Supporting Information

Facile Fabrication of Crack-Free Large-Area 2D WO_3 Inverse Opal Films by 'dynamic hard-template' strategy on ITO Substrate

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Section I Experimental details

Materials:

The non-cross linked monodispersed carboxyl polystyrene (PS) spheres aqueous suspensions (PS particles, 5.0 % w/v) were purchased from Spherotech Inc. Before using, they were diluted into 0.5 % w/v with equal volumes of ethanol and water. ITO coated glass substrates were ultrasonically treated for 15 min, successively in warm water, acetone, ethanol and deionized water. Tungsten powder (99.9 %), sodium dodecylsulfate (SDS), hydrogen peroxide (H_2O_2) (30 %), and H_2SO_4 (98 %) were reagent grade and purchased form Fisher Scientific Co. Ltd. All the aqueous solutions were prepared with Millipore water (resistance = 18.2 MΩ cm^{-1}). The glass substrates were cleaned in a piranha solution (30 % H_2O_2: concentrated H_2SO_4 = 3:7 v/v) at 100 ^oC for 15 min, and then washed with Millipore water.

Synthesis of WO_3 solution:

WO_3 solution was made by dissolving 0.9 g tungsten powder in 10 ml H_2O_2 (30 %). After the initial reaction, the mixture was left to stir at room temperature for 20 h to get a clear solution, and then refluxed at 100-110 ^oC for 20 min to get a clear yellowish solution. After getting rid of the excess H_2O_2 by stirring with a Pt wire, the solution was mixed with an equal volume of ethanol.

Fabrication of 2D PS opal:

To begin with, a clean glass substrate was placed on the bottom of a Petri dish. Millipore water was added so as to just submerge the substrate. Then, the PS spheres suspension (0.5 %w/v) was added drop-wise on the surface of the water in order to get a self-assembled monolayer of PS spheres on the water surface. Afterwards, a few drops of 2% SDS solution were added into the water from a corner of the dish. The PS monolayer was pushed aside and became tightly bonded, resulting in a 2D PS opal floating over the solution. Once the 2D self-assembly was achieved, the glass support was gently removed. The 2D PS opals were named as PS920, PS880, PS530, PS480 and PS410, for which the number refers to the diameters of the PS spheres used.

Infiltration of WO_3 by soft template strategy:

Once the PS opal was formed, a WO_3 solution was slowly injected into the water, just under the 2D PS opal monolayer. The volume of WO_3 solution changed with the size of the PS spheres used. For the 410 and 480 nm PS spheres, a 0.3 ml PS spheres suspension (0.5 %w/v) was used and the volume of the WO_3 solution was 7-8 ml (for 480 nm PS) and 5-6 ml (for 410 nm PS). For the 530,

880 and 920 nm PS spheres, a 0.5 ml PS spheres suspension (0.5 %w/v) was used and the volume of the WO_3 solution was 6-8 ml (for 920 nm PS spheres); 7-9 ml (for 880 nm), and 7-8 ml (for 530 nm).

After infiltration, a waiting time of 20 min was taken to get the WO_3 solution homogeneously infiltrated within the interstitial spaces of the PS spheres monolayer. Then the ITO or glass substrate was slided under the PS/WO_3 monolayer. Next, the solution was slowly sucked out in order to sink the film onto the substrate. After drying in air, it was further dried in an oven at 50 ^oC overnight. Before taking optical images and recording the UV-vis-NIR spectra, the composite films were heated at 150 ^oC for 5 h. The 2D PS-WO_3 composite films were named as PS/$WO_3$920, PS/$WO_3$880, PS/$WO_3$530, PS/$WO_3$480 and PS/$WO_3$410, in which the last three digits refer to the size of the PS spheres used in the film. In order to remove the PS spheres and get WO_3 IO films, the 2D PS-WO_3 composite films were treated in THF for 4 h, followed by heat treatment (150 ^oC) for 5 h. The obtained 2D WO_3 IO films were named as $WO_3$920, $WO_3$880, $WO_3$530, $WO_3$480 and $WO_3$410, in which the last three digits refer to the size of PS spheres used in the film.

