

## Electronic Supplementary Information (ESI)

# A Rapid and Scalable Strategy to High Quality Inverse Opal Tin Dioxide Porous Films

### Experimental Section

*Materials:* Sodium styrene sulfonate and SnF<sub>2</sub> were from Alfa Aesar Chemicals. NaHCO<sub>3</sub>, NaOH, styrene, potassium persulfate, CaCl<sub>2</sub>, hydrogen peroxide, ammonia and ethanol were from Sinopharm Chemical Reagent Co. Ltd. The styrene monomer was washed with NaOH solution and deionized water for several times respectively to remove the polymerization inhibitor. Potassium persulfate was purified by recrystallization in cold water. All other chemicals in this study were used as received without further purification.

*Synthesis of monodisperse PS microspheres:* The monodisperse polystyrene (PS) microspheres with narrow size distribution (< 5%) were synthesized by an emulsifier-free emulsion polymerization method.<sup>1</sup> In brief, an aqueous solution containing sodium styrene sulfonate as an emulsifier and sodium hydrogen carbonate as a buffer was kept at a temperature of 80 °C and stirred at 300 rpm. The purified styrene monomer was added into the solution. Then, purified potassium persulfate was introduced into the solution as an initiator. Finally, polymerization was performed under a nitrogen atmosphere for 12 h. By using different amount of emulsifier and buffer, 5 PS microspheres with different particle sizes were obtained. After polymerization, PS microspheres were concentrated by a centrifugation method, and then redispersed in a mixture of ethanol and water to obtain the colloidal suspension with a concentration of about 30% for fabricating colloidal crystals.<sup>2</sup>

*Preparation of CaO<sub>2</sub>·8H<sub>2</sub>O:* Briefly, 5.6g calcium chloride was dissolved in a mixture of 5mL water and 25mL 30% hydrogen peroxide. A solution of 5mL concentrated aqueous ammonia dissolved in 20mL cold water was added dropwise under stirring. After the mixture cooled in the ice water for half an hour to precipitate completely, the product was filtered, washed with cold water and grinded to a yellowish powder of CaO<sub>2</sub>·8H<sub>2</sub>O.

*Preparation of LPD precursor solution:* SnF<sub>2</sub> aqueous solution with a concentration of 0.3 M was poured into a beaker. And just before the LPD process, some amount of CaO<sub>2</sub>·8H<sub>2</sub>O was added into the solution, and formed a layer of precipitate cover the bottom of the beaker.

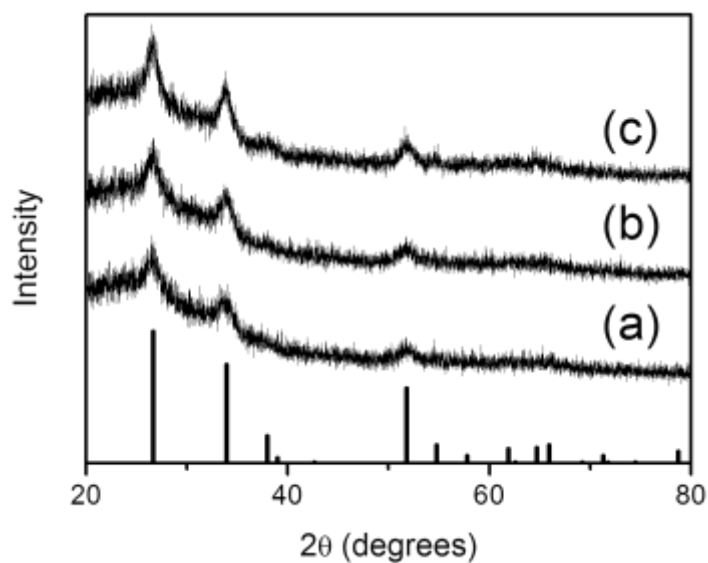
In this LPD process, the role of CaO<sub>2</sub>·8H<sub>2</sub>O as an additive of LPD precursor solution was investigated. When meeting with pure water, the CaO<sub>2</sub> will release oxygen gas, while mixing with SnF<sub>2</sub> aqueous solution, no bubble is observed and the solution turns milky opacity. Considering that the SnF<sub>2</sub> aqueous solution can be stable for a rather long time at room temperature,<sup>3</sup> CaO<sub>2</sub>·8H<sub>2</sub>O can accelerate the SnF<sub>2</sub> hydrolysis reaction as an oxidant. Another role of CaO<sub>2</sub>·8H<sub>2</sub>O as F<sup>-</sup> scavenger can be easily inferred from the solubility of CaF<sub>2</sub> and Ca(OH)<sub>2</sub>. As an experimental evidence, SnF<sub>2</sub> aqueous solution was kept at 60 °C with excess CaO<sub>2</sub>·8H<sub>2</sub>O for several hours. After filtration, F<sup>-</sup> can barely be detected in the supernatant. This improved LPD process only lasted for a short time about 30 min, which was significantly faster than the traditional LPD method.<sup>4</sup>

