Colloid Polym Sci (2008) 286:113–118
DOI 10.1007/s00396-007-1775-9

SHORT COMMUNICATION

pH and ionic strength responsive photonic polymers fabricated by using colloidal crystal templating

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Received: 30 March 2007 / Revised: 4 June 2007 / Accepted: 5 September 2007 / Published online: 27 September 2007

Abstract In this paper, monodispersed silica particles were synthesized using tetraethoxysiliane hydrolyzing in ethanol by a Stöber–Fink–Bobn method and then self-assembled on cleaning glass slides to form silica colloidal crystals. After photopolymerization of methacrylic acid mixing with ethylene glycol dimethylacrylate and hydrofluoric acid etching, the pH-responsive polymers were obtained with highly 3D-ordered macroporous structures templated by silica colloidal crystals. These polymers films can swell or deswell in response to external stimuli, causing a change of Bragg diffraction to read pH or ionic strength of various solutions by optical signals or electrochemical signals. As an application, they can be used as chemical sensors to detect pH or ionic strength variation of environment.

Keywords Colloidal crystal templating · Photonic polymer · Hydrogel · Sensor · Stimuli-responsive materials.

Introduction

Photonic crystals (PC) or photonic band gap materials have attracted rapidly growing interest because of their potential applications as diffractive optical devices, chemical and bio-sensors, high-density magnetic, and optical data recording materials [1, 2]. Colloidal crystal templating offers a simple and inexpensive chemical route to prepare highly ordered three-dimensional (3D) PC materials [3].

Generally, colloidal crystals can be formed by self-assembly of monodisperse silica particles by a vertical deposition method [4] in anhydrous ethanol. This method has many advantages; for example, colloidal particles can form highly ordered closed packing structure by self assembly, sizes of colloidal particles and thickness of colloidal crystals can be precisely controlled by chemical approaches, and silica particles can be easily etched away by hydrofluoric acid in ambient temperature. Therefore, silica colloidal crystals are usually used as templates to prepare photonic polymers with highly ordered 3D macroporous structures. On the other hand, hydrogels are usually designed to undergo reversible volume change in response to external stimuli such as solvent composition [5, 6], temperature [7, 8], pH, ionic strength [9], and antibody binding [10–13] due to their swelling or deswelling. Particularly, if these hydrogels have highly ordered 3D macroporous structure, such reversible volume change of hydrogels may cause the change of their periodic spacing of 3D-ordered structures, resulting in an interesting shift in Bragg diffraction wavelength. By means of variation of readable optical signals or electrochemical signals, these hydrogels with 3D-ordered macroporous structures can be used as chemical sensors to read easily and directly external stimuli. In this respect, Asher's team [14, 15] and Braun's team [16, 17] had done pioneering job using 3D-ordered macroporous hydrogels as chemical sensors to detect variations of pH, ionic strength, and glucose concentration.

In this paper, we synthesized monodispersed silica colloidal particles with tetraethoxysiliane hydrolyzing in ethanol by a Stöber–Fink–Bobn [18] method, and then

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these silica colloidal particles self assembled on cleaning glass slides by a vertical deposition method [4] to form colloidal crystals. The 3D-ordered macroporous hydrogel film was prepared by photopolymerization of a mixture of methacrylic acid (MAA), ethylene glycol dimethylacrylate (EGDMA), and 2, 2′-azobisisobutyronitrile (AIBN) templated by a silica colloidal crystal. The obtained photonic hydrogel film exhibits high sensitivity to pH or ionic strength variation, coupling readable optical or electrochemical signals to chemical responsive, which may supply an easy approach to test the variation of pH or ionic strength.

Experimental section

Materials and equipment

Tetraethoxysilane (TEOS) and ammonia are analytical grade and purchased from Beijing Chemicals. MAA, EGDMA, and AIBN are also analytical grade and obtained from Arcos Chemical Anhydrous ethanol (ETOH), before using, was distilled to remove excess water. Other affiliated chemicals are analytical grade and supplied by local commercial sources. All slides (5×2×1 mm) were soaked in H_2SO_4/H_2O_2 mixture for 12 h and then rinsed with deionized water and dried in air before use.

