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Cellulose photonic crystal film sensor for alcohols

Fengyan Wang[a], Zuogang Zhu[b], Min Xue[a,*], Fei Xue[a], Qiuhong Wang[a], Zihui Meng[a,*], Wei Lu[a], Wei Chen[a], Fenglian Qi[a], Zequn Yan[a]

[a] School of Chemical Engineering & Environment, Beijing Institute of Technology, Beijing 100081, PR China
[b] Beijing Municipal Institute of Labor Protection, Beijing 100054, PR China

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ABSTRACT

A novel photonic crystal sensor, a cellulose film with a three dimensional (3D) colloidal array embedded inside, was fabricated by infiltrating the voids of a 3D poly methyl methacrylate (PMMA) colloidal array with methyl cellulose aqueous solution, followed by thermal curing. When the obtained cellulose photonic crystal film sensor (CPCFS) was immersed in alcohols, including ethanol, n-propanol, isopropanol and n-butanol, its lattice constant and mean effective refractive index increased, which led to the redshift of the reflection of incident light. The redshift of this sensor had linear response to the concentration of alcohol vapors, while its structural color changed from blue to green visually. This CPCFS demonstrates promising potential as an on-site monitoring sensor for alcohols and an inexpensive and minimally invasive breathalyzer in the future.

1. Introduction

Nowadays, with the fast growth in economy and civilization, people pay more attention to the health issues which are adversely affected by serious environmental pollutions [1]. Among all the pollutants, volatile organic compounds (VOCs) have attracted more and more concerns in recent years. VOCs have high vapor pressure at room temperature and are difficult to disperse, which makes people easily be exposed to them for long term and eventually is harmful to human health. Alcohols, including ethanol, n-propanol, isopropanol and n-butanol, are the common compounds as VOCs. Ethanol is an important raw material in chemical industry, but long-term exposure to ethanol vapors leads to nausea, headache, dizziness and cancer [2–4]. Isopropanol is widely used in the manufacture of paints and printing, but the emission of isopropanol can be photochemical oxidants which cause "summer smog" and destroy the body's respiratory system and eyes. The serious toxicities of alcohols mean that it's in an urgent demand to develop sensor techniques to monitor them on site.

Monkawa et al. developed a high sensitive sensor with wide dynamic range localized surface plasma resonance for VOCs [5]. Deo et al. reported an ultrasonically sprayed nanostructured $CdSnO_3$ thin film to detect isopropanol vapors [6]. However, almost all conventional sensors involve high-cost and complicated process, and the response cannot be visually detected. Recently, Winther et al. developed a novel biosensor which detected alcohol vapor sensitively by immobilizing enzymes on a breathable electrode, but its output showed unstable with conventional long-term storage [7]. An easy-to-operate, stable and economical sensor technique is in an urgent need for the sensing of alcohols. Moreover, to control the drunken driving on the road, it is also pressing to develop a sensor to monitor ethanol in human body [8,9].

Colloidal arrays with periodically arranged 3D structures can be assembled from monodispersed colloidal particles [10,11]. In a perfect colloidal array, only the light of a certain wavelength can propagate through it, which suggests the existence of photonic band gap (PBG) [12,13]. If the PBG is located in the visible-light region, the light reflected by the colloidal array is visible to the naked eyes [12–15]. Sensors that utilize the optical properties and superior sensitivity of colloidal array have already been achieved. Asher's group developed an ammonia sensitive material by coupling the Berthelot reaction to the polymerized crystalline colloidal array (PCCA), which can be used as a point-of-care device for the detection of blood NH_3 concentration [16]. Recently, colloidal arrays incorporated with hydrogel have been reported for the sensing of alcohols [10,17,18]. For example, Zeng et al. developed a polyacrylamide inverse opal hydrogel to detect liquid alcohols [19]. However, the inverse opal hydrogels were synthesized by the templated hydrogel preparation, which uses colloidal array as nanoscale template at first, and then etches away the template to obtain an interconnected porous structure. Such procedure is time-consuming, and the composition of conventional hydrogel is

* Corresponding author. Tel./fax: +86 10 68913065.
E-mail addresses: minxue@bit.edu.cn (M. Xue), m_zihui@yahoo.com (Z. Meng).

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not environmental friendly. In addition, the usability of hydrogel materials after long term storage cannot be guaranteed either.

As one of the most versatile biopolymers in nature, cellulose nanocrystals (CNCs) extracted from wood pulp or cotton were assembled into a chiral nematic liquid crystal in water [20,21]. The obtained order can selectively reflect circularly polarized light that has a wavelength matching the pitch [22]. Some researchers have already fabricated free-standing films with mesoporous structures using CNCs as templates for the applications including catalysis, separation and sensing [23,24]. Simultaneously, other cellulose derivatives were doped into the microstructured optical fibers to increase the sensitivity of sensor probe or for imaging *in vivo* [25–27]. Sahcear et al. reported a new strategy to build large-scale solvent-responsive elastomeric opal films, in which hard-soft core-interlayer-shell (CIS) beads were used to prepare paper-supported elastomeric opal films with remarkably distinct iridescent reflection colors. Due to the high porosity of the paper-sheets used, these composite films could be easily swelled by various solvents. The swelling changed the crystalline lattice of the opals which provoked a tremendous photonic band gap shift and also enhanced the brilliance of these colors. This approach became the basis of a whole family of polymer-based soft sensors with a fascinating optical response [28].

