

Electronic Supplementary Information

Large-scaled formation of calcite inverse opal induced by the calcite single crystal substrate

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Experimental

The calcite single crystals were purchased from Yongzhou Natural Glass Company. Polystyrene with surface functional group (240 nm) of –COOH and –NH₂ were synthesized according to the references of 1 and 2. NH₄CO₃ were supplied by Alfa Aesar. All the water used in the experiments was Milli-Q ultra-pure water.

The PS colloids with different surface functional group were convectively self-assembled to form 3D colloidal crystals on calcite single crystal substrate. Typically, the calcite single crystal were inserted vertically into the beaker containing 3 ml PS suspension (0.1%, v/v), and allowed to dry at constant temperature of 60 °C. The PS colloidal crystals were annealed at 90 °C for 30 min to enhance its mechanical stability.

The colloidal crystals along with the calcite single were immersed in the CaCl₂ solution (50 mM) in the beaker. The beaker was sealed in a desiccator containing 1 g NH₄CO₃ powder. The desiccator was placed in an environment at 25 to 30 °C for 12 h. The calcite crystal was taken out from the beaker and rinsed with ultra-pure water for 3 times to remove the floating free calcite

particles from the surface. The PS templates were removed with toluene and the calcite crystals were annealed at 500 °C.

Both TEM (JEOL, JEM 2011, 100 kV) and SEM (Hitachi, S4300, 15 kV) characterization were performed to characterize the morphologies and the crystalline features of the calcite inverse opals. The optical image was captured with an Olympus microscope (MX40) equipped with a charge coupled device (CCD) detector connected to the computer, and the UV-Vis reflection spectroscopy was obtained with optical fiber spectrometer (AvaSpec-128).

References:

1. J. Wang, J. Hu, Y. Wen, Y. Song, L. Jiang, *Chem. Mater.* **2006**, *18*, 4984.
2. Z.-F. Liu, T. Ding, G. Zhang, K. Song, K. Clays, C.-H. Tung, *Langmuir* **2008**, *24*, 10519.

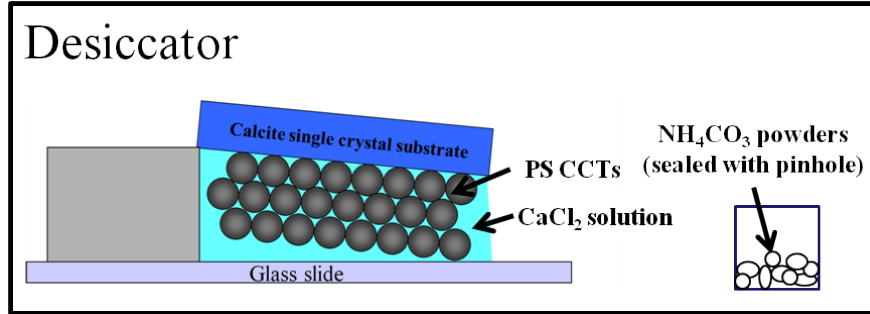


Fig.S1 The scheme of experimental setup for the growth of calcite inverse opal (IO).

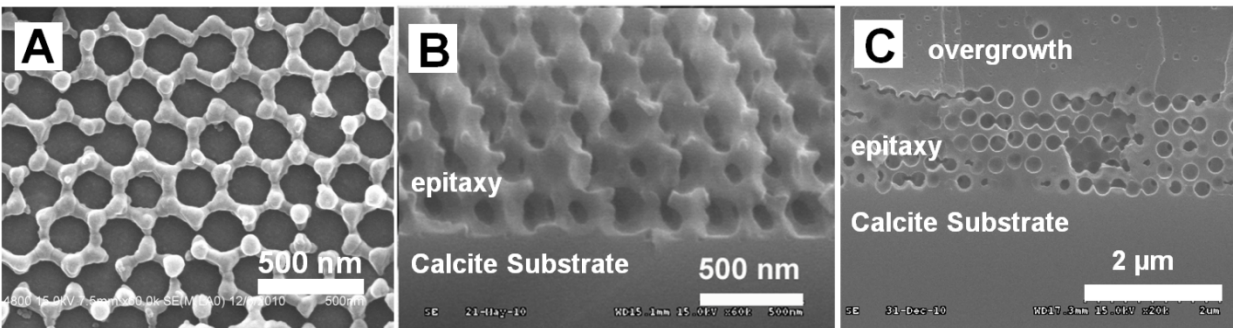


Fig. S2 The growth of calcite crystals started from the substrate of calcite single crystals to the top of the colloidal crystals templates (CCTs). The SEM images of the samples are taken after calcinations. (A) after 5hrs growth, only a monolayer of calcite crystals of 2DOM structure was formed; (B) after 12hrs growth, calcite crystals of IO structure was formed; (C) after 24 hrs growth, an additional layer of calcite crystals overgrew on the surface of the IO.

