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# Diffraction efficiency in reflection holograms stored in photopolymers doped with metallic nanoparticles

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## ABSTRACT

The storing of volume holographic reflection gratings in eco-friendly photopolymers represents a challenge at present since they can be used in many important applications such as sensors and holographic optical elements. The main goal of this work was record unslanted volume holographic reflection gratings in a low toxicity poly(vinyl alcohol)-based photopolymer called Biophotopol. The composition of the photopolymer layers was optimized in a first stage. Subsequently, the holographic material was doped with high refractive index Platinum nanoparticles in order to increase the refractive index modulation during the recording stage. Results obtained were analysed as a function of the Platinum nanoparticles concentration used. Maximum diffraction efficiencies of 28% was reached when a concentration of 0.58 nanomoles of Platinum nanoparticles per gram of poly(vinyl alcohol) was employed.

**Keywords:** Holography, Reflection holograms, Photopolymers, Low toxicity materials, Platinum nanoparticles

## 1. INTRODUCTION

In Holography, there are several types of materials useful for the holographic recording and reconstruction process. The most important characteristics required for a holographic material are, among others, high energy sensitivity and resolution, low production cost, self-healing and low toxicity. Although each type of material has some of these characteristics, there is no single material that satisfies all of them. Therefore, the appropriate material must be chosen according to the application required. Currently, photopolymers are the most relevant holographic materials, as they are the ones that meet most of these characteristics. The interest in storing volume holograms in photopolymers has increased enormously due to their applications in industry, the medical field, security, sensors, or renewable energy. Due to the wide variety of applications in reflection holography, this topic is now more relevant than ever. The interest in reflection holograms has increased in recent years due to the demand for materials with enough resolution for high spatial frequency recordings.

Nowadays, society demands scientific development based on green materials. The production of environmentally compatible photopolymers is one of the main focuses of holography research teams. Many poly(vinyl alcohol)-based photopolymers used to have acrylamide as a monomer. However, due to its toxicity, new photopolymer materials try to substitute this dangerous component for a monomer such as sodium acrylate used in Biophotopol. This material is a low-toxicity poly(vinyl alcohol)-based photopolymer patented by the Holography and Optical Processing Research Group at the University of Alicante.<sup>1</sup> Biophotopol was optimized for the recording of transmission holograms,<sup>2,3</sup> but its response to the recording of reflection holograms is not as good as it could be. One of the most important parameters in the characterization of holograms is the diffraction efficiency ( $DE$ ). Obtaining high values of this parameter is of vital importance in most applications. One way to increase  $DE$

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values is by doping the holographic materials with nanoparticles.<sup>4-7</sup> In this work, we study the response of undoped and doped Biophotopol layers with high refractive index Platinum nanoparticles (Pt NPs). First, the photopolymer layers (PL) were optimized by varying their components to find the highest response in terms of *DE*. Subsequently, these optimized PLs were doped with different concentrations of Pt NPs and their *DEs* were measured.

## 2. HOLOGRAPHIC MATERIAL

Undoped Biophotopol layers with an average refractive index of  $n \sim 1.5$  were obtained from a photopolymer solution. This solution was composed of poly(vinyl alcohol) (PVA) as an inert binder polymer ( $M_w = 130000$ , hydrolysis degree = 87.7%), sodium acrylate (NaOA) as polymerizable monomer, triethanolamine (TEA) as coinitiator and plasticizer, sodium salt 5'-riboflavin monophosphate (RF) as sensitizer dye and *N,N'*-(1,2-dihydroxyethylene) bisacrylamide (DHEBA) as crosslinker. The solvent used was water as all components were soluble. The fabrication process of Biophotopol layers is showed in Fig. 1. The volume of the starting NaOA solution and the DHEBA mass were changed to obtain photopolymer solutions with different mole ratios of these compounds. The moles of the other compounds were kept fixed. The photopolymer solution was manually deposited over levelled thin and flat glass plates ( $n = 1.5255$  at  $\lambda = 589$  nm,  $6.3 \times 6.3$  cm<sup>2</sup>, thickness of 0.55 mm, Marienfeld GmbH & Co. KG, Lauda-Königshofen, Germany) under red light in which the material was not sensitive. The deposited solution was left inside a climatic chamber (Climacell 111, MMM Medcenter Einrichtungen GmbH, Munich, Germany) with controlled conditions ( $60 \pm 5\%$  relative humidity and  $20 \pm 1$  °C). The details of the drying process are described in section 4. A curing time of 6 min was selected for carried out the curing process of the Biophotopol layers after recording process. The physical thickness of the PLs was  $160 \pm 1$  μm.

