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Improving the performance of methylene blue sensitized photopolymer by doping with nickel ion

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ABSTRACT

Holographic performance of an economically cheap metal ion doped photopolymer material is presented. We investigated the effect of incorporation of nickel ion into the methylene blue sensitized poly (vinyl alcohol)/acrylamide (MBPVA/AA) photopolymer system. The composition and preliminary characterization of the developed photopolymer material is reported. The presence of nickel ion improves the diffraction efficiency, stability of the material and it operates in a wide range of spatial frequencies (550–2000 lines/mm) at exposure energy of 100 mJ/cm^2. When nickel ion concentration was 0.01 mM, maximum diffraction efficiency of 84% at exposure energy of 100 mJ/cm^2 with spatial frequency 1335 lines/mm could be achieved for gratings recorded using wavelength of 632.8 nm. The material showed panchromaticity with more than 70% diffraction efficiency in both blue and green regions. Effects of humidity and temperature on the stored gratings were studied by keeping films in different environmental conditions. Suitability of recording large area holograms was also explored.

1. Introduction

Photopolymers are considered as key materials for holographic applications like data storage and holographic optical elements [1–5]. Photopolymers deserve much attention because of low cost, response in real time, high diffraction efficiency, controllable film thickness, stability and ease of optical processing. PVA-acrylamide based photopolymer materials are widely used because they have very good holographic characteristics [6,7]. These materials are self-developing so that they can find advantage in many holographic applications like holographic display, holographic data storage and holographic optical elements. As compared with the conventional storage materials, holographic data storage demands high capacity and low cost. Meanwhile, holographic optical elements have the ability of lens and mirror functions in single device, and it can be easy to integrate with new energy systems like solar cell and concentrators [8].

Many attempts were made by our research group as well as other researchers to improve the holographic performance of photopolymers by changing dyes and incorporating materials like organic cross-linkers, nanoparticles, and metal salts [9–14]. Metal ion doped photopolymers are found to improve the properties of the holograms like diffraction efficiency and environmental stability. It is reported that metal ions such as chromium (Cr^{3+}), copper (Cu^{2+}), ferric (Fe^{3+}), silver (Ag^{+}), nickel (Ni^{2+}) have been doped in the polymer matrix in order to improve the holographic properties. Most of the metal ion doped holographic recording materials requires some types of fixing process for achieving high diffraction efficiency and stability, while those that required no fixing process had poor sensitivity and diffraction efficiency [11,12]. John et al. developed copper doped methylene blue sensitized poly (vinyl alcohol) (MBPVA)–acrylamide films [15]. Gratings could be recorded on the films with diffraction efficiency of only 20% at an exposure of 500 mJ/cm^2. The diffraction efficiency of this photopolymer system could be enhanced by replacing copper ions with chromium ions. The diffraction efficiency of the system achieved a diffraction efficiency of 42% after self enhancement; but it falls down to the initial value of 21% after 3 months [16]. Pramitha et al. proved that incorporation of silver ions into the photopolymer system could improve the holographic parameters like diffraction efficiency, energy sensitivity and also could use thus as a potential storage material [17,18]. More than 75% diffraction efficiency could be attained at exposure energy of 80 mJ/cm^2. Gratings recorded in these films could be stored for more than a year with good diffraction efficiency. Gratings with more than 60% diffraction efficiency could be recorded even after four months of preparation. In addition, photopolymer system with different

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metallic salts could play the role of conducting films. In 2008, Fontanilla-Urdaneta et al. have done the diffraction efficiency study of holographic gratings in $NiCl_2{\cdot}6H_2O$ doped dichromated poly (vinyl alcohol) [19]. They reported the effect of electric potential on holographic recording. The maximum diffraction efficiency reached in that material was only 1.034%. In 2011, the same group examined the voltage effect in the same material by varying the thickness of the film [20].

In this context, our aim was to develop another competitively promising metal ion doped photopolymer material which should be cost effective and free from post processing techniques. A photopolymer system similar to that developed and reported earlier by Pramitha et al. [17] was used, but with the essential difference that silver dopant was replaced with nickel dopant which is four times cheaper than silver dopant. The dopant concentrations as well as the holographic recording parameters of this material was optimized, so as to fabricate amply dimensioned media at low cost and good optical clarity with more than 80% diffraction efficiency.

2. Experiments and results

2.1. Photopolymer solution preparation

The photopolymer system consists of poly (vinyl alcohol) (PVA) as binder [CDH, Mol.weight-125,000, purity-99.25%], acrylamide (AA) [Merck, purity >99%] as monomer, triethanolamine (TEA) [Merck, purity >99%] as initiator, and methylene blue (MB) [Merck, purity >82%] as sensitizer with an additional dopant nickel chloride [Universal Laboratories Pvt. Ltd, purity >97%]. The photopolymer solution was prepared by mixing 0.38 M AA, 0.05 M TEA, 0.014 mM MB, and 0.01 mM nickel chloride with 10% PVA solution.