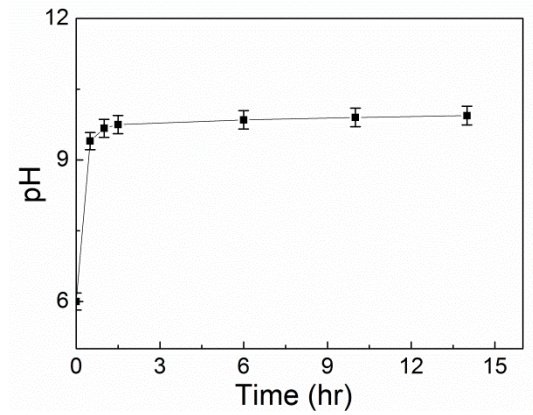


Fig. S3 The change of pH of the CaCl_2 solution at different time of incubation

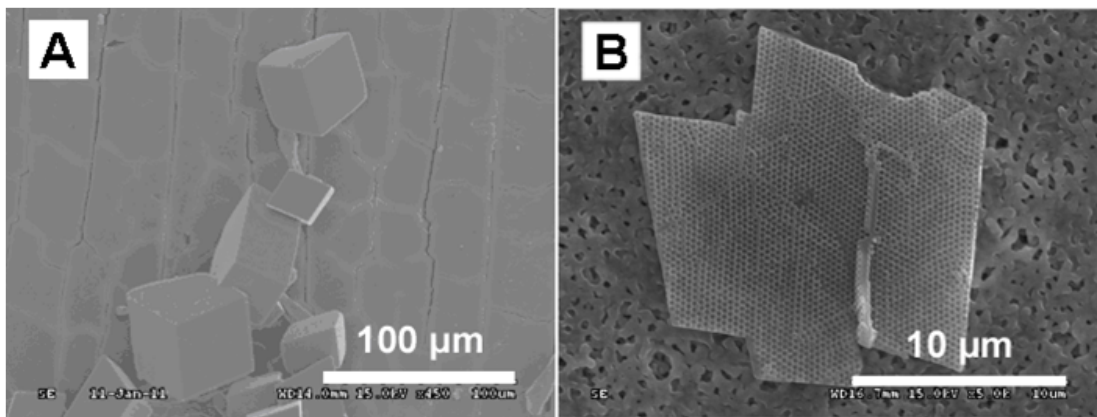


Fig. S4 The growth of calcite crystals in CCTs without the presence of calcite single crystal substrate. (A) The SEM image of calcite crystals on the surface of CCTs; (B) The calcite single crystals with 2D surface patterns imprinted by the surface of the CCTs.

