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Photopolymers: beyond the standard approach to photosensitisation

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A photopolymerizable material for use in the visible normally consists of a dye sensitizer, a free radical generator, monomer/monomers and, optionally, a binder, and is prepared usually as a dry or liquid film. Upon illumination with light of appropriate wavelength, a photopolymerisation reaction is triggered, leading to a change in the film's refractive index. Because the presence of the dye is essential, the film is usually made sensitive to light during its preparation. Here we separate the film preparation and the sensitisation processes. In this way the photopolymerisation process can be used to detect dye labelled analytes, providing an alternative to fluorescence detection methods that offers visual, easy to interpret information. Our approach also allows for a precise control of the spatial location of the photoinduced refractive index changes that can be utilised for holography, lithography and photonic device fabrication.

Keywords: photopolymers, optical lithography, dye deposition lithography, holographic sensors, DNA sensing

1. Introduction

Photopolymers have been known since the 1950's [1,2] and following years of development have been used in recent years in applications such as holographic sensors [4,5], holographic data storage [6-8], fabrication of holographic optical elements [9], security holograms [10], electro-optical switchable devices [11], and some non-imaging applications such as adhesives, coatings and inks [12]. Because the lasers and the optical systems for work in the UV are very expensive, the majority of the photopolymers have been designed to respond to visible light. To enable this the photopolymer system includes a dye sensitizer [3] whose role is the absorption of visible light and transfer of the absorbed energy to the appropriate co-sensitiser so that polymerization can be initiated. Choosing the correct sensitising dye and its concentration are matters of extreme importance when optimum light sensitivity and efficiency of the photopolymerisation process are sought. It has been assumed intuitively that optimal sensitisation would be obtained when the dye sensitizer has maximum access to the other photopolymer components. For this reason and to ensure homogeneity, the dye is normally added to the liquid photopolymer mixture at the preparation stage. However, if the dry photopolymer layer is permeable enough and the sensitiser is chemically stable outside the layer there appears to be no fundamental reason why the dye could not be added at a later stage. It is assumed that after deposition on the layer surface the sensitiser will diffuse into the layer and thus be able to interact with the other components at the holographic recording stage. There are key requirements for a photopolymer system suitable for external sensitisation in this way. First, the unsensitised dry layer must be characterised by a high permeability, thus allowing for a relatively rapid diffusion of the externally deposited sensitiser. This in turn will impose limitations on the lateral resolution of the sensitised areas. Depending on the particular application of the method a

compromise between the requirement for high lateral resolution and grating thickness providing higher diffraction efficiency would be needed. Another requirement concerns the physicochemical stability of both the photopolymer and the sensitiser before mixing. In the present article we demonstrate that such an approach to photosensitisation of photopolymers in which the sensitiser is added at a later stage is practically feasible and could be useful for a number of different applications such as sensing and optical device fabrication.

2. Methodology

Figure 1 depicts the basic idea behind the novel approach to photosensitisation. Initially an unsensitised photopolymer solution is prepared by mixing all the components except for the dye sensitiser. The solution is then deposited on a glass substrate and left to dry. Then the dye sensitiser is deposited in a dry or liquid form only in specific locations on the dry film. The film is then illuminated by light and the refractive index of the photopolymer changes. There are two possible scenarios for the result depending on the structure of the light (Fig.1).

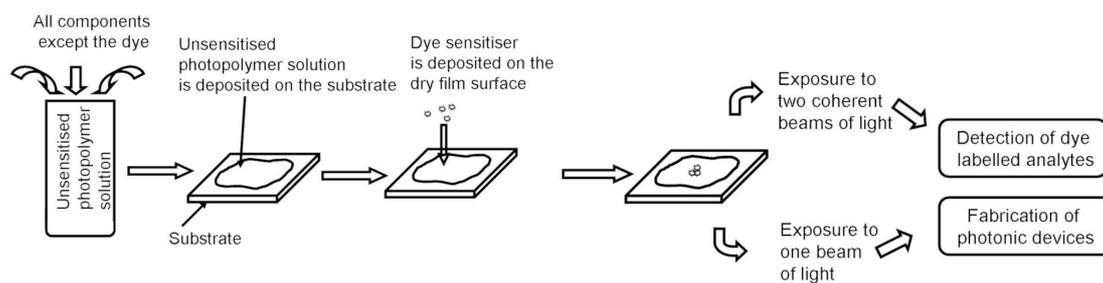


Fig.1 Principle of dye deposition photopolymerisation and its application in a) detection and b) device fabrication

A diffraction grating can be produced by spatially modulating the illuminating light. This is readily achieved by using an interference pattern produced by two coherent

laser beams. Depending on the configuration of the two recording beams the grating could be either a transmission or reflection grating. The familiar rainbow effect produced by a transmission diffraction grating is readily observed in white light. In the case of a reflection grating, a specific single colour is observed when illuminated with white light. Examination in white light in both cases would therefore reveal the presence and the exact location of the dye. Going a step further, one could use the dye molecules to label analyte molecules and have the film activated by a labelled analyte which will therefore be visually detected by the production of a holographic diffraction grating.