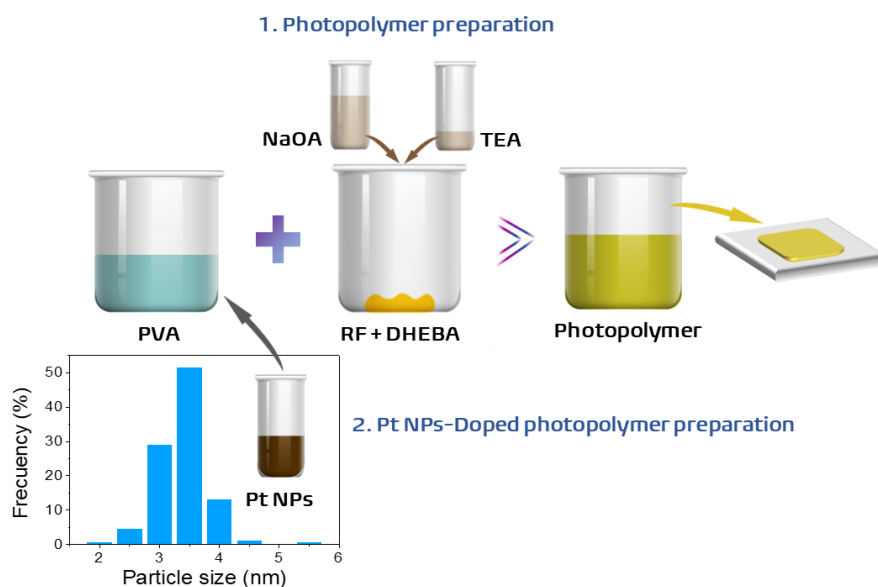


Figure 1: Preparation process of the photopolymer layers and frequency distribution of the size of the Pt NPs.

Pt NPs-doped Biophotopol layers were obtained from the optimized composition of the photopolymer solution. The Pt NPs are introduced into the photopolymer when the PVA solution is prepared. Colloidal quasi spherical Pt NPs was synthesized using a previously described methodology.<sup>8</sup> In brief, a solution containing stridium citrate and the Pt metallic precursor ( $H_2PtCl_6$ ) both at a concentration of  $2.5 \times 10^{-4}$  M was reduced by ice cold and freshly prepared sodium borohydride ( $NaBH_4$ ) solution (0.1 M), with a  $NaBH_4$  to Pt ratio of 6. The  $NaBH_4$  solution was added to the solution under vigorous stirring. The stirring was slowed down after 30 s and the solution was keep unperturbed for the next 30 min. TEM experiments were performed with a JEOL, JEM 2010 microscope working at 200 kV. The sample for TEM analysis was obtained by placing a drop of the dispersed

solution onto a Formvar-covered copper grid and evaporating it in air at room temperature. The diameter size of the NPs (Fig. 1) was estimated to be about  $3.4 \pm 0.4$  nm. All compounds were purchased from Sigma-Aldrich (Madrid, Spain).

### 3. HOLOGRAPHIC REFLECTION SETUP AND MEASUREMENT OF DIFFRACTION EFFICIENCY

Fig. 2 shows the experimental holographic setup used for the recording process of the holographic gratings. A solid-state laser (Genesis CX, Coherent, Santa Clara, CA, USA) emitting at  $\lambda = 460$  nm was used. First, the beam laser is spatially filtered and collimated. Then, this beam is split into two secondary beams, the object and reference beams, using a beam-splitter. The two laser beams were spatially overlapped at the sample, reaching symmetrically by the opposite sides at the photopolymer layer with a recording angle  $\alpha_o = \alpha_r = \alpha = 75.1^\circ$  with respect to the normal incidence. The ratio of intensities between both reference and object beams was 3.3:1. A total recording intensity (sum of both intensity beams measures in the hologram plane) of  $3.00 \pm 0.08$  mW/cm<sup>2</sup> was used and the exposure times were varied to obtain different values of radiant exposure ( $H$ ). According to Bragg's law for symmetrical transmission geometry (Eq. 1), holograms were recorded at a theoretical spatial frequency of 4988 lines/mm (period  $\Lambda = 0.200$   $\mu$ m).

