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Hierarchical opal grating films prepared by slide coating of colloidal dispersions in binary liquid media

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ABSTRACT

There are active researches on well ordered opal films due to their possible applications to various photonic devices. A recently developed slide coating method is capable of rapid fabrication of large area opal films from aqueous colloidal dispersion. In the current study, the slide coating of polystyrene colloidal dispersions in water/i-propanol (IPA) binary media is investigated. Under high IPA content in a dispersing medium, resulting opal film showed a deterioration of long range order, as well as a decreased film thickness due to dilution effect. From the binary liquid, the dried opal films exhibited the unprecedented topological groove patterns with varying periodic distances as a function of alcohol contents in the media. The groove patterns were consisted of the hierarchical structures of the terraced opal layers with periodic thickness variations. The origin of the groove patterns was attributed to a shear-induced periodic instability of colloidal concentration within a thin channel during the coating process which was directly converted to a groove patterns in a resulting opal film due to rapid evaporation of liquid. The groove periods of opal films were in the range of 50–500 μm, and the thickness differences between peak and valley of the groove were significantly large enough to be optically distinguishable, such that the coated films can be utilized as the optical grating film to disperse infra-red light. Utilizing a lowered hydrophilicity of water/IPA dispersant, an opal film could be successfully coated on a flexible Mylar film without significant dewetting problem.

1. Introduction

Three-dimensional (3D) photonic crystals of submicrometer wavelength range have gathered much attention due to its potential applications to photonic devices such as microlasers [1,2] optical waveguides, and chemical sensors [3,4]. Among various fabrication strategies for the 3D photonic crystal scaffolds, artificial opal films are frequently utilized as they can be readily obtained from self-assembly process of monodisperse microspheres (diameter = 0.1–1 μm) in the liquid media. If the surface of microsphere is polar enough to be dispersed in water, strong capillary forces between microspheres induce the ordered arrangements of the particles into an opal film upon water evaporation. The resulting opal film exhibits shiny reflective color, so called structural color depending on the particle size due to Bragg diffraction of visible light from the periodic [1 1 1] facets of face centered cubic (fcc) crystalline structure within the opal film. Various fabrication methods for capillary-induced opal films have been developed such as dip-coating [5–8], direct-coating [9,10], and capillary method [11–13]. Dip-coating method has been commonly adopted since it provides high quality opal films, while the process is too slow and consumes too much colloidal dispersion. In the capillary methods, the colloidal dispersion is filled within the capillary channel and subsequently dried. This method is much faster than dip-coating, and the resulting opal film conforms to the shape of capillary channel. Recently, direct coating method has been reported to be capable of rapid fabrication of large area opal films. P. Jiang and coworkers utilized Doctor Blade™ to spread the colloidal suspension which subsequently dried to form well-ordered opal film with area of 10 cm^2 within 30 min [14]. Lee et al. have also demonstrated a slide coating method in which a large area polymeric opal films were fabricated less than an hour by supplying hot air to the colloidal suspension between the slide glasses to accelerate water drying. This method was simple yet effective way to produce polymer opal films [15] or binary films of polymer opal and TiO_2 nanoparticles filling the interstices [16]. In slide coating

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method, colloidal dispersions have been prepared in water to maximize the capillary force. However, it is desirable to test various polar solvents or their mixtures as dispersing agent of the colloidal particles to extend the applicability of the coating method.

In this study, the polystyrene (PS) colloidal dispersions in water/alcohol binary mixture are slide-coated on glass substrate by controlling the alcohol content. Morphological changes and surface structures of the resulting opal films accompanied in the course of film coating process are rigorously characterized [15].

2. Experimental

2.1. Synthesis of PS colloids

Spherical PS colloidal particles with two different particle sizes were synthesized by a typical emulsion polymerization method using potassium persulfate (PPS, Aldrich) and sodium dodecylsulfate (SDS, Aldrich) as a radical initiator and a surfactant respectively. Synthetic details are almost the same as described in the previous report [17]. Owing to the sulfate groups of PPS, the surface of the resulting colloidal particles is negatively charged in water, and therefore a stable aqueous colloidal dispersion is obtained. The synthesized PS particles were dialyzed using a semipermeable cellulose membrane (MWCO 12,000–14,000, MFPI) within deionized water for 2 weeks for purification, and the final aqueous dispersions contained 10 wt% solid contents. Two PS colloidal systems synthesized in this study were PS240 and PS 280 indicating that the average diameters of the PS colloids are characterized to be 240 nm and 280 nm respectively by using scanning electron microscopy (SEM, S-4700, HITACHI).

