

Divalent metal ion-sensitive holographic sensors

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Abstract

A holographic sensor for real-time detection of divalent metal ions (Ca^{2+} , Mg^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+}) has been fabricated by incorporating a chelating monomer into a hydrogel matrix. A methacrylated analogue of iminodiacetic acid (IDA) was prepared and co-polymerised with hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EDMA) as a cross-linker to form polymer films. A silver-based reflection hologram was incorporated into the hydrogel by diffusion followed by holographic recording using a frequency-doubled Nd:YAG laser. Changes in the replay wavelength of the hologram were used to characterise the swelling behaviour of the matrix as a function of its chemical composition and concentration of analyte in the media. The effects of active monomer, cross-linker, pH and ionic strength on the swelling of the matrix and on metal detection sensitivity have been studied. Polymers containing >10 mol% of chelating monomer and 6 mol% of cross-linker showed significant responses (46.3 nm) within 30 s at an ion concentration of 0–40 nM. The selectivity of the holograms towards the different ions tested was $\text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. The sensor showed fully reversible responses, permitting real-time monitoring of calcium ion efflux during the germination of *Bacillus megaterium* spores.

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1. Introduction

Much effort has been devoted to decrease the expense and time that are associated with the study and optimisation of fermentative and cell culture bioprocesses in the pharmaceutical, fine chemicals, food and environmental industries. The development of miniaturised analytical devices simultaneously monitoring different analytes in these bioprocesses offers the opportunity to increase throughput, reduce sample size, lower operating costs, make single-use disposable devices and improve portability. Among key analytes of interest are the divalent metal ions, which play an important role in biological processes carrying out a wide range of tasks such as oxygen transport, carbon dioxide fixation, phosphate, methyl and electron transfer, hydrolysis and the stabilisation of the structure of proteins and enzymes [1]. In addition, uncontrolled human activities have made heavy metal ions an environmental and human health

risk by the virtue of their toxicity at very low concentrations and persistent nature. Consequently, rapid methods for the detection of metal ions are required for monitoring chemical and biological processes.

Many methods have been developed for the analysis of metal ions including atomic absorption [2], fluorescence spectrometry [3] and inductively coupled plasma mass spectrometry (ICP-MS) [4]. However, whilst all these technologies are highly sensitive, they are time-consuming and require expensive instrumentation and large sample volumes. In the last few years, there has been an increased interest in circumventing these problems by developing new analytical methods [5–17] and fabricating mass-producible, inexpensive and small sample volume sensors for real-time monitoring of divalent metal ions.

Optical chemosensors have been developed for the detection of metal ions in which changes in absorbance or fluorescent properties of different chelating compounds are determined when binding the metal. Other approaches exploit changes in diffraction, which generates a visual colour change [18,19]. This has been achieved by the formation of a crystalline colloidal array of polymer spheres of diameter

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~100 nm within a hydrogel that swells or shrinks reversibly in the presence of the analyte [20,21]. This system has been made sensitive to Pb^{2+} , Ba^{2+} and K^{+} by co-polymerisation of 4-acryloyl-aminobenzo-18-crown-6 into the hydrogel and to other metal ions such as Cu^{2+} , Co^{2+} and Zn^{2+} using 8-hydroxyquinoline as a chelating ligand [22–24]. Although this system is an attractive approach, the preparation of the iridescent charged array is labour-intensive.

In the previous work, our group proposed the use of reflection holograms as integrated systems that comprise not only the analyte-selective “smart polymer” but also the optical interrogation and reporting transducer [25–31]. The holographic gratings act as sensitive wavelength filters diffracting the light with a wavelength governed by the Bragg’s equation:

$$m\lambda = 2nd \sin \theta$$

where m is the diffraction order, λ is the wavelength of light in vacuo, n is the average refractive index of the system, d is the diffracting plane spacing and θ is the angle of illumination.

