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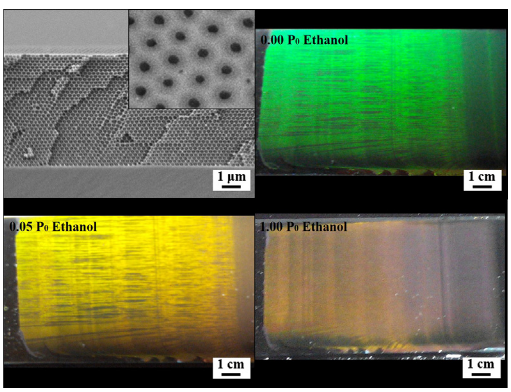
Regular Article

Reusable macroporous photonic crystal-based ethanol vapor detectors by doctor blade coating

Ya-Ling Ko [a], Hui-Ping Tsai [b], Kun-Yi Lin [c], Ying-Chu Chen [a], Hongta Yang [a,*]

[a] Department of Chemical Engineering, National Chung Hsing University, 145 Xingda Road, Taichung City 40227, Taiwan
[b] Department of Civil Engineering, National Chung Hsing University, 145 Xingda Road, Taichung City 40227, Taiwan
[c] Department of Environmental Engineering, National Chung Hsing University, 145 Xingda Road, Taichung City 40227, Taiwan

GRAPHICAL ABSTRACT



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ABSTRACT

This research reports the development of sensitive and reversible vapor detection by using three-dimensional macroporous photonic crystals. A scalable and roll-to-roll compatible doctor blade coating technology is utilized to fabricate flexible macroporous poly(ethoxylated trimethylolpropane triacrylate) (PETPTA) films with hexagonal close-packed pores which are interconnected. The pores are then coated with a layer of poly(2-hydroxyethyl methacrylate) (PHEMA) to create macroporous PHEMA/PETPTA films. The condensation of vapors in the PHEMA coated macroporous films leads to the increase of both the PHEMA swelling degree and the effective refractive index of the diffractive medium, resulting in the red-shift and amplitude reduction of the optical stop bands. The optical measurements reveal that the diffraction from the as-prepared macroporous photonic crystals sensitively monitors the vapor pressure of ethanol since the PHEMA layer displays a great volume dependence on ethanol due to a decreased Flory-Huggins mixing parameter. The dependence of the diffraction wavelength on vapor pressure and the reproducibility of vapor sensing have also been investigated in this study.

1. Introduction

To address rapidly-growing environmental issues and reduce increasingly serious chemosensory irritations in humans, detection and monitoring of volatile chemicals is critical for environmental

* Corresponding author.
E-mail address: hyang@dragon.nchu.edu.tw (H. Yang).

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monitoring, industrial emission control, chemical leak detection, and process monitoring applications [1–3]. Among various volatile chemicals, ethanol is one of the most concerning solvents, which is extensively used in the manufacturing industry, and commonly used as a biofuel additive for gasoline [4]. The ethanol vapor can lead to significant air pollution, involving substantial risks to biodiversity and adverse effects on human neurobehavioral functions [5,6]. Therefore, there is an urgent demand on ethanol vapor sensor developments.

In recent years, various semiconductors, conducting polymers, and electricity-based sensors have been extensively exploited for detecting ethanol vapor [7–9]. Nevertheless, the sensing methodologies suffer from complicated detection processes, high operating temperature, sensitivity to environmental factors, slow responses, and expensive detection equipments, which seriously restrict their developments [10–12]. In contrast, optical chemical sensing displays several advantages over other sensing methods, such as immunity to electromagnetic interface, low toxicity, non-invasiveness, and relatively inexpensive [13–15]. Owing to the novel structural colors and unique optical properties, photonic crystals, periodic dielectric structures with a forbidden gap for electromagnetic waves, have been explored for use in chemical vapor detections [16–18]. Capillary condensation of a condensable vapor in the voids of photonic crystals results in an increase of the effective refractive index of the diffractive medium, leading to a red-shift of the optical stop bands [19]. The reflection wavelength shift exhibits a linear relationship with vapor partial pressure, indicating that the colorimetric method offers a promising platform for chemical vapor sensing [20].

