

## Supplementary Information

### Template Synthesis of Ordered Arrays of Mesoporous Titania Spheres

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### Experimental:

*Synthesis of silica colloidal crystal (opal):* Silica opal was prepared by published methods.<sup>S1</sup> Monodisperse silica spheres with a diameter of ca. 290 nm, and 180 nm were initially prepared from hydrolysis of tetraethoxysilane (TEOS). The spheres were then formed into close-packed lattices through a sedimentation process over several months. This precipitate was then sintered at 120°C for 2 days and then 750°C for 4 hours, producing a robust opalescent piece that could be readily cut into smaller sections.

*Preparation of PMMA mesh (inverse opal):* A piece of silica opal was immersed in methyl methacrylate (MMA) monomer with 1 wt.% benzoyl peroxide (BPO) as an initiator. Polymerization was initially carried out at 40°C for 10 h and then 60°C for 12 h. Excess poly(methyl methacrylate) (PMMA) on the opal was removed by wiping the exposed opal surface clean with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The silica opal spheres were removed using a 10 wt.% HF solution (24 h) to obtain a freestanding PMMA mesh.

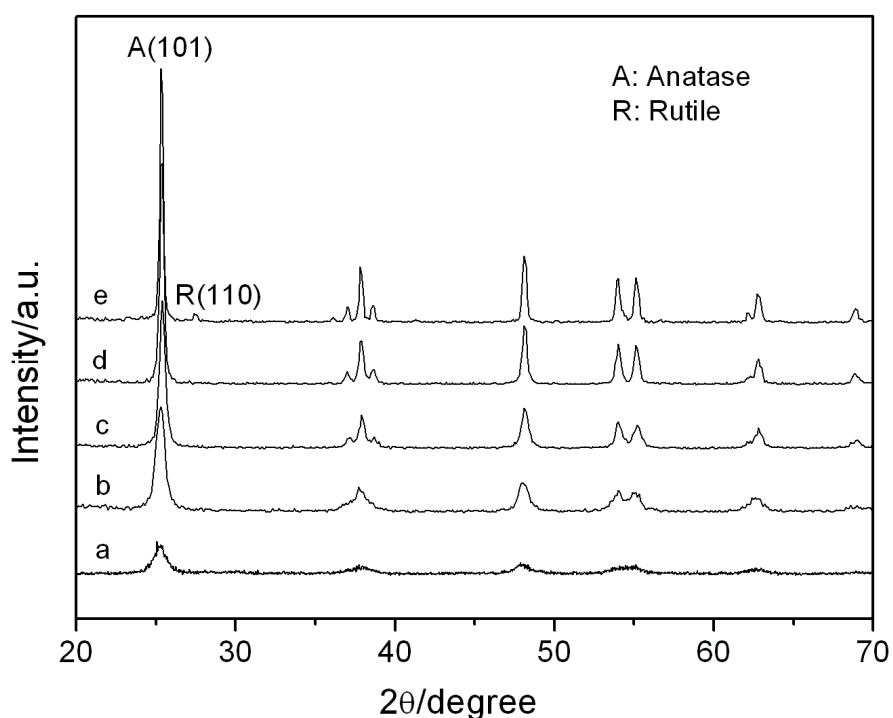
*Fabrication of three-dimensionally (3D) ordered arrays of TiO<sub>2</sub> spheres:* Titanium tetraisopropoxide was used as the titanium source, and amphiphilic triblock copolymer Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) was used as the mesopore-directing agent. The titania precursor solution was typically prepared as follows: 2.84 g titanium tetraisopropoxide was dissolved in 2.4 g concentrated HCl (37 wt.%) at room temperature under stirring, then a solution of 1.16 g P123 (Aldrich) dissolved in 3.7 g ethanol was added; the mixed solution was stirred at room temperature for 1 further hour to form a clear solution. Then the titania precursor solution was infiltrated into the spherical macropores of the PMMA mesh by immersing the mesh in the precursor solution for 4 h. After that, the precursor-filled PMMA mesh was removed from the solution, and then aged at room temperature for 3 days. Ordered mesoporous TiO<sub>2</sub> sphere arrays were obtained by heating the precursor/PMMA composite in open air to 400°C at 1°C /min., followed by a 4-h soak to remove the PMMA mesh template and the triblock copolymer surfactant.