Morphology and microstructure of silica colloidal crystals and photonic hydrogel films was observed by a Hitachi S-6700 field emission scanning electron microscope. Optical Bragg diffractions were checked by a UV-spectrometer (Lambda35, PerkinElmer). The photopolymerization was performed in a UV light (FUSI Electric ST3) with 16 W. The electrochemical studies were performed utilizing cyclic voltammetry. The electrochemical cell consisted of a glassy carbon working electrode, a calomel reference electrode, and a platinum electrode binding with the photonic polymer film. The potential was varied from 0.6 to −0.1 V at a scan rate of $0.2\ \mathrm{V\ s^{-1}}$, and the current was measured by a potentiostat interfaced to a Pentium computer.

Monodispersed Silica colloidal particles synthesis

The synthesis of monodispersed SiO_2 particles was based on Stöber–Fink–Bobn method. First, 8.74 g TEOS and 180 ml anhydrous ethanol were mixed in a 250 ml clean Erlenmeyer flask, stirring intensively with a magnetic beater, and then pouring slowly 15.4 ml ammonia and 4.46 g deionized water. After 24 h, the monodispersed colloidal particles were obtained by centrifugation and redispersion using anhydrous ethanol for three times. The size of SiO_2 particles is about 200 nm.

Colloidal crystals template formation

The monodisperse silica particles were dispersed in anhydrous ethanol to form a colloidal solution with weight concentration of about 1% and then allotted into 10 ml cleaning vials. A cleaning glass slide (50×20 mm) was put vertically into each vial. After complete volatilization of ethanol, silica colloidal crystal was formed on both sides of the glass slide. During that time, it was very important to avoid vials from shake and airflow disturbance. Normally, there were few to tens of layers of silica arrays on glass slides depending on concentration of colloidal solution; the thickness of colloidal arrays could be controlled by adjusting concentration of colloidal solution.

Preparation of photonic hydrogel films

For preparation of photonic hydrogel films, MA and EGDMA were used for the formation of matrix materials, as they have polar groups of carboxyl and carbonyl, which make the obtained hydrogel films exhibit well hydrophilicity. Figure 1 is the schematic illustration of the preparation of photonic hydrogel films using colloidal crystals templating (Fig. 1a) and the crosslinked network of hydrogel (Fig. 1b). Before polymerization, 4 ml MAA (47.16 mmol) was fully mixed with 2 ml EGDMA (10.59 mmol) as crosslinker and 0.01 g AIBN (6.1 mmol)

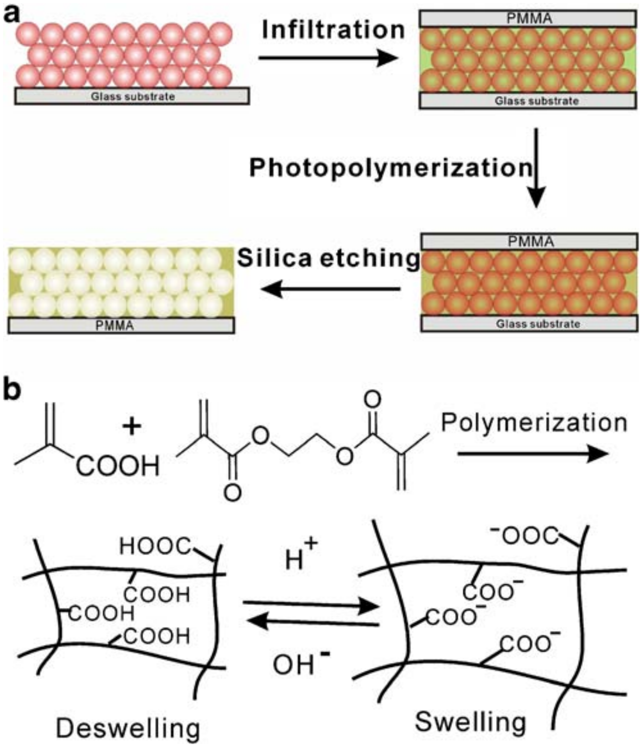

Fig. 1 Schematic illustration of the preparation of photonic hydrogel films using colloidal crystals templating (**a**), chemical structures of monomers and the crosslinked network of hydrogel (**b**)

