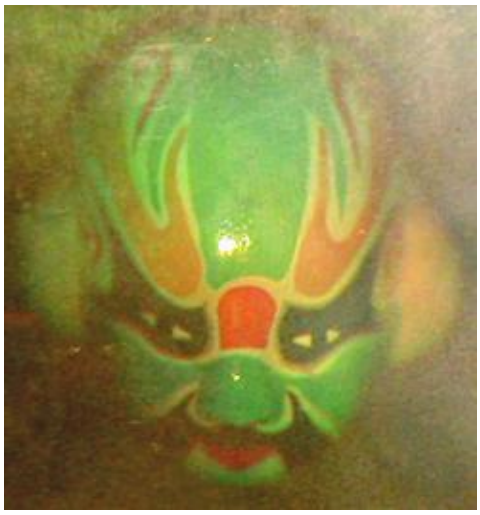

Fig. 6 The photograph of a white-light-illuminated Lippmann color hologram

It should be mentioned that DCG hologram has poor environmental stability. When exposed to ambient environment, the diffraction efficiency of unprotected DCG hologram would decrease very quickly. In order to prevent the degradation of DCG hologram, we developed two kinds of methods to isolate the ambient humidity. One is called physical sealing, which uses polymer coatings or optical epoxy resin to seal hologram physically [15]. The other is called chemical sealing, which employs chemical reagent ninhydrin to react with amino and carboxyl groups, the strong

humidity-adsorbing groups in gelatin and responsible to the environmental instability of DCG holograms, and modify them to hydrophobic aldehyde groups [16]. Both methods can prevent DCG holograms from water vapor damage and obviously improve the stability of diffraction efficiencies.

4. CONCLUSIONS

In this paper, a high-quality single-layer panchromatic dichromated gelatin is presented for the recording of three-dimensional true-color volume holograms. It has wide spectral response within the visible light region, high photosensitivity up to 20 mJ/cm^2 for three-primary-color laser lines, high diffraction efficiency up to 85%, and high spatial resolution up to 4000 lines/mm, etc. The Lippmann color holograms with high color saturation, high brightness and low noise are recorded successfully. We believe that the panchromatic gelatin material can be a new and good candidate for the practical applications of high-quality true-color display holography, holographic anti-counterfeiting, as well as holographic optical elements.

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