$$\Lambda = \frac{\lambda}{2\sqrt{n^2 - \sin^2\alpha}} \quad (1)$$

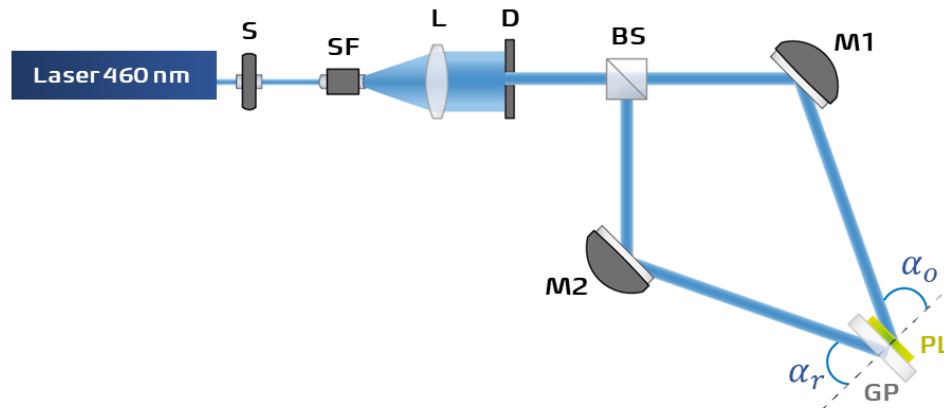


Figure 2: Holographic setup for reflection gratings. S: shutter; SF: spatial filter (microscope objective and pinhole); L: lens; D: diaphragms; BS: beam splitter; M: mirrors;  $\alpha_o$ ,  $\alpha_r$ : object and reference recording angles; PL: photopolymer layer; GP: glass plate.

The  $DE$  experimental values were obtained as a function of the photopolymer layer transmittance with ( $T_{pg}$ ) and without ( $T_p$ ) the recorded reflection grating (Eq. 2). The transmission spectra at normal incidence upon the photopolymer layer was measured with a double beam spectrophotometer (V-650, Jasco). The maximum diffraction efficiency ( $DE_{max}$ ) was obtained for the lowest value of  $T_{pg}$ .

$$DE = \frac{T_p - T_{pg}}{T_p} \quad (2)$$

## 4. RESULTS AND DISCUSSION

### 4.1 Optimisation of drying time and composition of undoped photopolymer layers

The optimum drying time was first studied. Fig. 3a shows the mass loss of an undoped PL when an initial amount of  $1.0317 \pm 0.0001$  g of photopolymer solution with composition P4 (Table 1) was deposited over a glass

plate and introduced in the climatic chamber. The greatest rate of mass loss occurs during approximately the first 5 h. From this time, the drying speed decreases. The mass of the undoped PL remains practically constant from 13 hours. The highest diffraction efficiency was reached when the photopolymer layers has finished its drying process and its mass remains stable in time.<sup>9</sup> Taking into account that the amount of water in each solution varies slightly, a drying time of 16 h was selected for all the undoped-PLs prepared from the photopolymer solutions whose compositions are indicated in Table 1.

Table 1: Composition of photopolymer solutions in molarity. PVA in g/mL.

Composition	PVA (g/mL)	NaOA (M)	TEA (M)	RF ( $\times 10^{-3}$ ) (M)	DHEBA ( $\times 10^{-3}$ ) (M)
P1	0.115	0.384	0.033	1.2	0.0
P2	0.111	0.503	0.032	1.2	2.0
P3	0.109	0.599	0.032	1.2	4.0
P4	0.106	0.676	0.031	1.1	5.9

Once the drying time was fixed and in order to find the best composition, the  $DE_{max}$  values were measured as a function of  $H$ . The results are shown in Fig. 3b to  $H$  values between 15 and 140  $\text{mJ}/\text{cm}^2$ . The P1 and P2 photopolymer layers had a similar behaviour. Its highest  $DE_{max}$  values were  $4.2 \pm 0.6\%$  and  $7.0 \pm 0.6\%$ , respectively, at 107  $\text{mJ}/\text{cm}^2$ . The same sensitivities ( $DE_{max}$  vs  $H$  slope) were obtained with the P3 and P4 photopolymer layers for a  $H$  range of 15 to 45  $\text{mJ}/\text{cm}^2$ . The highest  $DE_{max}$  obtained for P3 was around  $9.5 \pm 4\%$  at 76.4  $\text{mJ}/\text{cm}^2$ . From this value, a decrease in  $DE_{max}$  was measured. P4 was the photopolymer solution in which the highest  $DE_{max}$  value was achieved. This value was of  $16.3 \pm 0.9\%$  at  $H$  of 137  $\text{mJ}/\text{cm}^2$ .