2.2. Slide coating of colloidal dispersions

As shown in Fig. 1(a), the apparatus for slide coating has a very simple configuration composed of top and bottom slide glasses, Teflon™ tape spacers (thickness ~ 200 μm) attached on each side of a bottom slide which is slowly pulled out by a syringe pump (KD scientific) at the controlled speeds. An aqueous PS dispersion was mixed with 2-propanol (IPA, 99%, Aldrich) at various mixing ratios, and then was infiltrated to a thin space between two slide glasses. As the bottom substrate moves out at a programmed speed, the colloidal self-assembly takes places at the drying front aided by hot air blown onto the drying film surface. The coated opal films were analyzed by SEM and a digital single lens reflex (DSLR) camera (DSLR-A550, SONY). The reflectance of a film was measured using a fiber optic UV–Vis spectrometer (AvaSpec, Avantes) connected to the reflected light microscopy (L2003A, Bimeince) through an objective lens (20×/0.30NA) as shown in Fig. 1(b). In each measurement, the raw data of reflected signal from the sample were referenced by a silver mirror (Edmund optics).

3. Results and discussion

The PS particles were initially dispersed in water, and subsequent addition of alcohol changed the physical property and the concentration of the dispersion. For both PS240 and PS280, the five colloidal dispersions in water/IPA with 25%, 40%, 50%, 60%, and 75% of IPA volume ratios were prepared, which respectively contained 7.5%, 6%, 5%, 4%, and 2.5% of PS particles. Those dispersions were slide-coated on clean glass slides at an optimized coating speed of 1 mm/min which provided the best film quality compared to other coating speeds [18]. (see Fig. S1 in supplementary material for the films prepared at various speeds.) Shown in Fig. 2(a)–(e) is the photographs of the opal films from the five dispersions of PS280 in order of increasing IPA content exhibiting red reflective colors owing to the Bragg diffraction of light from fcc (1 1 1) planes of opals. (The five sequential films from PS240 are shown in Fig. S2.) The color becomes less intense as the IPA content increases in the dispersion due to weakening in long-range order of colloidal crystals. The surface morphologies of the opal films are shown in Fig. 2(f)–(j) which reveal gradual deterioration of the hexagonal packing and increasing tendency of the defect densities with increased IPA content. For Fig. 2(f)–(j), the loosened hexagonal packing and occurrence of the linear dislocations such as the breakage of hexagonal lattice are dominant among which Fig. 2(j) (a film from 75% IPA) is most serious. The cross-sections of the films shown in Fig. 2(k)–(o) also present the changes in opal film qualities, along with the thickness decreases due to the dilution effect. Relatively random orientation of the colloidal film from a 75% IPA dispersion resulted in a weakening of a red reflective color. The quality of the opal film represented by the reflective color can be more rigorously traced by reflectance measurement of light under normal incidence, in which peak reflectance (λ_{peak}) has a linear relationship with particle size (d) by a modified Bragg equation as shown in Eq. (1) [15]:

$$\lambda_{peak} \sim 1.633 \cdot d\left(f_{PS} \cdot n_{PS}^2 + f_{air} \cdot n_{air}^2\right)^{1/2} = 1.633 \cdot d \cdot n_{eff} \quad (1)$$

where f and n_{eff} stand for the filling factor and the effective refractive index of the opal film. For a perfect fcc lattice of PS with n_{PS} ~ 1.59, one can assume $f_{PS} = 0.74$ and n_{eff} will approximately be 1.46. In Fig. 3(a), the typical reflectance spectra from five PS240

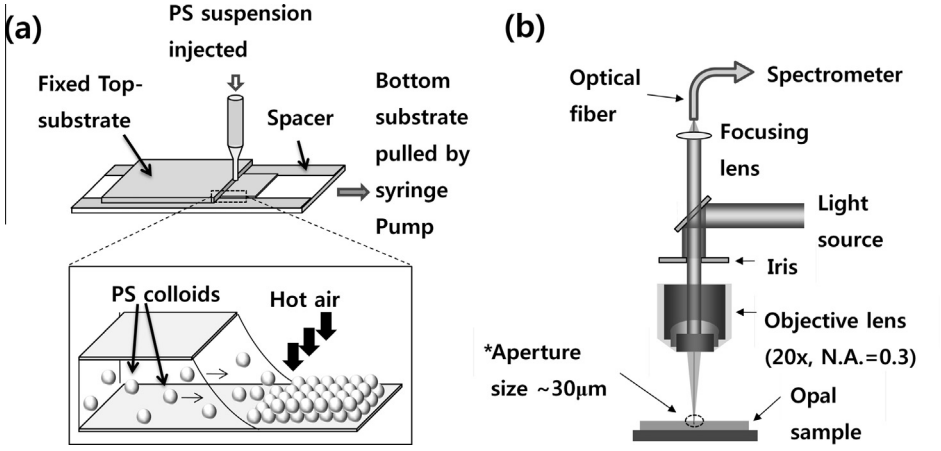

Fig. 1. Schematic illustration of (a) slide coating of PS dispersion and (b) reflectance measurement by UV–Vis spectrometer coupled with optical microscope.