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Rapid on-chip integration of opal films and photonic gel sensor array via directed enhanced water evaporation for colloidal assembly

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ABSTRACT

We developed a fabrication method for colloidal photonic crystal films and arrays with high quality and uniform thickness without need for any lithography. The method, “directed enhanced evaporation for colloidal assembly” (DEECA), employs a two-step process: a capillarity-induced infilling of an aqueous dispersion of colloidal particles within the thin two-dimensional (2D) channel arrays, followed by enhanced evaporation of water through the inlet, leading to laminar flow of the colloidal dispersion and subsequent colloidal crystallization. DEECA was confirmed to be a fast, precise and a cost-effective process with minimum loss of colloidal particles for preparing multiple opalline scaffold structures toward on-chip integrated photonic bandgap device arrays. To prove this, 2D arrays of poly(hydroxyethylmethacrylate) (PHEMA)-based inverse opal (IO) photonic gel pH sensors were fabricated via templated-photopolymerization of the precursor mixtures within the DEECA cells. It was confirmed that on-chip integrated photonic gel pH sensor arrays could be successfully implemented by using opal templates prepared via DEECA. DEECA could also be utilized for opal-templated fabrication of TiO_2 inorganic IO film arrays on a glass substrate.

1. Introduction

For the past decade, two-dimensional (2D) and three-dimensional (3D) close-packed structures of submicron-sized colloidal particles have been extensively studied since they are useful scaffold structures for various photonic crystal devices, such as photonic gel sensors [1–6], reflective displays [7], solar cells [8–10], and others [11–13]. Three-dimensional close-packed colloidal crystals, which are also known as synthetic opals, can be fabricated by spin coating [14], vertical deposition [15,16], and direct coating [17,18] from charge stabilized colloidal suspensions in aqueous media. The driving force of the close-packed structure of synthetic opal is primarily based on the capillarity of evaporating water [19]. When a synthetic opal is fabricated via the capillary force of drying solvent, the colloidal crystal film produced usually possesses a face centered cubic (FCC) {111} facet parallel to the glass substrate, which has the least surface energy compared to other facets. Such {111}-faceted colloidal crystals can be effectively utilized as templates for highly reflective photonic crystals. The synthetic opal film can either be formed on a flat substrate or in between two glass plates. As an example of the former, fabrication of colloidal crystal films was demonstrated by spin-coating a concentrated colloidal dispersion in liquid mixtures with varying composition [14]. Depending on the spin rate and solvent composition, large-area colloidal crystals were obtained with controlled crystalline orientations and film thicknesses. Jiang et al., reported that controlled drying of a colloidal suspension enables vertical coating of a high-quality opalline colloidal crystal on a glass substrate [16]. The method has been improved by Vlasov et al., by applying thermal agitation of the suspension to prevent sedimentation of the colloidal particles during vertical coating [15]. Park and coworkers reported a rapid fabrication of colloidal crystal films by vertical coating of a colloidal suspension via solvent evaporation aided by nitrogen flow [20,21]. However, the vertical coating methods produce a large amount of wasted colloidal dispersion after the coating process. Recently, we presented a horizontal coating process with continuous addition of colloidal suspension, which

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exhibits rapid colloidal crystallization without significant loss of the colloidal suspension [18]. A simple design of the coating device enabled rapid fabrication of a large-area colloidal crystal ($2 \times 2\,cm^2$) within 20 min, and the colloidal crystal film could also be coated on a flexible polymer film by preparing a colloidal dispersion in an alcoholic medium [22]. A major drawback of the coating methods mentioned thus far is that it is difficult to obtain a uniform opal film with a predefined thickness, and therefore the infilling of functional materials within the opal template can be tricky. An opal film with a desired thickness can be fabricated by crystallizing the colloidal dispersion within a thin 2D channel. Park et al., have developed a method to fabricate large-area opal films with a defined thickness and area by flowing an aqueous colloidal dispersion within a rectangular space while water is drained through a lithographically defined thin channel [23]. An opal film within a flow cell can be appropriately used as a scaffold structure for the subsequent formation of functional devices such as inverse opal (IO) hydrogel sensors. However, the fabrication time to obtain a $1\,cm^2$ opal film was several weeks because of the slow drainage of water through the thin channel. Miguez et al., developed a method called assisted directed evaporation-induced self-assembly (ADEISA), where the exact addressing of a colloidal crystal within a very thin channel was demonstrated toward sophisticated photonic bandgap devices [24]. In this study, we demonstrate a simple and rapid fabrication method for 2D opal film arrays, in which enhanced water evaporation induces rapid colloidal self assembly within individual channels on a single substrate. The usefulness of the opal film arrays was tested by utilizing them as template structures for the fabrication of IO photonic gel sensors.

