Visual detection of carbonate ions by inverse opal photonic crystal polymers in aqueous solution

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Materials and chemicals

Acrylic acid (AA), ethylene glycol dimethylacrylate (EGDMA), ammonia, and tetraethoxysilane (TEOS) were purchased from Alfa Aesar. 2,2'-Azobis(isobutyronitrile) (AIBN) were obtained from Arcos Organics. Anhydrous ethanol, anhydrous methanol, hydrofluoric acid and other affiliated chemicals were all obtained from Beijing Chemical Industries. All of the solvents and chemicals used were of analytical quality and were used without further purification unless indicated. Common glass slides (Microscope slide, 76.2 mm long, 25.4 mm wide, 1 mm thick) were purchased from Sail Brand (Shanghai, China). Polymethyl methacrylate (PMMA) slides (25 mm long, 15 mm wide and 1mm thick) were from local suppliers. Common glass slides were cut to the same as the PMMA slides, and were treated with and immersed in a H_2SO_4/H_2O_2 mixture (7:3, v/v) for 24 h, followed by rinsing with deionized water and anhydrous ethanol in an ultrasonic bath several times before dried with nitrogen. All 5 mL vials for the formation of colloidal crystal templates were treated as well.

Characterization

The morphology and microstructure of the silica colloidal crystals and photonic films were characterized using the scanning electron microscope (SEM, model JEOL S4800). Optical Bragg diffractions were tested by a fiber spectrometer (AvaSpec-2048, Avantes). These spectra were taken with light impinging perpendicular to the film and, hence, also to the (111) planes of the opaline lattice. The diameter of collection spot was approximately 1.5 mm. The photopolymerization was performed in UV light (Jiapeng limited company, Shanghai) at 24 W. The color change of the IOPPs films

was recorded using a common digital camera.

Formation of photonic crystal templates

The highly uniform silica colloidal microspheres were synthesized by using an approach based on the Stöber method with certain modifications as follow. In a typical preparation process, anhydrous ethanol (100 mL), deionized water (6 mL) and ammonia (4 mL) were mixed in a 250 mL flask and stirred gently with a magnetic stirrer at 35℃ in a water bath for 20 mins. Then TEOS (6 mL) was quickly added and the resulting reaction mixture was left for 8 h. The size of the silica particles can be tuned in the range of 180–360 nm by changing certain experimental parameters. The monodispersed silica particles were obtained by centrifugation followed by rinsing 8 times using anhydrous ethanol to expunge the residues. The resulting product was then dispersed in anhydrous ethanol (Volume concentration 1%), and transferred into 5 mL vials. A glass slide was well-cleaned by rinsing with deionized water and ethanol several times before dried with nitrogen, and then was put vertically into a vial for colloidal crystal growth. After the solvent was evaporated completely, templates of close-packed face-centered cubic (fcc) colloidal crystals were obtained. In this work, monodispersed silica spheres with a diameter of about 220 nm were used (Fig. S1).

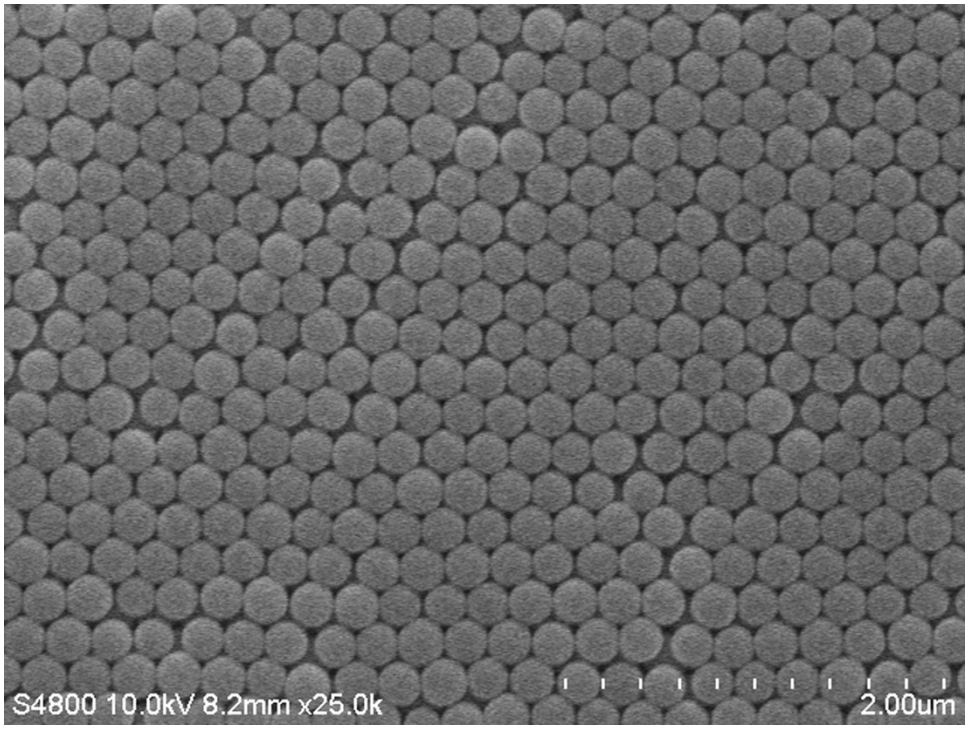

Fig. S1: SEM image of the used colloidal crystal template.