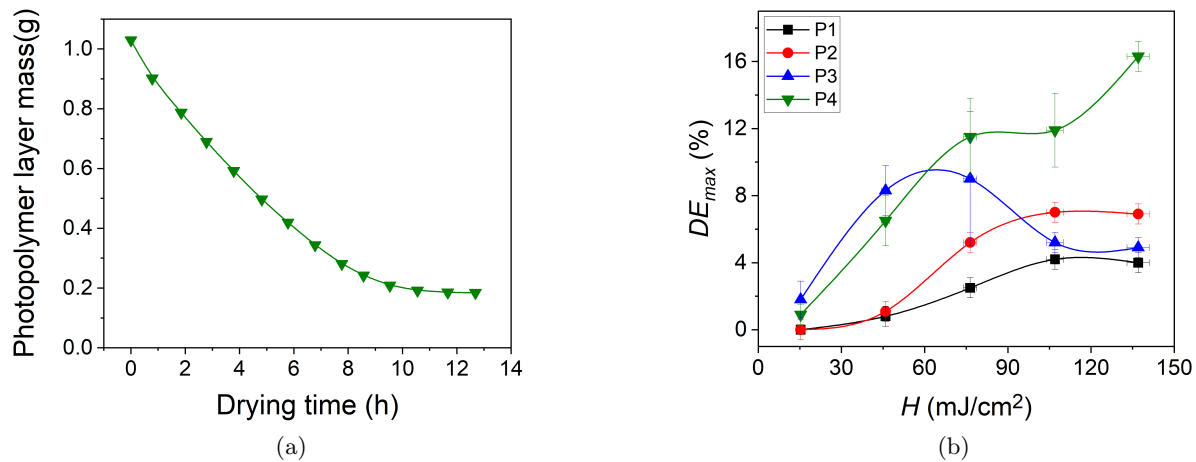


Figure 3: (a) Mass loss of a photopolymer layer when an initial amount of 1.0317 g of photopolymer solution is deposited over a glass plate. (b) Maximum diffraction efficiencies as a function of radiant exposure for undoped photopolymer layers with different composition. Errors are  $\pm 0.0001$  g in the photopolymer layer mass and  $\pm 0.017$  h in the drying time.

#### 4.2 Measure of diffraction efficiency as a function of Pt NP concentration in the photopolymer layer

Once the composition of photopolymer solution and the drying process were optimised, doped PL with different Pt NPs concentration were prepared. The composition of the P4 photopolymer solution was used and the Pt NPs were added to the initial PVA solution. The concentrations of Pt NPs used in this work are shown in Table 2. In order to define a correct unit of measurement, these concentrations were expressed in nanomoles of Pt NPs per gram of PVA. Fig. 4a show the transmittances as function of wavelength for Pt NPs-doped photopolymer layers. The transmittance decreases slightly as the Pt NPs concentration increases. However, there was no notable difference in the transmittance values for these doped PL.

Table 2: Concentration of Pt NPs prepared.

Pt NP-doped Photopolymer	Concentration (nmol Pt NPs/g PVA)
P4	0.00
PtP4a	$0.12 \pm 0.03$
PtP4b	$0.29 \pm 0.07$
PtP4c	$0.42 \pm 0.09$
PtP4d	$0.58 \pm 0.13$
PtP4e	$0.75 \pm 0.17$

The influence of  $H$  on  $DE_{max}$  was studied for all Pt NPs-doped PL. The results are shown in Fig. 4b. The values corresponding to the P4 undoped PL were added for a better comparison. As clearly observed in Fig. 4b, there is not a great improvement for the highest  $DE_{max}$  values achieved ( $\sim 18\%$ ) in the PLs with a low concentration of Pt NPs (PtP4a, PtP4b and PtP4c). The behaviour for PtP4b and PtP4c were similar throughout all range of  $H$  used.  $DE_{max}$  values achieved for these PLs were higher compared to those obtained for P4 and PtP4a in  $H$  range of 15 to 76  $\text{mJ}/\text{cm}^2$ . The trend of the  $DE_{max}$  values for the two doped PLs with the highest concentration of Pt NPs was different. When PtP4d was measured,  $DE_{max}$  increased rapidly until it reached its highest value of  $28 \pm 5\%$  at  $H$  of 76.4  $\text{mJ}/\text{cm}^2$ . From this value, the  $DE_{max}$  decreased. For PtP4e,  $DE_{max}$  increased until its highest value of around  $21 \pm 4\%$  at  $H$  of 107  $\text{mJ}/\text{cm}^2$ .