as initiator in 3 ml anhydrous ethanol. The homogeneous monomers mixture was dropped onto silica colloidal crystals until the colloidal crystals became transparent, indicating successful infiltration. Redundant precursors were removed by covering a clean PMMA slide (1.5 mm thick). The remaining mixture was photo polymerized in an ice-bath environment under an UV light for 50 min. Afterward, the sandwich of glass, hydrogel, and PMMA was soaked in 1% hydrofluoric acid for 30 min to separate double slides and fully etch away silica colloids. The obtained hydrogel films on PMMA substrates were rinsed by deionized water for three times and then soaked in a neutral phosphate buffer (0.01 M, pH=7.6) for UV-vis detection.

Electrochemical behavior of photonic hydrogel films was performed with a PG310 (HEKA Electronic, Dr. Schulz GmbH) electrochemical station. The conventional electrochemical cell consists of three electrodes with a platinum electrode (diameter 10 mm) enwrapped with Teflon as working electrode, a platinum wire (diameter 0.1 mm) as counter electrode and a Ag|AgCl|KCl (salt) electrode as reference electrode. For all cases, the electrolyte is a mixture of 0.2 M K_2SO_4 and 2 M $K_4[Fe(CN)_6]$, scan rate is 100 mV/s, $n=3$. before scanning, the electrolyte was degassed by argon for 15 min.

Results and discussion

Influence parameters to colloidal crystals and photonic hydrogel films

The colloidal crystal templates with highly ordered closed packing structure are formed by self-assembly of monodisperse silica particles in anhydrous ethanol. One of the most important factors is the monodispersity of the prepared colloidal particles. Imperfect monodispersity of particles can produce serious disorders and dislocations in templates. These defects lead to strong random scattering of incident light so that the crystal templates cannot generate strong optical signals due to weakly Bragg diffraction. Improvement of the monodispersity of the particles is a critical way to obtain templates with high quality and strong optical response. The monodispersity of colloidal particles is mainly affected by the different formula. Early studies indicated that TEOS hydrolysis was a rate-limiting reaction. Once the supply of TEOS exceeds its hydrolytic rate under the reaction condition, the monodispersity of the system will be destroyed. Keeping appropriate rate of the hydrolysis and condensation of TEOS is the prerequisite for the effective control of the formation process of monodisperse particles. On the other hand, the entire appliances used must be very clean and anhydrous. Furthermore, excess ammonia and water may destroy the monodispersity of silica particles.

Two scanning electron microscopy (SEM) images shown in Fig. 2 demonstrate the morphologies of the silica colloidal crystals. Figure 2a is a top view of a silica colloidal crystal. It is clearly seen that the silica colloidal crystal possesses a face-centered cubic (fcc) close-packed structure with the (111) plane parallel to the substrate surface. An analysis of spatial structure indicates that each lattice point of the fcc connects with two different kinds of (111) planes, such as (111¯) and (11¯1), and one (100) kind of plane, such as (010) and (001), etc. Figure 2b is a side view of the colloidal crystal; it is clear that the thickness of this sample is about 13 layers. The thickness of the silica colloidal crystals is apparently a function of both the colloidal concentration in anhydrous ethanol and the evaporation speed of ethanol. Either of these two factors can be used to control the number of layers.

As mentioned above, the silica colloidal crystals were used as templates to form photonic polymers with inverse opal structures. After the colloidal templates removal, the hydrogel polymer films with 3D-ordered macroporous structures were formed. SEM images shown in Fig. 3 reveal these highly ordered arrays of pores. These films have well-defined 3D-ordered macroporous structures and large internal surface areas. Moreover, these macropores

