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Signal intensity enhancement of laser ablated volume holograms

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ABSTRACT

Conventional volume holographic gratings (VHGs) fabricated in photosensitive emulsions such as gelatin containing silver salts enable the facile visualization of the holographic image in ambient lighting. However, for the fabrication of holographic sensors, which require more defined and chemically-functionalised polymer matrices, laser ablation has been introduced to create the VHGs and thereby broaden their applications, although the replay signal can be challenging to detect in ambient lighting. When traditional photochemical bleaching solutions used to reduce light scattering and modulate refractive index within the VHG are applied to laser ablated volume holographic gratings, these procedures decrease the holographic peak intensity. This is postulated to occur because both light and dark fringes contain a proportion of metal particles, which upon solubilisation are converted immediately to silver iodide, yielding no net refractive index modulation. This research advances a hypothesis that the reduced intensity of holographic replay signals is linked to a gradient of different sized metal particles within the emulsion, which reduces the holographic signal and may explain why traditional bleaching processes result in a reduction in intensity. In this report, a novel experimental protocol is provided, along with simulations based on an effective medium periodic 1D stack, that offers a solution to increase peak signal intensity of holographic sensors by greater than 200%. Nitric acid is used to etch the silver nanoparticles within the polymer matrix and is thought to remove the smaller particles to generate more defined metal fringes containing a soluble metal salt. Once the grating efficiency has been increased, this salt can be converted to a silver halide, to modulate the refractive index and increase the intensity of the holographic signal. This new protocol has been tested in a range of polymer chemistries; those containing functional groups that help to stabilize the metal nanoparticles within the matrix yield more intense holographic signals as the integrity of the fringe is more protected with increasing metal solubility.

1. Introduction

Volume holographic gratings (VHGs) fabricated in photosensitive emulsions, such as silver halide salts within a gelatin emulsion, produce intense holographic signals that enable images to be detected visually in ambient lighting [1,2]. One limitation of these VHGs for use as sensors is the polymer matrix, which is normally hydrophilic and unable to detect analytes such as hydrocarbons, which require hydrophobic matrices for absorption. The use of laser ablation to generate VHGs in a wide range of hydrophilic and hydrophobic polymers, containing a variety of metal salts or dyes, has significantly broadened the application of such sensors [3–9]. Furthermore, a number of the steps currently used in photochemical processing can be eliminated to increase their cost-effectiveness [9,10]. Even so, their application can be limited, however, by the low intensity of the holographic signal in some polymer matrices, which makes visualization of sensor response challenging without the use of a spectrometer or a bright white light source. Traditional methods such as reversal or rehalogenation bleaches, used to increase signal intensity of photochemically produced VHGs, results in the loss of intensity in ablated holograms. This research advances a hypothesis to explain the loss of intensity associated with the use of these bleaching agents and provides an alternative post-processing regime to increase the peak intensity of ablated VHG sensors.

Whilst the exact mechanism that generates the volume

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diffraction grating within the emulsion is not fully understood, it is thought to result from an in situ reduction in the size of the metal particles and the formation of alternating light and dark fringes (high-low index modulation) [7]. The fabrication process begins with diffusion of a metal salt solution into a polymer matrix. If the choice of solvent is optimized for the polymer matrix, the metal salts are likely to diffuse homogenously through the depth of the polymer and on reduction, the metal nanoparticles are distributed randomly as a colloidal suspension. Following exposure from a coherent light source, metallic nanoparticles are arranged in periodic fringes to form a VHG [9].

The sensor response is linked to either a swelling of the polymer matrix and/or changes in refractive index, which generates a shift in wavelength and changes in intensity of the holographic signal [3–10]. If the polymer swells, either due to solvent being drawn into the polymer or electrostatic repulsion of charges, or there is an increase in refractive index, the diffracted light can be shifted to longer wavelengths. Likewise, a decrease in refractive index or a contraction of the polymer causes the diffracted light to be shifted to shorter wavelengths. The diffraction grating therefore acts as a reporter, and calibration of the holographic response enables accurate detection and quantification of the analyte using a spectrophotometer.