Herein, we constructed a sensor by embedding a 3D colloidal array inside the cellulose film, and investigated its response to VOCs, such as alcohols, formaldehyde, toluene and acetone. Compared with the conventional photonic crystal with 3D inverse opal structure, the preparation process of this cellulose photonic crystal film sensor (CPCFS) was easy-to-operate and cost-efficient, which only needs self-assembling and following curing. This cellulose-based photonic crystal sensor is expected to become a promising sensing material for the *in situ* detection of alcohols by the naked eye.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) was purchased from J&K Scientific Ltd and treated with Al_2O_3. Potassium peroxydisulfate (KPS) was obtained from Xilong Chemical Co. Ltd. Methyl cellulose (MC) was obtained from Aladdin Industrial Inc. Methanol, ethanol, n-propanol, isopropanol, n-butanol, toluene, trioxymethylene, acetone and sulfuric acid (98%) were purchased from Beijing Chemical Plant, and hydrogen peroxide (30% water solution) was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. Glass slides (20 × 20 mm) were obtained from Weiss Experiment Products Co. Ltd. and washed with H_2SO_4/H_2O_2 (7/3, v/v) solution for 12 h, followed by being rinsed with ultra pure water in an ultrasonic bath for three times before usage [29].

2.2. Apparatus

The reflection spectra were recorded using an Avaspec-3648TEC optical fiber spectrometer (Avantes) with an AvaLight-DH-S-BAL light source and a FC-UV600-2-SR fiber optic reflection probe. The assembly of colloidal array was carried out within a Safe HWS-150 incubator (Haishu). The heating process was carried out in a DNP-9022 electro-thermal incubator (Jinghong). SEM images were obtained from a QUANTA FEG 250 field emission scanning electron microscope (FEI). The Z-average diameter was measured using a Zetasizer dynamic light scattering (DLS) device (Malvern).

2.3. Fabrication of CPCFS

The monodispersed PMMA colloidal particles were prepared according to the literature [29]. MMA (6 ml) and ultra pure water (139 ml) were mixed and heated in a four-neck round-bottom flask which was equipped with a nitrogen inlet tube, a water cooled reflux condenser, a mechanical stirrer and a digital thermometer. The initiator KPS (0.3 g dissolved in 5 ml ultrapure water) was added into the mixture at 80 °C. The stirring rate was kept at 300 rpm and nitrogen was bubbling to remove oxygen throughout the reaction. Monodispersed PMMA colloidal particles obtained after 45 min. The suspension was separated by centrifugation at 6000 rpm for 5 min with discharging the supernatant. Particles were cleaned with ultra pure water for three times.

The process of CPCFS fabrication was shown in Scheme 1. After self-assembly of PMMA particles on the surface of glass slides, the obtained opal was infiltrated with methyl cellulose aqueous solution (3% g/ml) and was subsequently incubated in an incubator at 60 °C for 3 h.

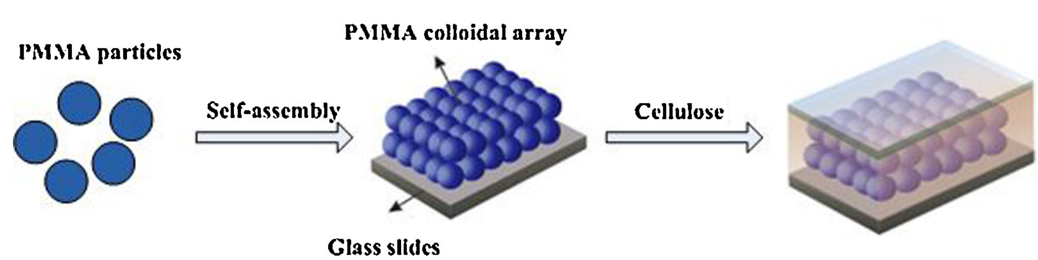
2.4. Detection of VOCs by CPCFS

The obtained CPCFS was cut into 7 × 7 mm in size. To investigate the response of CPCFS to liquid alcohols, we first recorded the original reflection wavelength of CPCFS by optical fiber spectrometer, and then fixed it at the bottom of weighing bottle (50 mm × 30 mm). After that, alcohols were added and the reflection wavelength was measured. All of the experiments were repeated for three times. To respond to the saturated alcohol vapors, the CPCFS was attached to the inner side of the lid of a weighing bottle (50 mm × 30 mm), which was sealed after the injection of 1 ml solvents. When the bottle was saturated by vapors, the reflection of the cellulose film was recorded. In order to detect vapors of different concentrations, the CPCFS was fixed inside an air bag (0.5 l). After that, the air bag was filled with nitrogen to the specific volume, and different volumes of alcohols were injected into the air bag through an injection port. After the complete evaporation of alcohols, the CPCFS was taken out from the air bag and its reflection wavelength was recorded immediately.

3. Results and discussions

3.1. Characterization of CPCFS

The SEM image (Fig. 1(a and b)) shows a periodicity and uniformity in the prepared CPCFS. The mean diameter of PMMA particles



Scheme 1. Fabrication of CPCFS.