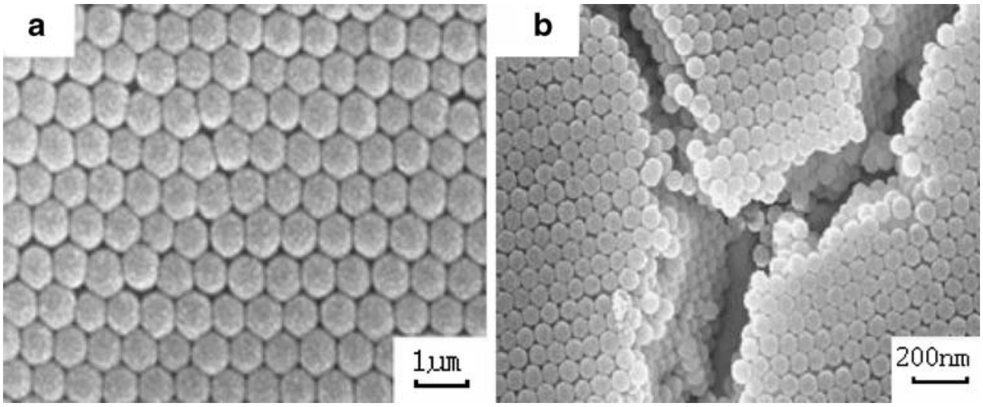

Fig. 2 SEM images of the colloidal crystals formed from silica spheres **a** top view and **b** side view

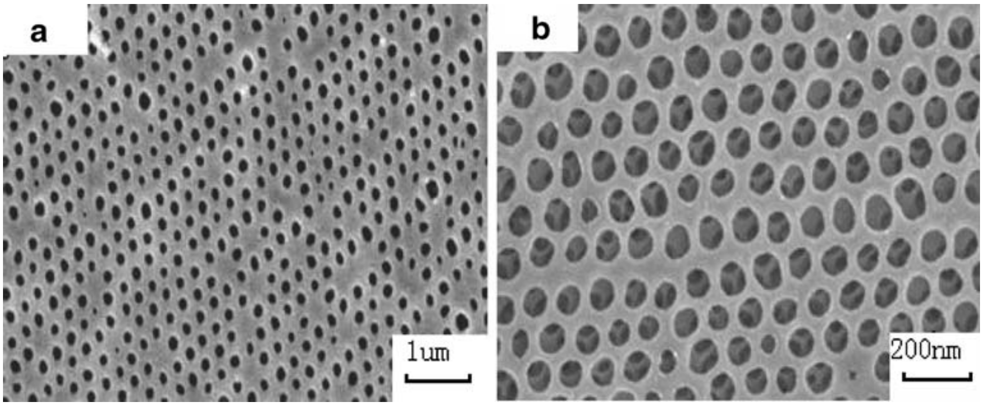

Fig. 3 SEM images of the inverse opal photonic hydrogel films **a** top view **b** side view

inside films are interconnected (Fig. 3b), which is favorable to reduce the response time on chemical stimuli by significantly shortening the diffusion path of swelling solvent. The structure of these photonic hydrogel films is mainly defined by colloidal crystal templates, so the size and the arrangement order of air pores within hydrogel films are full replica against their templates. If the disorders and dislocations exited in these templates, the highly ordered pore arrays and their optical responsive properties cannot be achieved in the synthesized photonic films.

Optical properties of silica colloidal crystals and photonic hydrogel films

Optical properties of silica colloidal crystals and inverse opal hydrogel films have been studied in many literatures. The colloidal crystals or inverse opal structures have the 3D-ordered periodic structures, and thus, their optical diffractions can be depicted by Bragg's law [19]:

$$\lambda = 2n_{\mathrm{eff}}d = (8/3)^{1/2}\left(\sum{}_{\mathrm{i}}n_{\mathrm{i}}^{2}V_{\mathrm{i}} - \sin^{2}\Phi\right)^{1/2}D$$

where d is the periodic spacing, n_{eff} is the effective refractive index of mixing dielectric, n and V are, respectively, the refractive index and the volume fraction of each component phase, Φ is the angle between the incident beam and the sample normal, and D is the center-to-center distance of particles arrays in the colloidal crystals. The optical property of these colloidal crystals and the photonic hydrogel films prepared in our work was checked by using a UV-vis spectrometer and shown in Fig. 4. Comparing two figures, both the colloidal crystal and the photonic polymer film have the absorbance peak almost at the same position (495 nm). However, the signal of photonic film was less strong than that of the colloidal crystal. The reason may be that the colloidal crystal is a rigid film, which can generate intensive optical signal, but the photonic hydrogel film is a flexible film and thus its optical signal is shallower.