For the VHG recording, the grating vector, $\boldsymbol{K}_G$, is defined as, $\overrightarrow{\boldsymbol{K}_G} = \overrightarrow{\boldsymbol{k}_1} - \overrightarrow{\boldsymbol{k}_2}$, where $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ are the wavevectors of the interfering plane waves, as shown in Fig. 1(a). When the angle, 2θ, between these two waves $\rightarrow$ π, a reflection VHG is formed. The period of this sinusoidal fringe, Λ, is given by

$$\Lambda = m\frac{2\pi}{\left|\overrightarrow{\boldsymbol{K}_G}\right|} = \frac{m\lambda}{2\bar{n}\sin\left(\frac{2\theta}{2}\right)}$$

where $\bar{n}$ is the effective refractive index of the medium, m (integer) is the spectral order, λ is the illumination wavelength and $2\theta = \pi - \phi$. This will produce a sinusoidal modulation of the effective refractive index of the medium, the response of which is dependent on the material sensitivity. When illuminated with white light, the VHG selectively filters light according to the Bragg phase-matching condition, $\overrightarrow{\boldsymbol{K}_G} = \overrightarrow{\boldsymbol{k}_i} - \overrightarrow{\boldsymbol{k}_R}$, where $\boldsymbol{k}_i$ and $\boldsymbol{k}_R$ are the wavevectors of the incident and reflected waves, as shown in Fig. 1(b), with further details shown in ESI, Fig. S1.

Optimal narrowband reflection is achieved when the optical thickness of each layer in the stack is a quarter-wavelength. The strength of the holographic peak signal, formed by constructive interference of the partial reflections from each fringe plane, is dependent on the number of fringes and the modulation depth of the refractive index [11,12]. The effective refractive index of the high index fringes is highly dependent on both the particle size and fill fraction of the metal nanoparticles and an optimum set of parameters can be modelled to maximise grating efficiency and hence holographic intensity [12,13].

The main difference between VHGs produced by photochemical and laser ablation methods is the timing of the reduction of the

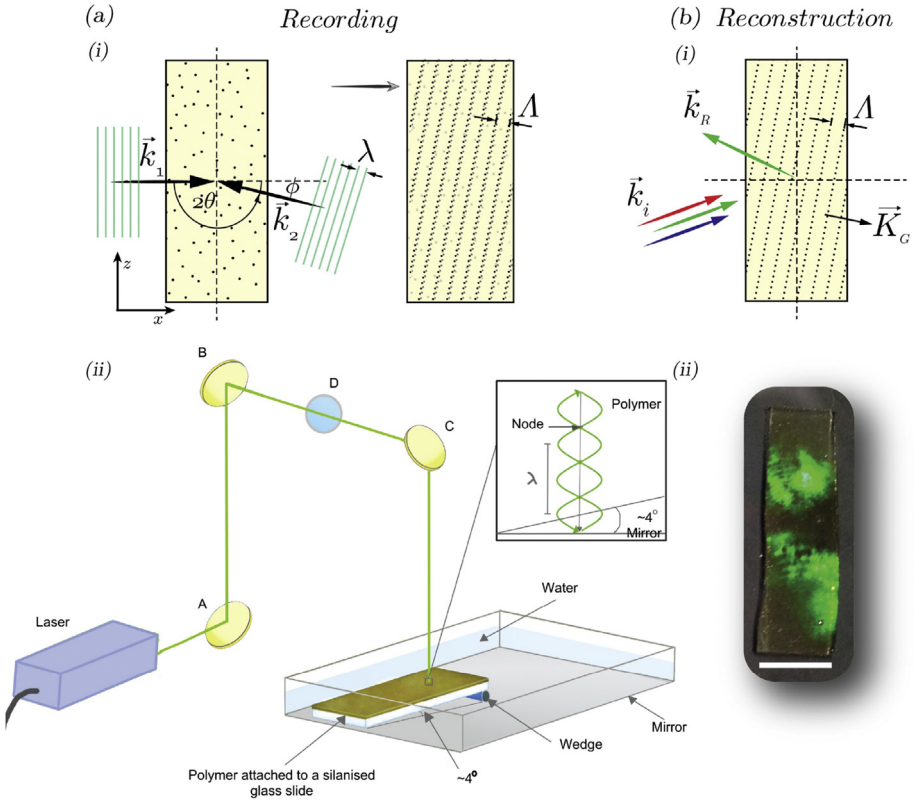

Fig. 1. Fabrication of Bragg reflection holograms. (a) Recording: (i) Schematic of holographic sensor recording process whereby the interference of two plane waves producing a periodic refractive index modulation of the medium. (ii) Nd:YAG pulsed laser generated a laser beam, which was directed by dichroic mirrors (A,B,C) and a spreader quartz lens (D), passed through the polymer and was reflected back by the mirror placed on the bottom of the plastic dish and running beneath the glass slide. The polymer on a silanised glass slide was placed on a 4° wedge lying on top of the mirror. The polymer was ablated either dry or immersed in deionised water to generate a hologram.(b) Reconstruction: (i) Reconstruction schematic highlighting the Bragg-phase matching condition. (ii) Photograph of a typical final sensor immersed in water bath, white scale bar ~3 cm.