If only one beam is used for illumination, the local change in the photopolymer refractive index is spatially homogeneous. No diffractive effect is observed in this case but the refractive index change can be patterned to produce photonic structures that will confine, focus or direct the light propagating through them.

Figure 2 illustrates the process of recording and probing of a transmission (Fig.2 a,b) and a reflection (Fig.2 c,d) diffraction grating. The photopolymer layer is locally sensitised and then illuminated with two coherent beams of light (Fig.2 a, c) to record a diffraction grating. Upon illumination (Fig.2 b, d) with a probe beam at the appropriate angle, a diffracted beam is observed. One important aspect of the described method of detection is that it exploits an inherent amplification in the form of a chain polymerisation reaction triggered by a single excited dye molecule, leading to polymerisation of thousands of monomer molecules. A second important aspect is the intrinsically high sensitivity of this detection method due to the fact that an optical signal is produced in a direction in which no light was previously propagating and thus the signal to noise ratio could be very high.

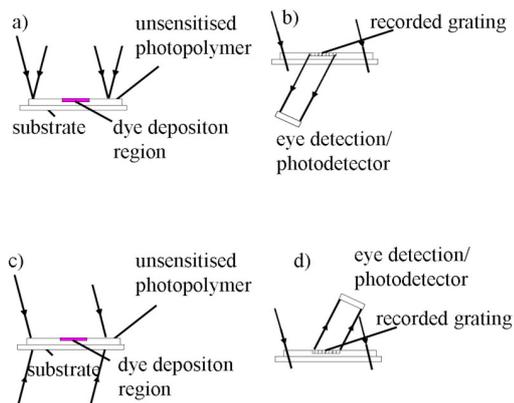


Fig.2 Recording and probing of a transmission (a), (b) and a reflection (c), (d) grating recorded by dye deposition holography.

3. Experimental

In order to verify that it is possible to record a hologram by dye deposition on a dry photopolymer layer, we used a photopolymer developed and optimised for various holographic applications at the Centre for Industrial and Engineering Optics [13-15]. The photopolymer contains 0.6 g acrylamide, 0.2 g N,N'methylene bisacrylamide, 2 ml triethanolamine and 17.5 ml of 10 % w/v polyvinylalcohol stock solution. Films of thickness 30 - 180 μm were obtained using volumes of between 0.5 and 2 ml of the photopolymer solution, gravity settled on a microscope glass slide and dried for 24 hours. Stock solutions of 0.5 or 1 μl of dye varying in concentration from 10^{-3} to 10^{-8} M were deposited on the layer surface by means of a micropipette and left for time intervals ranging from 15 min to 24 hours. Transmission gratings with 1000 l/mm spatial frequency were recorded using interference patterns obtained from the frequency doubled output of NdYVO₄ laser ($\lambda=532\text{nm}$) and intensities ranging from 10 to 30 mW/cm^2 and exposure time ranging from 20 s to 120s.

4. Results and Discussion

Examples of transmission diffraction gratings recorded in the areas where the dye was deposited (Fig.3 a) are shown in Fig.3 b.