Optical response of hydrogel films to various pH and ionized strength

Photonic films made from hydrogel polymers enable swelling or deswelling in aqueous solution due to environment conditions change, such as pH or ionized strength variation. In our case, these hydrogel films contain a large amount of carboxyl functional groups inside, of which carboxyl groups can be deprotonated when OH^{-} ions diffuse from the bulk solution into the gel phase driven

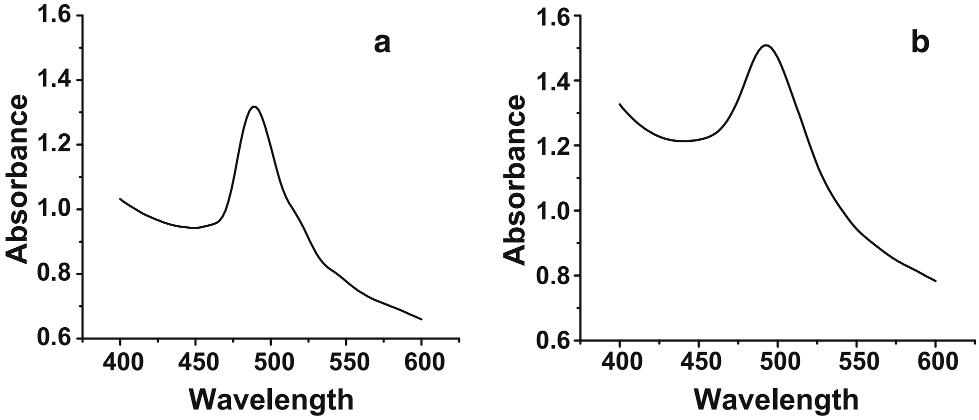

Fig. 4 UV-vis absorption spectra. **a** Colloidal crystal template, **b** photonic formed polymer film

by a concentration gradient. As a result, the osmotic pressure within the gel increases to drive the hydrogel swelling. On the opposite, the hydrogel polymers are deswelling in acidic solution because the deprotonation process is restrained to produce a reverse osmotic pressure from bulk acidic solution to gel phase. The pH-dependent optical diffractions of the photonic hydrogel films were checked by using the UV-vis spectrometer. Absorbance spectra were obtained by immersing these slides into phosphate buffer solution with different pH. Figure 5 shows their diffractive spectra. As the pH increasing, it is clear that their diffractive peaks are also shifted to longer wavelength, i.e., from 460 nm at pH=3.67 to 540 nm at pH=10.87. According to Bragg diffractive equation above, the shift of diffractive peaks is caused by the change of *d*, indicating the photonic film swelling. As a consequence, it can be inferred that these hydrogel films have a blue shift of diffractive peaks in acidic solution due to deswelling and a red shift of diffractive peaks in basic solution due to swelling.

On the other hand, this interesting shift phenomenon of diffraction can be also observed in ionic strength variation. By varying the concentration of NaCl in phosphate buffer solutions, the effect of ionic strength on diffraction response was studied and plotted in Fig. 6. The absorbance peak of one hydrogel film has a red shift from 485 nm in pure phosphate buffer to 525 nm in 1 M NaCl buffer, which means the hydrogel swelling. The reason is also ascribed to the variation of osmotic pressure resulting in hydrogel swelling. With the increase of the concentration of NaCl in buffers, much more free Na^+ can diffuse into gel phase and anchored onto polymer network, resulting in a difference of Na^+ concentration inside and outside the gel, thus generating a bigger osmotic pressure between gel phase and bulk solution, so the diffractive peak of the photonic hydrogel film can gradually shift to longer wavelength.

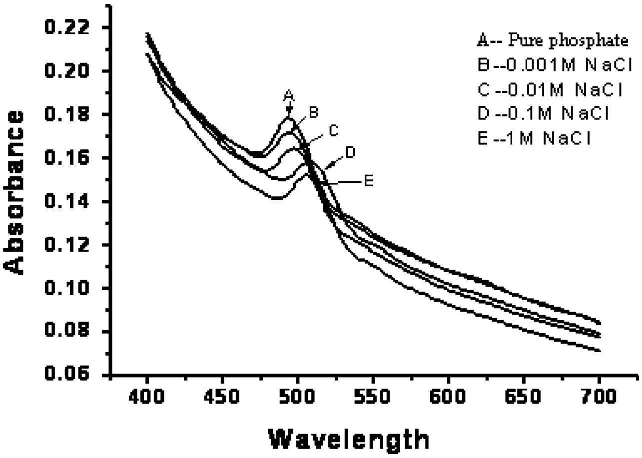

Fig. 6 Ionic strength response of one photonic hydrogel film in phosphate buffers on variation of NaCl concentration