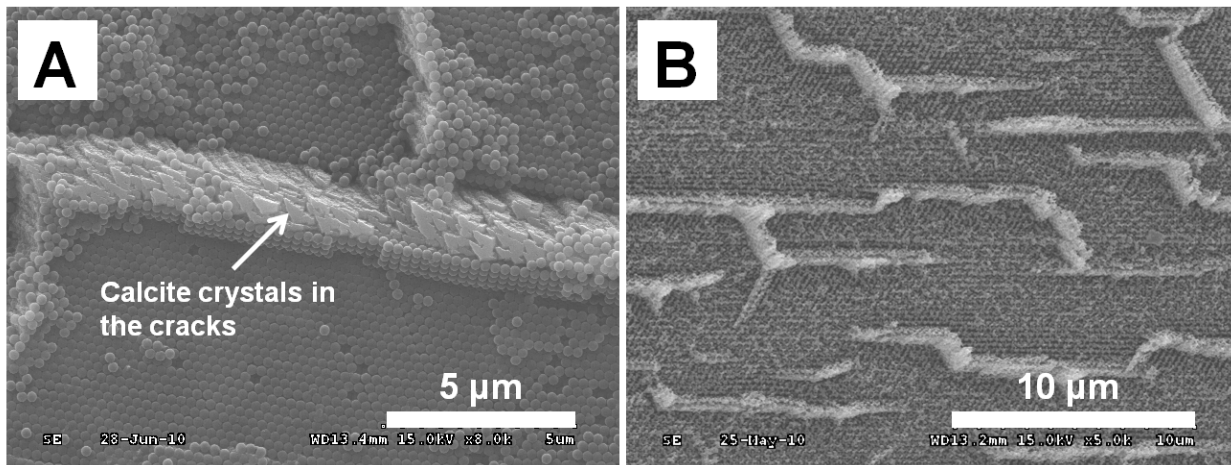


Fig. S5 The SEM images of (A) the growth of calcite crystals within the cracks of the CCTs and (B) the large-scaled image of calcite IO after removing the templates.

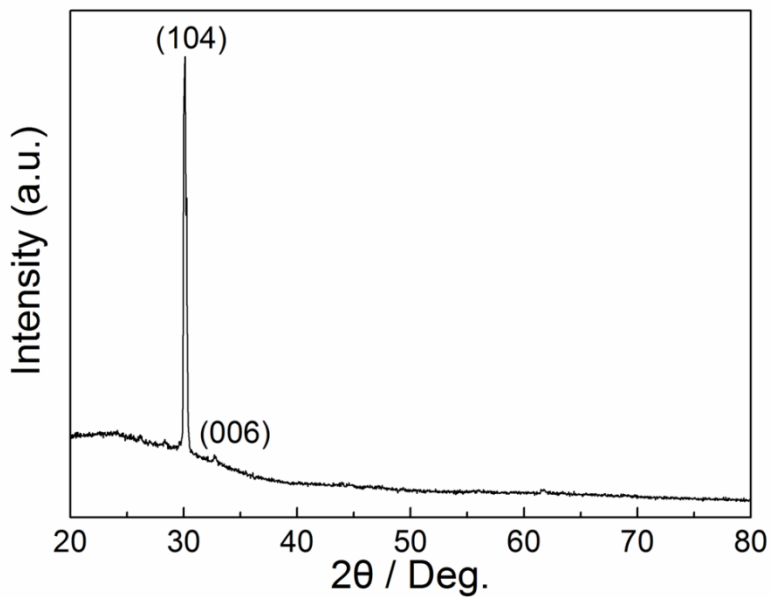


Fig. S6 The XRD patterns of the IO pieces of calcite crystals after sonication down from the substrate.

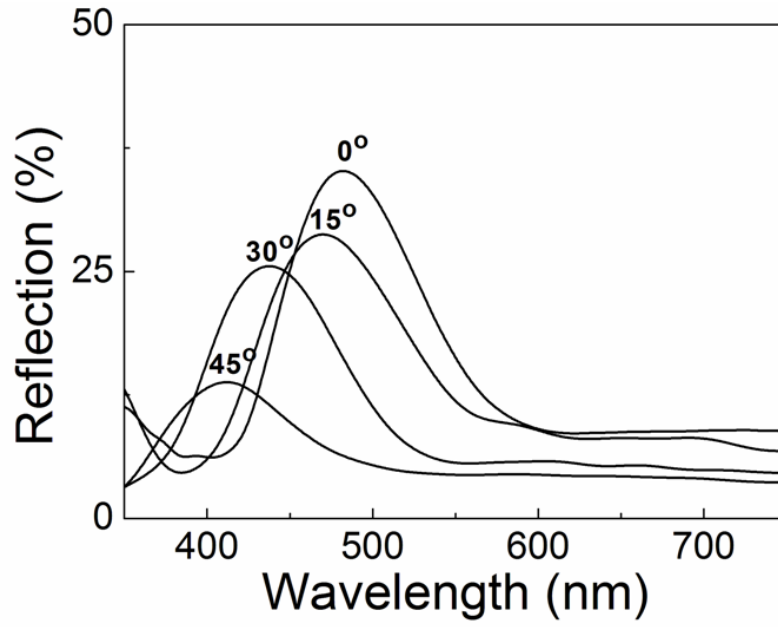


Fig.S7 Multi-angular characterization of the IO calcite crystals. The angle value is from the direction of incidence to the normal direction.