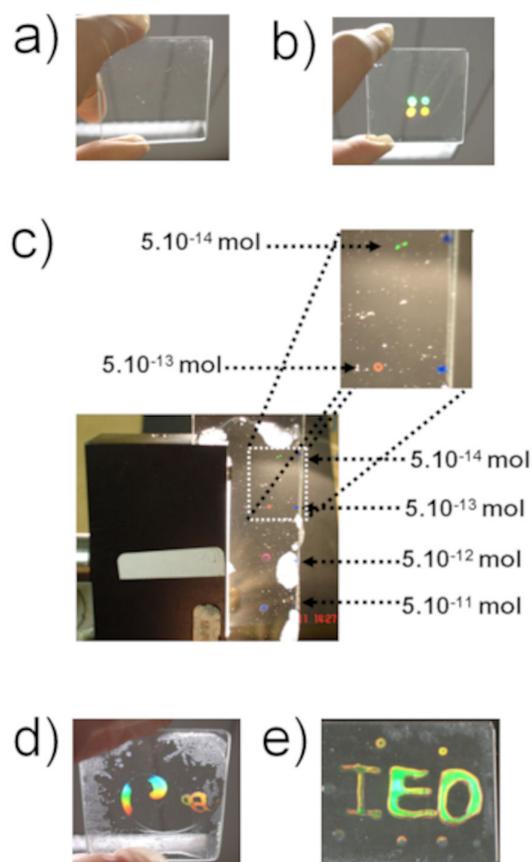


Fig.3 a) shows a photopolymer sample which has been sensitised but not exposed to laser light. The sensitised areas are not seen by eye because the dye concentration is very low. b) Following exposure to two interfering coherent light beams, transmission holographic gratings are recorded in sensitised areas (viewed in white light). c) Transmission holographic gratings recorded in photopolymer layer deposited on top of dye-labelled DNA molecules immobilised on a substrate. Arrows indicate areas in contact with dye-labelled DNA exposed to holographic recording. d) A transmission and e) a reflection grating recorded in the areas where the dye was deposited using a paintbrush.

A list of dye sensitizers absorbing at 532 nm and characterised by the high triplet quantum yield necessary for effective free radical generation and consequently efficient photopolymerisation was studied in order to determine the lowest concentration that can be detected. It was established that dye (Erythrosine B, Eosin Y, Eosin – 5 isothiocyanate) concentrations as low as 10^{-7} M can be visually detected by recording a transmission diffraction grating.

Having proved that the dye deposition sensitisation of photopolymers works well when the dye molecules are not attached to other molecules, the next step was to prove that the same principle applies when the dye is used as a label for another

molecule to be detected. The sample used in this experiment was purchased from Invitrogen and contained 17-mer single stranded DNA molecules labelled with Eosin-5-isothiocyanate at a concentration of 10 mM. Solutions (0.5 μ l) containing dye labelled DNA with concentrations from 10^{-3} to 10^{-9} M were deposited on a premium microarray substrate (ArrayIt, SuperEpoxy 2). Thus the amount of DNA molecules deposited in each location was varied between 0.5 nmols to 0.5 fmols. A separately prepared unsensitised dry photopolymer layer was peeled from a microscopic glass substrate and deposited on top of the substrate on which the dye labelled DNA was immobilised. The sandwich structure thus obtained was exposed to an interference pattern. The results from this experiment are shown in Fig. 3 c. It is seen from the figure that there are diffraction gratings recorded in the photopolymer layer in the areas where it has been in contact with the dye labelled DNA. 50 fmol of DNA were detected by the naked eye without significant optimisation of the dye label, photopolymer composition or recording conditions. As the total volume of the DNA sample deposited on the microarray surface in this case was 0.5 μ l, the smallest amount of DNA that was detected in this experiment was 50 fmol (approximately $3 \cdot 10^{10}$ molecules). For comparison the widely used technique of fluorescence detection is extremely sensitive ($5 \cdot 10^5$ molecules can be detected in a single spot $24 \times 24 \mu\text{m}^2$), but it can be very expensive, requiring skill in maintenance and operation and in the analysis of the results. We should emphasise that there is plenty of scope for optimisation of the described holographic detection method. Since the dyes currently developed for labelling biological molecules are usually characterised by high fluorescence quantum yield, they will not necessarily be the optimum sensitizers for photopolymerisation. In order to maximise the sensitivity, dye labels with high triplet yield and long lived triplet states must be sought. The actual composition of the

photopolymer could also be altered and this will provide additional flexibility when improved sensitivity is targeted. Using liquid instead of dry unsensitised layers could additionally improve the sensitivity of the detection method, because in this case the depth of diffusion of the sensitiser would not be a limiting factor for the layer thickness utilised during holographic recording. The diffraction efficiency of the recorded hologram depends on both the refractive index modulation and the thickness of the hologram, For a given diffraction efficiency a hologram with an increased thickness would allow the detection of a smaller refractive index modulation. Because the light induced refractive index modulation involving very few sensitising molecules, is expected to be proportional to their number, an increased hologram thickness would mean an increased sensitivity. The main advantage of the described detection method compared with the standard fluorescence-based detection method is that it can provide visual, easy to interpret information. Even should optimisation of the photopolymer composition fail to provide sensitivity matching that of fluorescence detection, the addition of state of the art photodetection systems with high directional sensitivity is likely to provide superior sensitivity.