*Fabrication of PS opal template:* Glass slides were used as the substrates. Before use, it was cleaned with water and ethanol in advance. The substrates were placed on a horizontal table, and adhesive tapes (Scotch, approximately 50 $\mu$ m) were served as spacers. The PS colloidal suspension was dropped onto an edge of the substrates, then spread rapidly and evenly on the substrates by doctor-blading technique using a glass rod. Without heating or air flow, ethanol and water evaporated completely in a few minutes, while the PS colloidal crystal films were self-assembled onto a glass substrate.

Generally, *fcc* and *hcp* structures are distinguished by their close-packed planes. Both *fcc* and *hcp* are composed of close-packed planes layer by layer. The layer order in *fcc* is ABCABC while in *hcp* is ABABAB. Considering this evidence is not intuitive, we use another judging method here. As we know, *fcc* structure has a higher symmetry than *hcp* structure. In *fcc*, 4 different planes belong to {1 1 1} family of crystal planes show the hexagonal-packed structure, while in *hcp*, only [0 0 1] plane shows that. The top view SEM images of opal templates show a hexagonal-packed structure, and so do the sectional SEM images of Fig. 1c and Fig. 1d. Obviously, the hexagonal-packed plane in sectional SEM image is not parallel to the plane in top view. So the 3D structure of opal templates is *fcc* rather than *hcp*.

*Fabrication of inverse opal SnO<sub>2</sub>:* The glass slide with PS colloidal crystal template was vertically submerged in the SnO<sub>2</sub> LPD solution, which then were kept at a temperature of 60 °C. After 30 min, the samples were rinsed thoroughly with deionized water and dried in air at room temperature. Generally, the PS opal templates were removed by calcination in air. The temperature was increased at a rate of 10 °C /min to 450 °C and stabilized at 450 °C for 1 h, then cooled to room temperature, leaving behind an inverse opal SnO<sub>2</sub> structure.

*Characterization of opal and inverse opal structure:* The polydispersity of the prepared PS microspheres were measured by a Zeta Plus (Brookhaven Instrument Corp.). The crystal structure of inverse opal SnO<sub>2</sub> film was investigated by X-ray diffraction (XRD, MacScience, M18X-AHF) using the Cu K $\alpha$  radiation. The diameter of the prepared PS microspheres, the morphologies of the PS opal and SnO<sub>2</sub> inverse opal films were obtained with scanning electron microscopy (SEM, FEI, XL30 S-FEG). Generally, 10 particles in SEM images were collected for the diameter measurement. The reflectance spectra of the PS opal templates were measured by a home-made optical microspectroscopy setup.<sup>5</sup> Generally, 3 samples with the same PS particles size were prepared for the optical measurement. The transmittance spectra of the SnO<sub>2</sub> inverse opal were measured by a Shimadzu, UV-2550 spectrophotometer with an integral sphere.



**Fig. S1** XRD patterns of inverse opal SnO<sub>2</sub> films at different calcination temperatures: (a) 450°C, (b) 550°C, (c) 650°C.

#### References

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