Synthesis of inverse opal photonic crystal polymers (IOPPs) films

AA (5 mmol), EGDMA (1 mmol) and AIBN (0.02 g) were sufficiently mixed in anhydrous methanol (1 mL). The homogeneous mixture was degassed with nitrogen for 5 min to remove the dissolved oxygen and then was individually added drop wisely on the edge of the colloidal templates which were covered with PMMA slides. The precursor solution was infiltrated into the voids of the colloidal templates by capillary forces. Once the colloidal crystal template became transparent, a successful infiltration process was completed. After the removal of excess precursors, photopolymerization was performed in an ice bath under a UV light at 365 nm for 3 h. The colloidal templates were frozen in a 3D network of polymers. The films were immersed in 1% hydrofluoric acid for 4 h to separate the double slides and fully etch the silica particles. The substrate of PMMA exhibited resistance from damage in the hydrofluoric acid solution. Thus, the inverse opal photonic crystal polymers were formed on the PMMA slides and then were rinsed thoroughly with deionized water several times. Finally, the resulting polymers were immersed in deionized water at room temperature till it reached a swelling equilibrium and then are ready for use (Fig. S2).

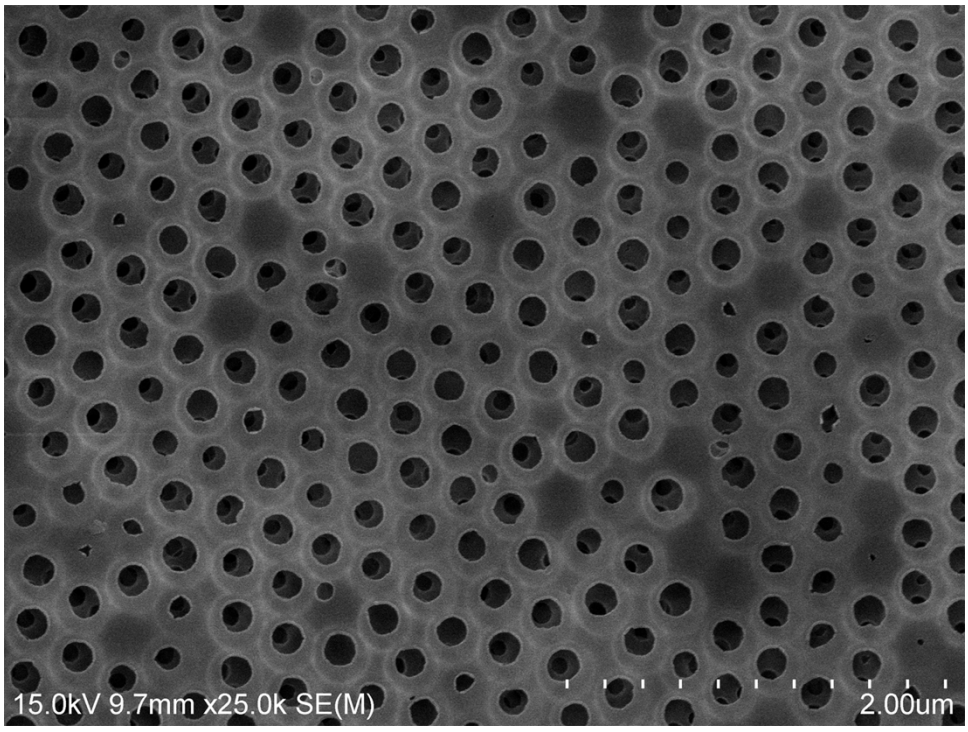

Fig. S2: SEM image of the formed IOPPs films.

Fig. S3: Optical response of the IOPPs films with CH_3COO^- and SO_4^{2-} as inference anions in CO_3^{2-} solution.

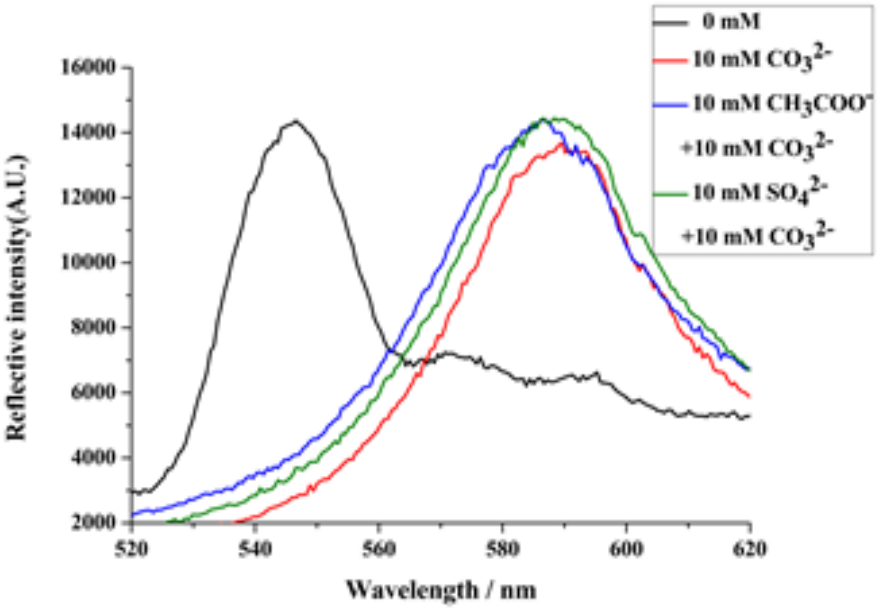

Fig. S3