2. Materials and methods

2.1. Preparation of PS μ-spheres, silica μ-spheres, and TiO_2 nanoparticles

Polystyrene (PS) μ-spheres with various particle sizes and narrow size distributions were synthesized by emulsion polymerization as reported elsewhere [25]. After purging temperature-stabilized deionized (DI) water under N_2 flow for 1 h, potassium persulfate (Aldrich) as an initiator and sodium dodecylsulfate (SDS, Aldrich) as a surfactant were added, followed by the quick addition of styrene (Aldrich), which had been filtered through activated alumina to remove the inhibitor. After finishing polymerization at 70 °C for 4 h, the as-synthesized polymer dispersion was filtered through pre-cleaned cotton fibers and poured into a semi-permeable cellulose membrane tube (MWCO 12,000–14,000, MFPI). The emulsion-filled tube was fully soaked in a 5-L beaker containing DI water. The low molecular weight impurities in the tube were removed in this manner. Fresh DI water was exchanged every 4 h until the resistivity of the DI water in the beaker reached 10 MΩ. The final aqueous dispersions contained ∼10 wt% of polymer μ-spheres. By controlling the amount of SDS in the reaction batch, seven PS μ-spheres with different particle sizes were synthesized. The average particle sizes characterized by scanning electron microscopy were 197 nm (PS 197), 226 nm (PS 226), 228 nm (PS 228), 238 nm (PS 238), 240 nm (PS 240), 260 nm (PS 260), 267 nm (PS 267), and 300 nm (PS 300), respectively. The average particle size and size distribution of the colloidal dispersion were characterized using an electrophoretic light scattering analyzer (ELS 8000, Otsuka electronics Co.). All the μ-spheres showed a size distribution with a standard deviation of 5%.

Silica μ-particles with two different sizes of 245 nm and 268 nm were synthesized by a typical Stober process [26]. First, a mixture A containing 0.8 M of ammonium hydroxide (Aldrich) in DI water and a mixture B containing 0.1 M (or 0.2 M) of tetraethylorthosilicate (TEOS, Aldrich) in ethanol (Aldrich, spectrophotometric grade) were prepared. Mixtures A and B were mixed with a 1:1 volume ratio with vigorous stirring at 30 °C, and the sol–gel reaction proceeded for 3 h. The precipitate was centrifuged at 4000 rpm for about 10 min, and then the sediments were washed with distilled water five times.

Organically modified TiO_2 nanoparticles with an average particle size of 2 nm were synthesized by the sol–gel method in the presence of acetylacetone as an organic modifier [27]. A mass of 5.006 g of acetyl acetone (AcAc) (Aldrich) was added to a round bottom flask containing 34.06 g of 1-butanol (Duksan Chemical) with vigorous stirring. Subsequently, 17.018 g of titanium *n*-butoxide (Aldrich) was slowly added, and then the solution turned bright yellow upon mixing. While maintaining the reactor temperature at 60 °C, 1.9022 g of *p*-toluene sulfonic acid (Aldrich) dissolved in 9 g of deionized (DI) water was added drop-wise to the precursor solution to conduct the sol–gel reaction for 24 h. The yellow product was precipitated in an excess amount of toluene, and the precipitate was subsequently centrifuged, washed with toluene and vacuum dried.

2.2. Fabrication of the multi-DEECA cell assembly

The cell assembly consisted of three major parts. All of the glass parts were cleaned with Piranha solution (H_2SO_4:H_2O_2 = 3:1 by volume) and rinsed with DI water several times prior to use. The bottom substrate was a flat rectangular glass plate ($4 \times 5\,cm^2$). The top glass plate of the same size had drilled holes (diameter = 1 mm) that were placed at the top centers of the individual cells, and it was rendered hydrophobic using 1 mM trichlorooctadecylsilane dissolved in 2,2,4-trimethylpentane (Junsei) for 20 min. In order to provide three thin spaces between two plates, 25-μm-thick Surlin® film was cut into 4.5 cm-long lanes with a width of 0.7 cm and a spacing of 0.3 cm between each lane, which had open ends for infiltration of the emulsion and drying. The Surlin spacer for five lanes was cut to have a width of 0.4 cm and a spacing of 0.3 cm between lanes. Each spacer was cut using a plotter pen (CC330-20, Grahtec) according to a simple bitmap drawing. The cleaned glass parts and a spacer were stacked as shown in Fig. 1(a), with the top glass placed slightly mismatched from the bottom substrate to leave room for colloid injection, and Surlin was hot-bonded to each glass using a hot-press apparatus at 70 °C to form ∼20-μm-thick channels.

2.3. Fabrication of IO photonic gel sensor array with different gel compositions

After degassing the colloidal dispersion of PS-228 by ultrasonication in a bath sonicator (SD-80H, Seong Dong), 2.4 μL of PS-228 colloidal dispersion was measured exactly and infiltrated into each channel, as shown in Fig. 1(b), which proceeded rapidly because of the capillary force. After every channel was filled with dispersion, the holes on the top cell were taped so that water evaporation occurred only on the front side of the channel. The evaporation of water induced FCC stacking of colloidal particles, which usually required 2–3 h (Fig. 1(c)). Fully dried PS opal films were annealed at 90 °C in a convection oven (LK-Lab Korea) to form necking between the neighboring particles (Fig. 1(d)). Next, three different monomer mixtures were prepared to be infilled within each opal film. Mixture 1 contained 2.5 g 2-hydroxyethyl methacrylate (HEMA, Junsei), 35 mg acrylic acid (AA, Junsei), 25 mg ethylene glycol dimethacrylate (EGDM, Aldrich), 75 mg Irgacure-651(Ciba specialty Chemicals), and 0.625 g DI water. Mixture 2 was the same as mixture 1, except that it contained 35 mg of methacrylic acid (MA, Aldrich) instead of AA, and mixture 3 was also the same except for 35 mg of vinylimidazole (VI, Aldrich) instead of AA.

An aliquot of about 1 μL of the each mixture was infiltrated within the opal templates, as shown in Fig. 1(e), and photo-