2.2. Layer preparation

Even though different methods were available for film coating, gravity settling method was adopted in this work. It is a common method in which manipulation of film dimension can be easily achieved. After stirring well, a fixed volume of solution was poured into glass plates of dimension $7.5 \times 2.5\ cm^2$ kept in a leveled tray and allowed to dry in darkness for 2–3 days under normal laboratory conditions. This resulted in a photopolymer film of thickness around 130 μm measured using Stylus profiler (Dektak 6M). The films are of uniform thickness at the central region.

2.3. Optical characterization

Optical characterization was done using spectrophotometer (JASCO-V-570 UV–VIS–NIR). The plot of absorbance versus wavelength for both metal doped and undoped MBPVA/AA solution is shown in Fig. 1. It is obvious that there is an additional peak in the doped sample around a wavelength of 400 nm other than the main peak at wavelength of 632 nm. It means that the material has become sensitive in shorter wavelength region also on the addition of nickel chloride into the photopolymer solution. Since the storage density is inversely proportional to the third power of wavelength, the additional peak at shorter wavelength can explore possibility of increasing data storage capacity.

2.4. Recording of holographic gratings

Transmission gratings were recorded in the film using the standard holographic set up shown in Fig. 2. A He Ne laser (Melles Griot, 15 mW) of wavelength 632.8 nm was used to store diffraction gratings. Using a spatial frequency filter and a collimating lens the diameter of the laser beam was increased to around 1 cm. The

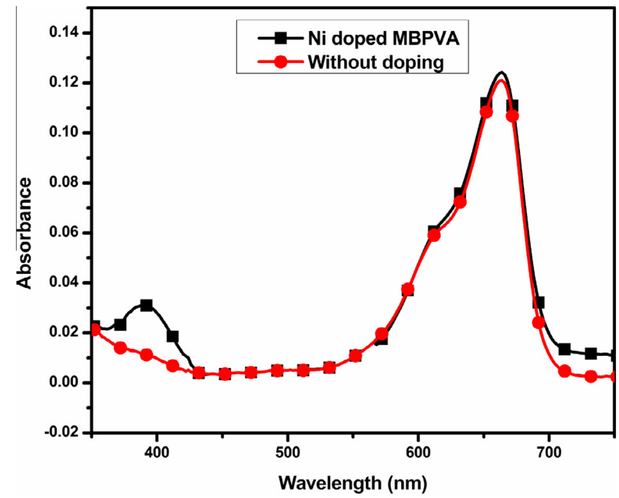

Fig. 1. Optical absorption of both metal doped and undoped photopolymer solution.

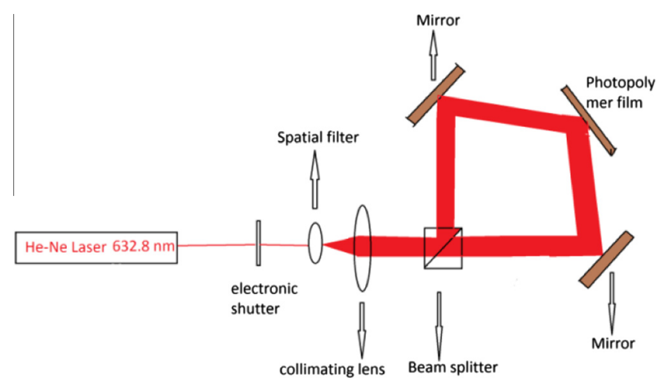

Fig. 2. Experimental set up to record holographic gratings.

laser beam was split into two beams of intensity ratio 1:1 using a cubic beam splitter. The two beams were recombined at the sample at required angle by an appropriate arrangement of two plane mirrors. The exposure time was controlled by an electronic shutter controller (Thorlabs SC10) placed in front of the laser. The working power of laser was 4 mW.

A laser beam (9 μW) with same wavelength was used to measure the diffraction efficiency of the recorded gratings. When the beam was positioned at Bragg angle, diffraction occurred from the gratings recorded on the photopolymer film. Ratio of the intensity of first order diffracted beam to incident beam was monitored using an optical power detector (Ophir PD 200) which gave the diffraction efficiency.

2.5. Possible photochemical process involved in the material

In the case of nickel ion doped photopolymer, the reason behind refractive index modulation is monomer diffusion due to photopolymerisation and photo-cross-linking. The possible free radical photopolymerisation mechanism for the developed material is described below. There are mainly three steps in a free radical photopolymer mechanism.

1. *Initiation*- When the material is exposed to light of suitable wavelength, sensitizer (MB) absorbs light and get excited. The singlet excited state is unstable so that it will undergo an intersystem crossing into a stable triplet state. The triplet state dye