To date, a number of photonic crystal-based ethanol vapor sensors have been developed and exhibit great advantages in miniaturization, portability, short response time, on-line monitoring capability, security and stability [21–23]. However, the developments of photonic crystal-based sensors are impeded by the inferior vapor adsorption abilities and thus the sensitivity of vapor sensing are restricted [24,25]. To solve the problems, distinct surface groups, reagent dyes, or chemical indicators are employed to offer photonic crystals different responding properties, which providing higher sensitivity and selectivity towards the ethanol vapor [26–28]. Nevertheless, most of the preparations are relative complex and the displacement assays are time consuming. Moreover, once the labeled analyte is exhausted, refilling is needed unless the sensor will only be used once or for a short period of time. Recently, three dimensional periodically structured hydrogels, which are responsive to various chemical stimuli, have also been widely used as optical chemical sensors. The hydrogel swells in the presence of certain analytes, increasing lattice spacing, and consequently the diffraction peak shift towards longer wavelength. A number of strategies have been investigated to fabricate three dimensional ethanol-responsive hydrogel photonic crystals [29–33]. Although the vapor sensing performances are improved, the application and removal of stimuli leads to complex deformation of hydrogels, causing inhomogeneous expansion/shrinking with different magnitudes in different directions [34]. The deformation of samples results in deteriorated optical sensitivities of hydrogel photonic crystals. Furthermore, compared to complex lithography-based fabrication technologies, the use of spontaneous crystallization of monodisperse colloidal particles as templates is a simple and inexpensive approach for developing photonic crystals [35–37]. Unfortunately, most of the existing colloidal self-assembly methodologies, including capillary force-induced self-assembly, evaporation-induced convective assembly, assembly at the air-liquid interface, gravity sedimentation, and electrical field-induced self-assembly, suffer from low throughput and are favorable only for low volume, laboratory-scale production [38–44].

In this study, we report a sensitive and reversible detection of ethanol vapor by using three dimensional macroporous polymer photonic crystals, which are fabricated by a scalable and roll-to-roll compatible colloidal self-assembly approach. Most importantly, the as-prepared ethanol sensors featuring a highly visible readout are portable, small, handy, and readily responsive.

2. Scalable fabrication of macroporous photonic crystals

Three-dimensional (3D) macroporous polymer photonic crystals are fabricated by a scalable doctor blade coating technology [45]. Typically, monodispersed silica colloids are first synthesized by the StÖber method and then dispersed in ethoxylated trimethylolpropane triacrylate (ETPTA) monomer with 2-hydroxy-2-methyl-1-phenyl-1-propanone as a photo-initiator [46]. The silica colloid volume fraction is controlled to be 74 vol.%. A doctor blade is introduced to spread the silica colloidal suspension uniformly on a glass substrate, and to offer a one-dimensional shear force to align silica colloids [47]. The suspension is then photopolymerized to obtain a silica colloidal crystal-polymer composite. As shown in Fig. 1, the embedded silica colloids can be etched away with a 1 vol.% hydrofluoric acid aqueous solution. The resulting macroporous polymer film is immersed in a mixture of 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MMA), polyethylene glycol (PEG), ethanol, and azobisisobutyronitrile (AIBN) as a photo-initiator, following by a spin-coating process to remove the HEMA mixture retained on the film surface. After storing in dark for one hour to allow residual ethanol to evaporate,

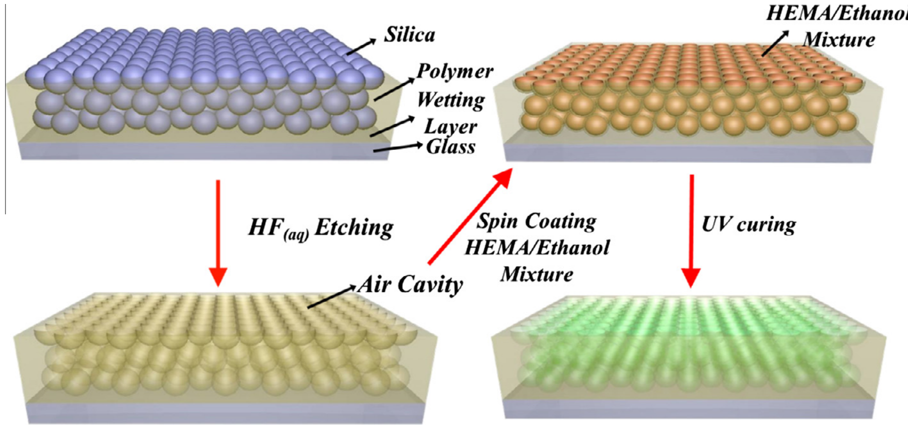

Fig. 1. The experimental procedure for fabrication of macroporous polymer photonic crystals.