Conventionally, the gratings are formed in a gelatin–silver halide photographic emulsion coated onto a glass or plastic substrate. They are fabricated by passing a single diverged laser beam through a holographic plate backed by a mirror. Interference between the incident and reflected beams followed by development and bleaching creates a set of fringes lying in planes parallel to the polymer surface which are approximately half a wavelength apart, within the 10 μm thickness of the polymer film. Under white light illumination, the gratings act by reflecting the light with a specific narrow band of wavelengths, hence, effectively behaving as a monochromatic mirror. The constructive interference of the partial reflections from each fringe gives a characteristic spectral peak. The peak reflectivity is dependent on the number of fringe planes and the modulation depth of the refractive index. As the grating is formed within the thickness of the smart polymer, any biological, chemical or physical change that makes the polymer swell or contract will change the spacing between fringes or the average refractive index generating changes in the wavelength and/or intensity of the reflection hologram. Several applications of this technology have been published previously showing that the holograms can be fabricated using any polymer matrix, either natural, synthetic or rationally designed to obtain sensors that respond to a wide range of analytes [25–31]. Recently, the technology has been adapted for the detection of monovalent metal ions using crown ether-substituted polymers [32]. A subsequent approach constructed pH-sensitive holograms using hydrogels that contain basic or acidic functionalities which, therefore, underwent changes in hydration as a function of the pH of the medium [33]. We report here a further application of this holographic sensing technology to the fabrication of sensors for divalent metal ions.

2. Experimental

2.1. Materials

All chemicals were of analytical grade unless otherwise stated. 2-Hydroxyethyl methacrylate (HEMA) (97%), iminodiacetic acid (IDA), ethylene glycol dimethacrylate (EDMA), dimethoxyphenylacetophenone (DMPA), hydroquinone, lithium bromide, methacrylic acid, silver nitrate (1 M, volumetric standard), silver perchlorate, zinc chloride, nickel chloride and calcium chloride were purchased from Aldrich. 2-(*N*-morpholino)ethanesulphonic acid (hydrate) (MES), 3-{[tris(hydroxymethyl)methyl]amino}ethanesulphonic acid (TES), chloroacetate, calcium nitrate tetrahydrate, iron(II) sulphate hexahydrate and sodium chloride were purchased from Acros Organics. Sodium hydroxide, cobalt chloride and magnesium chloride (1 M) were purchased from Sigma. Sodium thiosulphate (hypo), acetic acid (glacial), potassium chloride, magnesium sulphate, isopropanol, methanol as well as other common solvents were obtained from Fisher Scientific. Bicine was purchased from Avocado Research Chemicals. Methacryloyl chloride was purchased from Fluka. Glucose was purchased from ICN Biochemicals. Nutrient broth (NB) and tryptone soya broth (TSB) were purchased from Oxoid.

Microscope slides (Super Premium; 1–1.2 mm thick; low iron) were purchased from BDH (Merck). Aluminised, 100 μm polyester film (grade MET401) was purchased from HiFi Industrial Film. A UV Exposure Unit (555-279) was obtained from RS Components.

A frequency-doubled Nd:YAG laser (350 mJ, 532 nm, Brilliant B, Quantel) was used in hologram construction (note: high-energy class IV pulsed lasers such as this are potentially dangerous and appropriate protective clothing and safety glasses must be worn. The laser should be located and used according to local safety regulations).

Holograms were analysed using an LOT-ORIEL MS127i Model 77480 imaging spectrograph in a single channel mode with a 256 \times 1024 pixel InstaSpec IV CCD detector and processing software. Spectrometer calibration was achieved using a spectral calibration lamp (37-4405) purchased from Ealing Electro Optics. Optical density was measured using an UV-Vis scanning spectrophotometer from Shimadzu.

A bench pH meter (HI-213 pH/mV/C, supplied with glass electrode and temperature probe), pH 4.01, 7.01 and 9.18 calibration buffer solutions and electrode cleaning solutions were purchased from Jencons-PLS.

A Techware polymer-body combination pH electrode (6 mm diameter, catalog no. Z26, 627-2) was purchased from Aldrich. The apparent pK_a values of the holographic sensor pH response curves were determined from the point of inflection of curves fitted using sigma plot (Version 8; SPSS Science, Woking, Surrey, UK). The pK_a of ionisable monomers was determined using the standard titration methods.

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