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A bioinspired color-changing polystyrene microarray as a rapid qualitative sensor for methanol and ethanol

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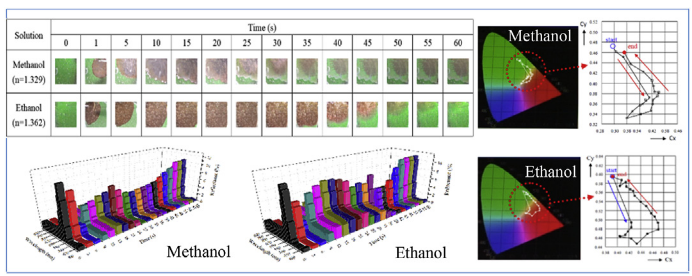
HIGHLIGHTS

- Opal-like array of polystyrene (PS) microspheres is synthesized by self-assembly.
- This periodic PS array is used as a rapid sensor for methanol and ethanol.
- Solvents are detected by routes of reflection coordinates in chromaticity diagram.
- They are also detected directly by naked eye based on change in color of sensor.
- The color change is irreversible for methanol but reversible for ethanol.

GRAPHICAL ABSTRACT



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ABSTRACT

Polystyrene (PS) microspheres were synthesized by emulsifier-free emulsion polymerization and arranged in an array of closely packed, opal-like photonic crystals by slow self-assembly through dip-coating. This periodic array of PS microspheres was then employed as a rapid qualitative sensor for methanol and ethanol. Both solvents could be detected rapidly based on the routes of their reflection coordinates in the chromaticity diagram or directly by the naked eye on the basis of the change in color within 1 min once a solvent sample had been placed on the PS photochromic sensor. This opal-like PS sensor can thus not only be employed as a rapid sensor for methanol and ethanol but can also be used as a powerful tool for the fast screening of illicit drugs and toxic chemicals during forensic investigations.

1. Introduction

In 2003, Parker et al. [1] reported that the elytra of the beetle *Pachyrhynchus argus* have properties similar to those of photonic crystals and have a structure similar to that of opal, exhibiting a uniform metallic luster from all viewing angles. Opal is not a perfect photonic crystal but is composed of many smaller crystals with different orientations, such that it can reflect light of different frequencies and produce beautiful structural colors. Owing to the interesting colors and related properties exhibited by biological structures, bioinspired photonic crystals are being explored for use in optical engineering [2], electronic microwave communications

Abbreviations: DRS, dynamic reflection spectra; FESEM, field-emission scanning electron microscopy; PS, polystyrene.

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[3], biomedical applications [4], and agricultural biotechnology [5].

The development of a rapid sensor for methanol and ethanol would be highly beneficial. High-performance liquid chromatography [6], gas chromatography [7], fuchsine sulfurous acid colorimetry [8], and chromotropic acid colorimetry [9] are the methods used traditionally to detect methanol. However, the pretreatments involved in these methods are time consuming and costly, and the testing procedures themselves are tedious.

In the past years, photonic sensors for liquid chemical species have been realized based on the shift in the balanced reflection peak and the change in their structural color. When a solvent infiltrates the voids of an opal solid, the effective refractive index of the entire colloidal crystal increases, because the air is replaced by the solvent, leading to a red shift in the reflection. The reflection wavelength exhibits a linear relationship with the solvent's refractive index, so that the simulated straight line can be used to distinguish between different solvents. There are numerous situations where chemical sensors that are small, portable, easy to handle, and capable of on-line monitoring a chemical species are needed; these should ideally have a visual (i.e., visible to the naked eye) readout. Sensors based on photonic crystals are promising in this respect, particularly because they are not affected by electromagnetic fields [10,11].

It has been reported that, when the wings of the butterfly *Morpho menelaus*, which are blue, are wetted with ethanol, the resulting change in their refractive index causes them to turn green. As the ethanol evaporates, the wings gradually turn blue again [12]. Inspired by the idea of developing photonic sensors similar to these wings, in this study, we fabricated a rapid, qualitative sensor for methanol and ethanol based on an array of polystyrene (PS) photonic crystals.

