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ScienceDirect

Photonics and Nanostructures – Fundamentals and Applications 19 (2016) 48–54

PHOTONICS AND NANOSTRUCTURES Fundamentals and Applications

www.elsevier.com/locate/photonics

Fabrication of titania inverse opals by multi-cycle dip-infiltration for optical sensing

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Received 10 October 2015; received in revised form 18 February 2016; accepted 22 February 2016
Available online 2 March 2016

Abstract

We have demonstrated a low-cost method to fabricate TiO_2 inverse opal photonic crystals with high refractive index skeleton. The TiO_2 inverse opal films were fabricated from a polystyrene opal template by multi-cycle dip-infiltration-coating method. The properties of the TiO_2 inverse opal films were characterized by scanning electron microscopy and Bragg reflection spectroscopy. The reflection spectroscopic measurements of the TiO_2 inverse opal films were compared with theories of photonic band calculations and Bragg law. The agreement between experiment and theory indicates that we can precisely predict the refractive index of the infiltrated liquid sample in the TiO_2 inverse opal films from the measurement results. The red-shift of the peak wavelength in the Bragg reflection spectra for both alcohol mixtures and aqueous sucrose solutions of increasing refractive index was observed and respective refractive index sensitivities of 296 and 286 nm/RIU (refractive index unit) were achieved. As the fabrication of the TiO_2 inverse opal films and reflection spectroscopic measurement are fairly easy, the TiO_2 inverse opal films have potential applications in optical sensing.

Keywords: Inverse opal; Optical sensing; TiO_2; Surface sol–gel process

1. Introduction

In recent years, tunable colors in opal and inverse opal (IO) photonic crystals (PhCs) have attracted enormous attentions for applications in chemical and biological sensing as well as surface-enhanced spectroscopy [1–5]. Such structures process the so-called photonic band gap (PBG) that forbids light within a range of frequencies to propagate through them, resulting in reflection [6]. For optical sensing, the modification of PBG occurs as the changes of lattice constants and/or average refractive index (RI) due to the infiltration of a liquid sample into the structure [7–13].

The PBG of opal and IO PhCs, which relates to lattice constant and average RI, can be predicted by Bragg

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http://dx.doi.org/10.1016/j.photonics.2016.02.004
1569-4410/

equation [14,15]. The wavelength of reflection peak at normal direction (1 1 1) planes is given by

$$\lambda_{peak} = 2d_{1\,1\,1}n_{eff}$$

where $d_{1\,1\,1}$ is space between (1 1 1) planes, and effective refractive index (n_{eff}) can be determined by RIs of spherical voids (n_{voids}) and solid backbone ($n_{backbone}$) with filling fraction of material (f) by the following expression [14,15].

$$n_{eff} = (1 - f)\,n_{voids} + fn_{backbone}$$

The pioneering work of Asher and coworkers, using the approach of polymerized colloidal crystal arrays (PCCAs), observed reflection peak change due to the alteration of opal lattice constants caused by the interaction of an analyte with an opal PhC [7,8,16]. However, there are limitations in the selection of materials and processes to form the PCCAs [11]. An alternative approach involves the change of average RI of opal or IO during the sensing process. According to Bragg's law, IOs are expected to have higher sensing sensitivity [10] because they have much larger void space (74%) than those of opal structures (26%), thus allowing larger variations in n_{eff}. Furthermore, it has been demonstrated that a higher difference in RI contrast between the IO backbone and the medium is beneficial to increase sensing sensitivity [9]. Thus, TiO_2 IO is a good choice, because TiO_2 material has high RI [17] which results in high RI contrast to fulfill the requirement of PhC sensors [18]. Furthermore, fabrication of TiO_2 IO is a simple and cost effective process, which can be obtained based on silica (SiO_2) or polystyrene (PS) opal templates [18,19].

Although fabrication methods for making high filling fraction IO structure such as electro-deposition, chemical vapor deposition (CVD), and atomic layer deposition (ALD) have been reported [19–21], electro-deposition of TiO_2 requires a high cathodic potential and a conductive substrate while the CVD and ALD methods are high-cost methods. It should be noted that an 88% high filling fraction was achieved by the ALD method for making TiO_2 IO structure [19]. Nevertheless, an alternative low-cost method is desirable.

In this work, TiO_2 IO films with skeleton of relatively high RI were fabricated by multi-cycle dip-infiltration-coating method. The fabrication process of the TiO_2 IO films includes two steps. First, large-area PS opal templates were prepared by the thermal assistant cell method. Second, a stepwise adsorption of alkoxide, so called "surface sol–gel process", was used to fabricate the TiO_2 IO films from the opal templates. To investigate refractive index sensitivity, different liquid samples with various RIs were filled inside the TiO_2 IO to produce a shift of the reflection peak. Analysis of the change of reflection peaks demonstrates that the TiO_2 IO exhibits high refractive index sensitivity to the infiltrated liquid sample. Since a change of effective refractive index inside the pores of the TiO_2 IO films will cause a shift of the peak wavelength in the Bragg reflection spectrum, the TiO_2 IO films have an application potential in chemical and biochemical sensing [9,10,13,22]. This work demonstrates the feasibility of using the TiO_2 IO films as an optical sensor for refractive index sensing.

2. Experimental

2.1. Chemicals

The following chemicals, absolute ethanol (J.T. Baker), methanol (J.T. Baker), titanium(IV) isopropoxide (Sigma), octadecyltrichlorosilane (Aldrich), and chloroform (Mallinckrodt), were used as received. Ultrapure water (18.2 MΩ/cm, Millipore) was used to prepare all aqueous solutions.

2.2. Fabrication of TiO_2 inverse opal

Fig. 1 shows a schematic illustration for preparation of TiO_2 IO films. First, PS opal templates with large area were fabricated by self-assembly processes with thermal-assistant cell method (Fig. 1(a)) [23]. The monodispersed PS spheres of 300 nm (4% w/v, IDC Latex) with 10 wt.% in water were injected into a confinement cell, which was composed of two glass substrates ($35 \times 25\ mm^2$) with 20 μm thickness of SU-8 photoresist spacers at the two edges. The top glass substrate was made hydrophobic by treatment with 3 mM octadecytrichlorosilane (ODTS, $CH_3(CH_2)_{17}SiCl_3$) for 20 min. The PS spheres were self-assembled on the bottom substrate by capillary force, and dried at room temperature (~25° C). The mechanical stability of the self-assembled layer of PS spheres was improved by heating at 105° C for 10 min. Then, the top substrate was removed and an opal template was obtained on bottom substrate.

Second, the TiO_2 precursor was infiltrated into the voids of the PS opal template (Fig. 1(b)) by dipping the PS opal template into a solution of 5% v/v of titanium(IV) isopropoxide ($Ti(i\text{-}OPr)_4$) in ethanol for 5 s, then the specimen was took out slowly and allowed to dry. Subsequently, the specimen was re-dipped into the solution and such a dipping and drying cycle was repeated for 15 times. Finally, we slowly heated the specimen in a vacuum oven for 2 h starting at room temperature until a final temperature of 500° C with a rate of