Fabrication of EC devices:

The EC devices were constructed in the following configuration:

ITO-coated-glass-1/WO_3 IO/ ICL[s1]/ITO-coated-glass-2,

where ITO-coated-glass-1 and ITO-coated-glass-2 are the two transparent electrodes (TEs) used to apply the electric field, WO_3 IO is the electrochromic layer and ICL is the ion conducting and electronically insulating layer. The ICL is applied on top of the WO_3 IO and the ITO-coated-glass-2 is gently pressed against this coating to ensure a uniform distribution of the ICL. After making the electrical connections, the EC device is ready for testing. The area of the EC devices was 2×2 cm^2.

Characterization:

Morphologies of the films were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700). Raman Spectroscopy was recorded at room temperature with a Jobin-Yvon Labram HR micro-analytical spectrometer equipped with a motorized xy stage and autofocus for the phase analysis. The spectra were generated with 17 mW, 1800 grooves/mm grating across the 0.8 m length of the spectrograph. The laser power was 4 mW at the sample surface. The spectral resolution is estimated to be less than 0.5 cm^{-1} for a slit width of 150 μm and a confocal hole of 300 μm. A Biochrom Ultrospec 2000 UV-vis-NIR spectrophotometer was used to record the optical transmittance spectra of the films and of the EC devices in their colored and bleached states.

[s1]: S. Balaji, Y. Djaoued, A.-S. Albert, R. Brüning, N. Beaudoin, J. Robichaud, J. Mater. Chem., **2011,** 21, 3940

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Section II : Figures and Tables

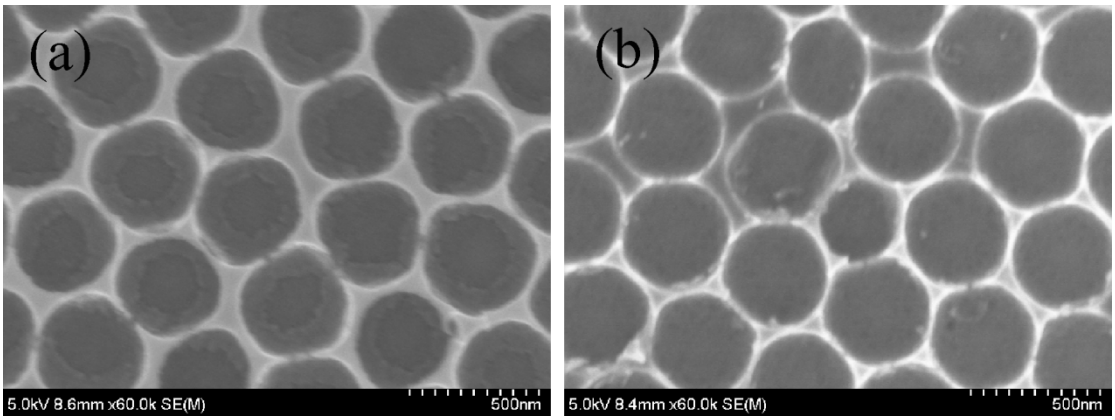


Figure S1 SEM images of WO_3 IO films on ITO substrates templated by 480 nm PS spheres: 8.0 ml (a) and 7.0 ml (b) of WO_3 solution used for the PS opals formed with 0.3 ml PS solution (0.5 %w/v/).

The average thickness of the WO_3 IO film templated by PS spheres of 880 nm diameter was measured from the SEM image was found to be around 650 nm.