Electrochemical response of photonic polymer films to pH variation

The sensitive response of photonic hygrogel films to pH variation can be also confirmed by cyclic voltametric experiments as shown in Fig. 7. In this experiment, a photonic hydrogel film was immobilized on a Pt work electrode and then soaked, respectively, in 0.1 M NaOH, 0.1 M HCl, and deionized water for 5 min. $K_4[Fe(CN)_6]$ was performed as a molecular probe to examine the electrochemical responsive effect. Three cyclic voltammetric curves were obtained after soaking the photonic polymer film in acid, base, and water. In three cases, the redox potential difference has almost no change, but the current difference has a big variation from acid to base. The reason is that the photonic film can swell in a basic solution while deswell in an acidic solution. When the hydrogel film swells in a basic solution, much more $\mathrm{Fe(CN)}_6^{4-}$ can pass through the multiporous hydrogel film to the Pt work

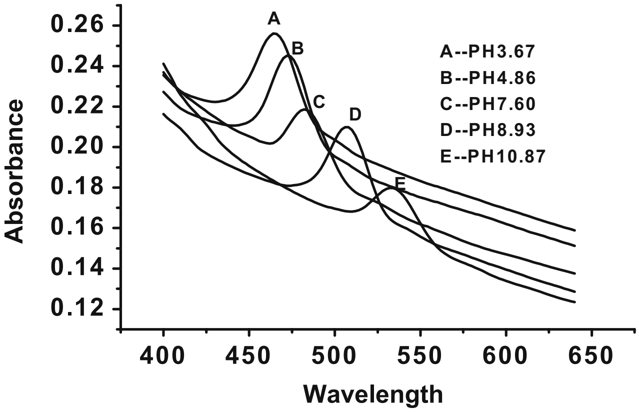

Fig. 5 pH response of one photonic hydrogel film soaking in phosphate buffers on pH variation

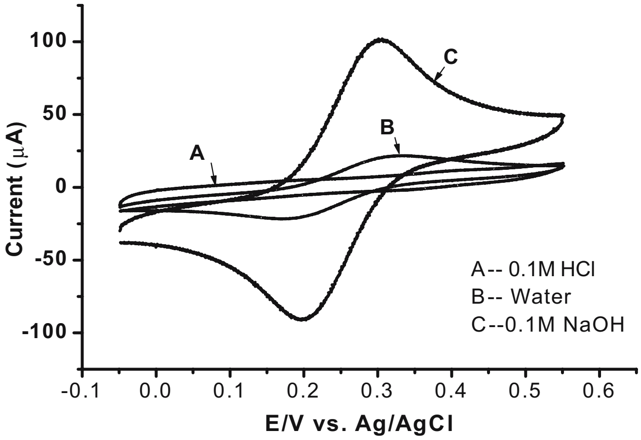

Fig. 7 Voltametric responses of the Pt electrode with the photonic hydrogel film on pH variation

electrode; on the opposite, the result is reversed in an acidic solution because of shrinkage of the film. The result indicates that the photonic polymer film exhibits different electrochemical response to pH variation.

Conclusions

In this paper, we present the synthesis and characterization of the robust and optically tunable polymer films templated by using colloidal crystals templating. These polymer films can swell and deswell, coupling readable optical signals or electrochemical signals on different pH or ionic strength stimuli, thus can be used as sensors with high sensitivity and quick response.

The structure and optical characterization of the photonic films by SEM and UV-vis spectrometer show that these polymer films have highly 3D-ordered macroporous structures, which can convert chemistry signals into readably optical signals directly by shift of Bragg diffractions without any other transducer. The preliminary results indicate that these photonic polymer films can be also used to test other environment stimuli, such as temperature and humidity.

Acknowledgement We gratefully acknowledge the financial support from the National Science Foundation of China (20473044, 20533050, 50673048), SRFDP (20060003080) and 973 Program (2006 CB806200).

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