*Characterization:* Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4700 FEG scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were carried out on a Hitachi H800 and a JEOL JEM-3010 transmission electron microscope, respectively (both operating at 200 kV). Powder X-ray diffraction (XRD) data were collected on a Shimadzu XRD-6000 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010 apparatus.

#### **References:**

S1 (a) N. D. Deniskina, D. V. Kalinin and L. K. Kazantseva, *Gem Quality Opals:*

*Synthetic and Natural Genesis*, Nauka, Novosibirsk, 1988 (in Russian); (b) A. P. Philipse, *J. Mater. Sci. Lett.*, 1989, **8**, 1371; (c) P. J. Darragh, A. J. Gaskin and J. V. Sanders, *Sci. Am.*, 1976, **234**, 84.



**Fig. S1** XRD patterns of TiO<sub>2</sub> sphere arrays calcined at (a) 400°C, (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C in air for 4 h.

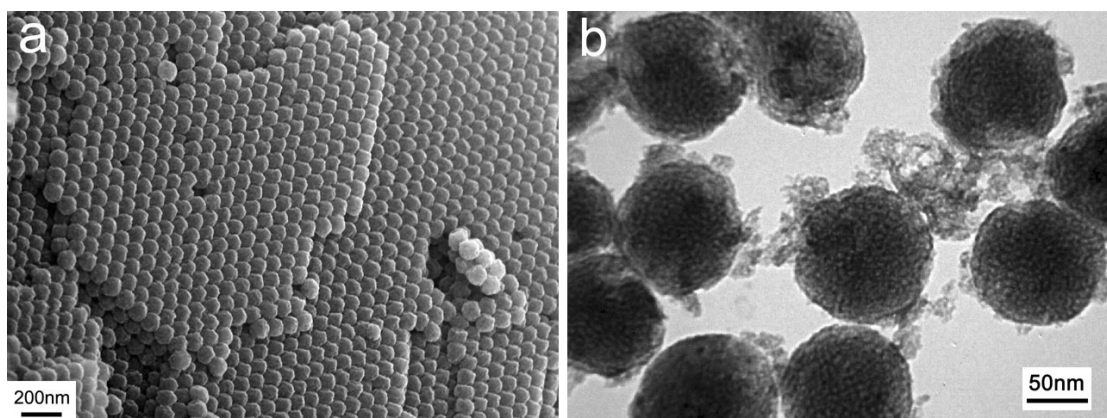
In the case of the TiO<sub>2</sub> sphere samples calcined at 400-700°C, all diffraction peaks can be assigned to the anatase phase of TiO<sub>2</sub>. As the calcination temperature increases, the anatase diffraction peaks become sharper, indicating the increase in crystallite size. When the TiO<sub>2</sub> sphere sample was calcined at 800°C, the phase transition started and small amount of rutile phase was observed in the sample. The effects of calcination temperature on phase composition and average crystallite size of TiO<sub>2</sub> are summarized in Table S1.

**Table S1** Effects of calcination temperature on phase composition and average crystallite size of TiO<sub>2</sub>

Calcination temperature (°C)	Crystallite phase <sup>a</sup> (%)	Crystallite size <sup>b</sup> (nm)
400	A-100	A-8.5
500	A-100	A-12.2
600	A-100	A-18.5
700	A-100	A-29.5
800	A-96/R-4	A-34.0/R-32.0

<sup>a</sup> Ratio of phase of TiO<sub>2</sub> based on XRD data, where A and R represent the anatase and rutile phases, respectively.

<sup>b</sup> Average crystallite size of TiO<sub>2</sub> determined by XRD using Scherrer equation.



**Fig. S2** (a) SEM image, (b) TEM image of mesoporous TiO<sub>2</sub> spheres made by using opal consisting of 180 nm diameter silica spheres as the starting template.

Using opal consisting of 180 nm diameter silica spheres as the starting template, ordered arrays of mesoporous TiO<sub>2</sub> spheres were obtained through the two-step replication process. The diameter of the mesoporous TiO<sub>2</sub> spheres shrinks to ca. 105 nm, but the spherical shape and ordered close-packed fcc structure as in the initial silica opal are kept as expected.