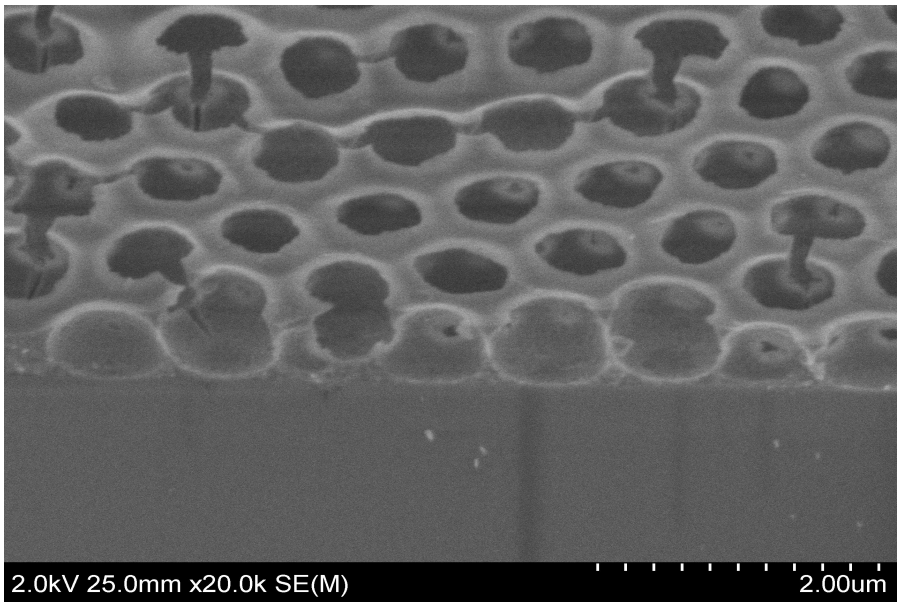


Figure S2. Cross-sectional scanning electron microscope image of a WO_3 IO film templated by PS spheres of 880 nm diameter. (Sample tilted at 47 °)

Table S1 Shrinkage of the WO_3 IO monolayers after heating at 150 ^oC

Sample name	$WO_3$920 nm	$WO_3$880 nm	$WO_3$530 nm	$WO_3$480 nm	$WO_3$410 nm
shrinkage	3.9 %	5 %	3.3 %	4.1	4.5 %

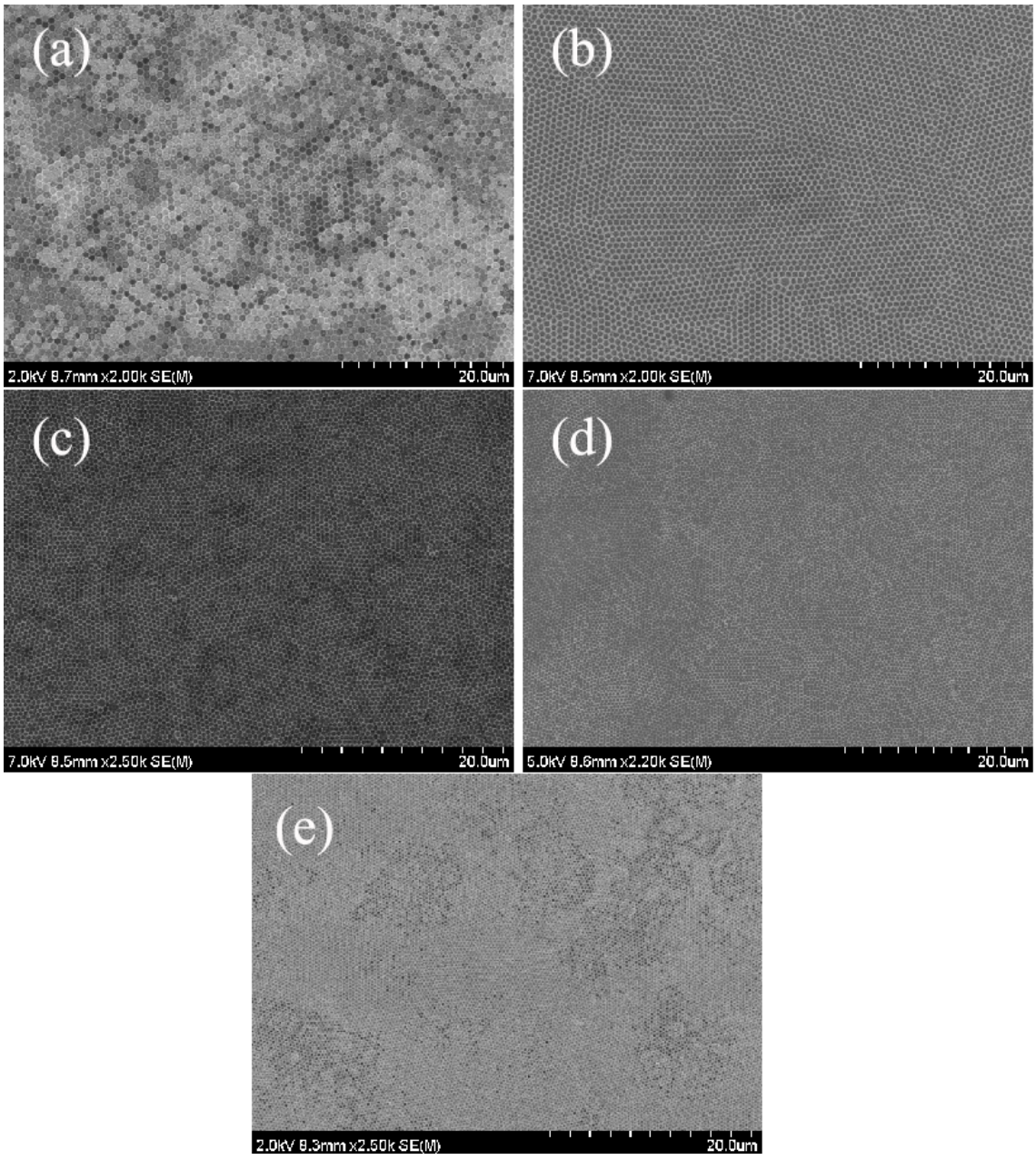
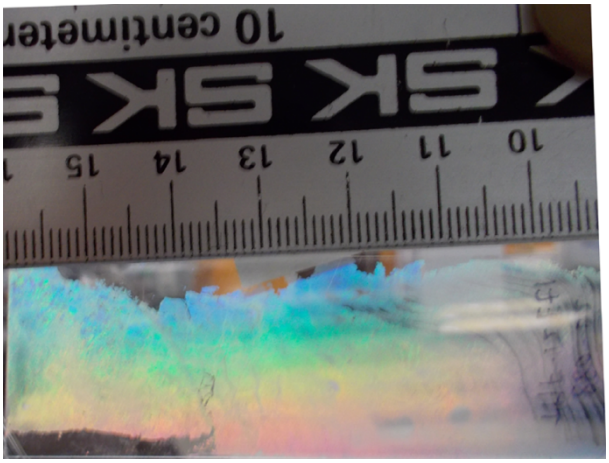