2. Materials and methods

2.1. Computing required PS particle size

Green light can be observed readily by the naked eye. If one wishes to ensure that green light ($\lambda = 495–510$ nm) is reflected by an array of PS photonic crystals, one can use Bragg and Snell's laws to calculate the required crystal size [13,14]:

$$D = \frac{\lambda}{2\sqrt{\frac{2}{3}\left(n^2 - sin^2\theta\right)}} \quad (1)$$

$$n = \sqrt{n_{sphere}^2 \times 0.74 + n_{air}^2 \times 0.26} \quad (2)$$

where D is the size of the PS microspheres, λ is the reflection wavelength of the PS photonic crystal array (or the opal-like structure), θ is the angle of incidence of the light, and n is the average refractive index of the PS photonic crystal array in Eq. (1). In Eq. (2), n_{sphere} is the refractive index of PS (n = 1.600) and n_{air} is the refractive index of air (n = 1.000). Based these equations, the size of PS microspheres such that they reflected green light was found to be 223–273 nm.

2.2. Fabrication of opal-structured PS sensor

The polymerization procedure used to form the array of PS microspheres was as follows. A mixture of deionized water (90 ml), styrene (10 ml), and 4-styrenesulfonic acid sodium salt (40 mg) was placed in a four-necked flask equipped with a reflux condenser and a mechanical stirrer. After the reaction mixture had been homogeneously mixed, its temperature was raised to 70 °C. Next, a deoxygenated aqueous solution of potassium persulfate (0.9 mg) was added to it. The emulsion polymerization process was stopped after 24 h. Owing to the hydrophobicity of the glass substrate surface, an oxygen plasma treatment was necessary. The oxygen plasma (PCD-150, All Real Technology Co., Ltd.) treatment was performed at a pressure of 300 mTorr using a 20 sccm oxygen flow and an electrical power of 100 W. Next, the PS suspension was diluted with deionized water to a concentration of 20 wt%, and the opal-structured PS microspheres were arranged on the hydrophilic glass surface at a dip-coating rate of 1 μm/s (see Fig. 1) [15].

2.3. Characterization of sensor

The average diameter and size distribution of the PS microspheres in water were determined using a Zetasizer system (Malvern 3000HS, UK). The morphology of the opal-like PS structure was examined with a field-emission scanning electron microscopy (FESEM) system (JEOL JSM-6700F, Japan), which was operated at an accelerating voltage of 15 kV in the secondary electron image mode. The samples were coated with a thin layer of gold by vapor deposition using a vacuum sputtering system (Sputter JEOL JFC-1100C) prior to FESEM characterization. The reflectance spectra and the routes in the Commission Internationale d'Eclairage (CIE)-1931 chromaticity diagram of the solvents tested were determined using a variable-angle multifunctional optical characteristics measuring system (HMT MF-630). This apparatus was equipped with a barium-sulfate-coated standard integrating sphere and a halogen light source. The HMT MF-630 is a high-resolution spectrometer capable of measuring the absorbance, transmittance, and reflectance of solid (film) samples for wavelengths of 300–1100 nm.

3. Results and discussion

3.1. Analysis of opal-like PS structure

3.1.1. Average size and size distribution of synthesized PS microspheres

The average particle size of the synthesized PS microspheres was 242 nm, as determined using the Zetasizer system. Their particle size distribution index was 0.006 (see Fig. 2), indicating that the PS particles were very uniform in size.

3.1.2. Analysis of surface of opal-like PS structure

Fig. 3(a) and (b) show SEM images of the surface and the cross-section, respectively, of the opal-like PS structure. Though a few local defects and vacancies existed in the PS microarray, most of the PS microspheres were uniformly dispersed and arranged in a compact and ordered periodic structure. The stacking thickness of the PS microspheres was approximately 3.63 μm (~15 layers), as evaluated from the SEM image in Fig. 3(b). This orderly arrangement of the PS microspheres was attributable to the balance between the van der Waals attraction and the electrostatic repulsion between the microspheres at the air/suspension interface. In order to improve the ethanol and methanol detection sensitivity of the PS structure, the thickness of the PS microarray was optimized; the optimal thickness was found to be approximately 3.63–4.84 μm (i.e., 15 to 20 layers in thickness). The stacking of an excessive number of PS layers can lead to cracking as well as inhomogeneities in the resulting opal film [16].

The stacking thickness of the PS microspheres on the substrate was the primary factor influencing the reflectance (R%). The PS microspheres arranged on the substrate tended to be white, since the PS suspension was a white emulsion. When the PS suspension concentration was increased from 20 to 100 wt%, the stacking thickness of the PS microspheres on the substrate increased. This