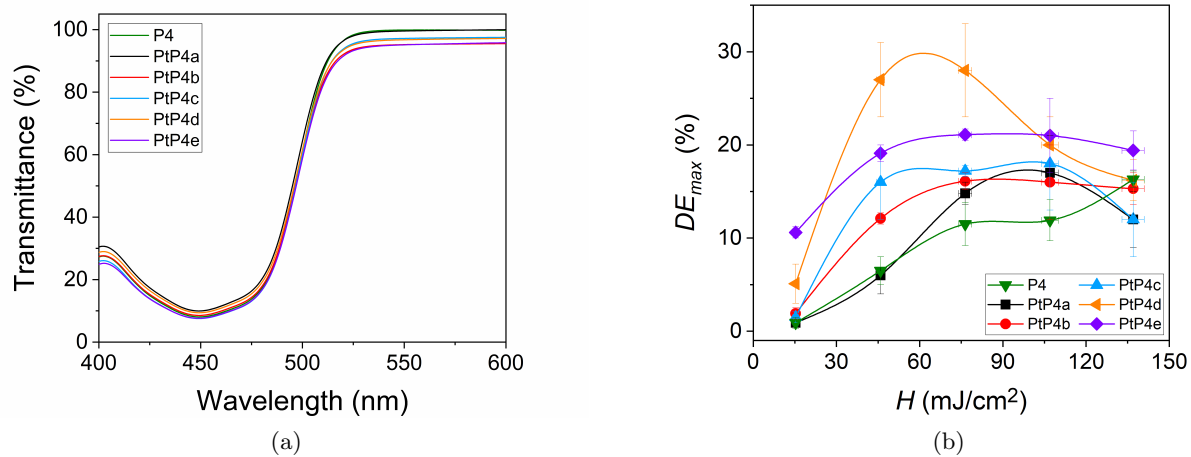


Figure 4: Transmittance as a function of the wavelength (a) and maximum diffraction efficiencies as a function of radiant exposure (b) for undoped and Pt NPs-doped photopolymer layers.

The highest values of  $DE_{max}$  obtained as a function of the concentration of Pt NPs are shown in Fig. 5.  $DE_{max}$  remains practically constant from 0 up to a concentration of 0.34 nmol Pt NPs/g PVA. From this value,  $DE_{max}$  begins to increase until reaching its highest value of  $28 \pm 5\%$  for a concentration of 0.58 nmol Pt NPs/g PVA. This behaviour can be explained by the different refractive index modulation between the bright and dark zones of the interference fringe pattern caused by the incorporation of metallic nanoparticles with a high refractive index. In the inset of Fig. 5 is shown a reflection grating stored in a PL with PtP4d composition.

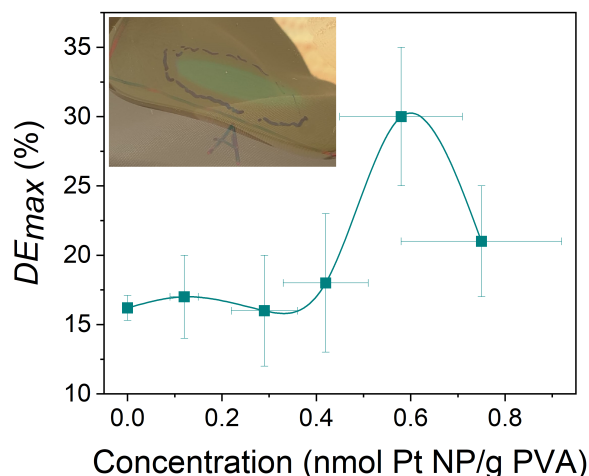


Figure 5: Maximum diffraction efficiencies as a function of the concentration of the Pt NPs. Inset is an image of the unslanted reflection gratings daylight illuminated.

## 5. CONCLUSIONS

Unslanted reflection holographic gratings of 4988 lines/mm have been stored in a low-toxicity and water-soluble photopolymer. The drying time and the optimal composition of Biophotopol layers were studied in terms of diffraction efficiency. The ratios of moles of sodium acrylate and DHEBA were changed while the moles of the other components were kept constant. The highest value of diffraction efficiency was obtained when the photopolymer solution with the highest amounts of sodium acrylate and DHEBA were used in the preparation of the layers. These optimized layers were doped with high refractive index Pt nanoparticles demonstrating that an increase in diffraction efficiency is produced. The highest diffraction efficiency value is reached for a concentration of 0.58 nmol Pt NPs/g PVA. The results indicate that it is possible to achieve high efficiencies in materials with high environmental compatibility opening the possibility to carrying out studies in which the type of nanoparticles will be changed and new components will be added to the Biophotopol.

## 6. ACKNOWLEDGMENTS

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