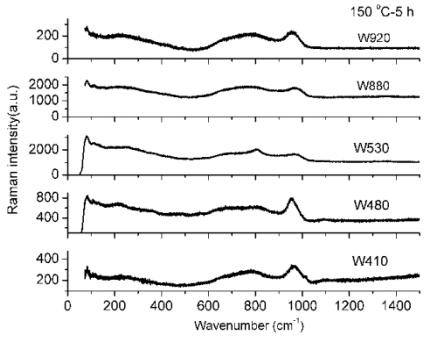
Figure S3 SEM images of WO_3 IO films templated by PS spheres of 920 nm (a); 880 nm (b); 530 nm (c); 480 nm (d) and 410 nm (e), showing crack-free samples.

(a)

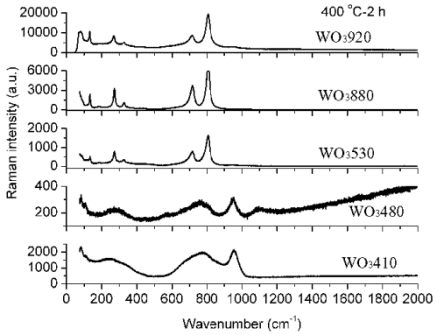


(b)

Figure S4 Optical images of WO_3 IO films on glass substrates (1 x 3 inches) templated by 410 nm (a), and 880 nm (b) PS spheres.



(a)



(b)

Figure S5 Raman spectra of WO_3 IO films heated at 150 (a) and 400 °C (b). Samples heated at 150 °C show the formation of amorphous WO_3, whereas at 400 °C, the $WO_3$920, $WO_3$880, and $WO_3$530 samples are crystalline and the $WO_3$480 and $WO_3$410 samples are still amorphous.

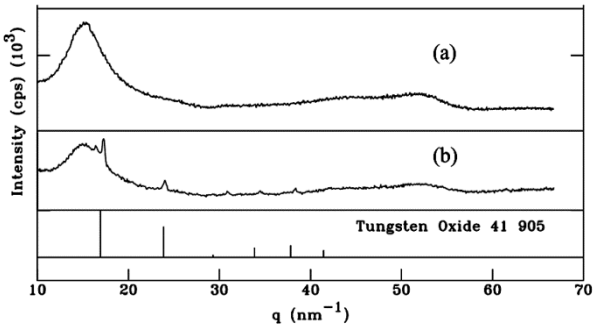


Figure S6 XRD patterns of $WO_3$880 IO sample heated at 150 ^oC (a) and 400 ^oC (b) showing amorphous WO_3 at 150 ^oC, and crystalline WO_3 (PDF-41-0905) at 400 ^oC.