Dye deposition sensitisation can also be used for precise localisation of photoinduced refractive index changes. There are two ways of illumination leading to different properties of the introduced refractive index changes. Firstly, if the illuminating light field is itself spatially modulated in intensity, a pronounced rainbow effect will be observed when white light is diffracted by a transmission grating, Fig. 3 d, or a single colour will be observed when the light is diffracted from a reflection grating, Fig.3 e.

Alternatively if one uses a spatially uniform light field no grating will be recorded but the refractive index of the recording material will be locally increased. This effect could be used fabricate different photonic devices. An example of such a device was

fabricated by dye deposition of a Fresnel phase plate pattern (Fig.4a,b) on a dry layer by means of a Dimatix Fujifilm materials deposition system.

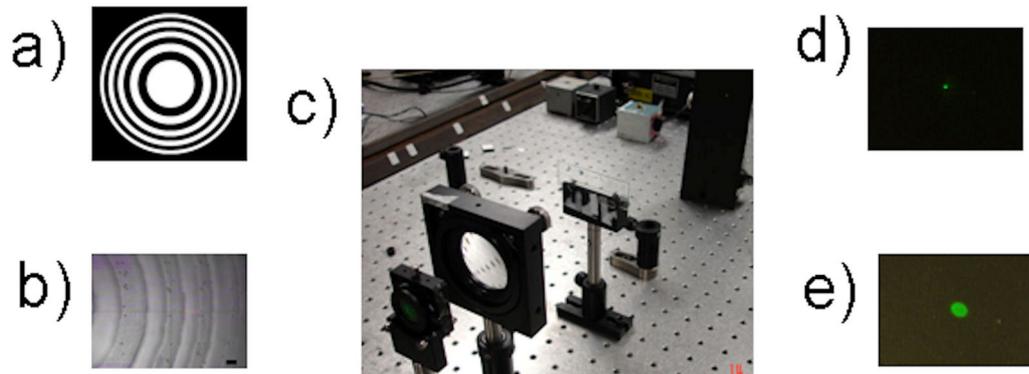


Fig.4 Fabrication of a Fresnel phase plate using the dye deposition method. a) the pattern b) printed on the photopolymer layer using Dimatix materials deposition system (the size of the bar is 100 μ m); c) probing the device with a collimated laser beam; d) the beam is focused when it passes through the optical device; e) the beam at the same location when the device is not in place.

The layer was left in the dark for 60 min and illuminated by a laser light of wavelength of 532nm. The intensity of the light was 5mW/cm² and the exposure time was 180s. The recorded structure was then illuminated by an attenuated 532 nm laser beam (Fig.4c). The beam was focussed after passing through the Fresnel plate (Fig.4d). This observation proves that the localised dye sensitised polymerisation has caused the expected patterned change of the refractive index. No focussing was observed when a printed but non-polymerised pattern was probed (Fig.4e). Using this approach light waveguides, couplers and splitters can be fabricated by a printing process that provides the required spatial resolution. Optical circuits can be similarly

designed and printed. At present the highest resolution commercially available is 10 μm provided by Dimatix but further improvements are anticipated.

5. Conclusions

In conclusion we present a novel approach for sensitisation of photopolymerisable materials that can facilitate precise spatial control over the light induced refractive index changes and can also be used in a detection method for dye labelled analytes.

This novel approach can open new horizons for a number of research areas summarised in Fig. 5. For

instance, the spatially controlled photopolymerisation and consequent change of the material refractive index could

find application in the fabrication of photonic devices such as

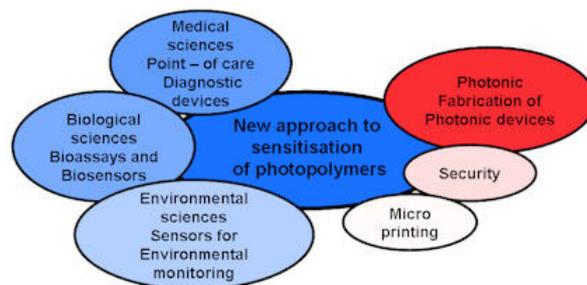


Fig.5 Research areas on which the new approach to sensitisation will have a significant impact.

waveguides, wave couplers and splitters. It could be used to advance security and microprinting applications. The holographic detection method can be applied in medical sciences for the design of point of care diagnostic devices, in biological sciences for the development of novel bioassays and biosensors and in environmental sciences for the development of sensors for environmental monitoring.

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