Electronic Supplementary Information

Hierarchically porous anatase TiO$_2$ coated-WO$_3$ 2D IO Bilayer film and photochromic properties

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Experimental details

Materials:
Polystyrene (PS) latex microsphere with diameter of 500 nm and 750 nm in aqueous suspensions (PS particles, 2.5 % w/v) was purchased from Alfa Aesar Inc. Before using, they were diluted into 0.5 % w/v with equal volume of ethanol and water. ITO coated glass substrates were ultrasonically treated for 15 min, successively in warm water, acetone, ethanol and deionized water and then annealed at 450 °C for 5 h. Tungsten powder (99.9 %), titanium isopropoxide (Ti(i-PrO)$_4$, TTIP), TPAOH (Tetrapropylammonium Hydroxide, 25 % in water), hydrogen peroxide (H$_2$O$_2$) (30 %), and H$_2$SO$_4$ (98 %) were reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All the aqueous solutions were prepared with deionized water. Surfactant, PEO-PPO-PEO (EO20PO70EO20, Ma=5800, P123) was purchased from Aldrich. The glass substrates were cleaned in a piranha solution (30 % H$_2$O$_2$: concentrated H$_2$SO$_4$ = 3:7 v/v) at 100 °C for 15 min, and then washed with deionized water.

Synthesis of WO$_3$ solution:
WO$_3$ solution was made by dissolving 2.0 g of tungsten powder in 20 ml H$_2$O$_2$ (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 90 °C for 2 h to get a clear orange solution. Then, the solution was mixed with ethanol with the final volume ratio of water:ethanol = 7:3.

Synthesis of TiO$_2$ solution:
2.4 ml TTIP was added into 60 ml of water and stirred for 1 h. The white precipitate resulting from the reaction was rinsed with distilled water and deionized water twice, respectively, to get a wet cake ofTiO$_2$. The wet cake was dispersed into 4 ml of deionized water mixed with 0.8 ml
TPAOH (25%, aqueous solution) and stirred for 20 min at room temperature. The mixture was then refluxed at 100 °C for 24 h, to get a translucent suspension.

The suspension above was added to a P123 ethanol solution (1 g P123 dissolved into 15 ml EtOH) drop by drop, and then stirred for another 24 h.

A TiO$_2$ suspension was thus obtained and it was used for dip-coating of the WO$_3$ IO film.

Fabrication of 2D PS opal:
The 2D PS opal prepared according to literature [see Ref. 18, 19 in the manuscript] with modification. Basically, a functionalized glass slide was deposited at the bottom of a glass beaker. Then, deionized water was added into the dish up to the upper surface of the glass slide. A hollow plastic ring was allowed to hang and float on the water surface. A PS spheres ethanol/aqueous suspension, 0.3-0.5 ml 0.5 wt.% (ethanol : deionized water was 1:1 in volume ratio) was added onto the glass slide drop by drop, spreading over the glass surface. Once the suspension contacted the surrounding water at the edge of the glass slide, the PS spheres spread rapidly onto the water surface and assembled into 2D arrays. The PS suspension addition was kept on until the 2D arrays consolidated and ‘fixed’ within the plastic ring. The opaque water under the latex film was then drawn out from a pipe fixed at the bottom of the beaker, and at the same time, DI water was added under the circle until the solution under the film become transparent.

Tungsten oxide 2D IO:
Once the PS opal monolayer formed and was cleaned by water, 8 ml of WO$_3$ colloid solution was injected into the water under the PS spheres. Once the PS spheres and WO$_3$ colloid solution stabilized (about 15 min), an ITO glass slide was introduced under the film, and the solution was sucked out to make the floating film sink down onto the ITO glass. The PS/WO$_3$ composite film was then heated overnight at 50°C and again at 150°C for 15 min to allow the film to stick well to the ITO glass. The PS spheres template was removed by applying a THF treatment for 2 h, yielding a WO$_3$:TiO$_2$ 2D IO film.

Hierarchically porous anatase TiO$_2$:WO$_3$ 2D IO bilayer film (WT500, WT750):
A mesoporous TiO$_2$ film was deposited over the WO$_3$ IO by dip-coating as follows: dipping speed, 75 mm/min; withdrawing speed, 75 mm/min; immersion time: 3 s; dipping 1 layer.

The obtained composite structure was calcined at 400 °C for 4 h.

The obtained films were named “WT500” and “WT750”, in which 500 and 750 refer to the size of the PS spheres.

TiO$_2$:WO$_3$ composite film (WT film) preparation:
For comparison purposes, conventional TiO$_2$:WO$_3$ composite films were also prepared following literature [s1] with modification. Details are as follows: dissolution of tungsten powder and titanium powder (molar ratio of Ti to W = 0.46) in an ice-cooled beaker containing a (2:1) mixture of hydrogen peroxide (30 vol.%) and glacial acetic acid: then, dip-coating this solution (one layer) on ITO glass substrates with a withdrawing speed of 65 mm/m. The obtained film was
calcined at 400 °C for 4 h.

Preparation of the ion conducting (IC) solution:
First, 0.67 g of lithium iodide (powder, 99.9%) and 0.127 g of iodine (99.8%) were mixed with 2 g of ORMOSIL and 2 ml of EtOH, after which the mixture was left to stir at room temperature for 3 hours. Then, 0.35 ml of acetic acid was added and allowed to mix for a minimum of 4 hours. The final transparent solution was viscous with a yellow/brown color, and was used for the ion conducting layers (ICL).

Photochromic device fabrication:
To prepare photochromic devices, the TiO$_2$-coated-WO$_3$ 2D IO on ITO substrate was immersed in 0.5 mM ethanolic dye solution of ruthenium ([cis-bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylate) ruthenium(II) bis(tetrabutylammonium)], N719) for 24 h at room temperature. The excess dye was washed away with ethanol$^{[2]}$.
The photochromic devices were constructed in the following configuration: ITO/TiO$_2$-WO$_3$ 2D IO-N719 dye/ICL$^{[3]}$, where ITO served as the transparent electrode, TiO$_2$-WO$_3$ IO is the photochromic layer and ICL is the ion conducting and electronically insulating layer. The ICL is applied on top of the TiO$_2$-WO$_3$ IO layer. The area of the PC devices was 2×2 cm$^2$.
For comparison purpose, a photochromic device based on the mesoporous TiO$_2$-WO$_3$ composite film was also similarly fabricated having the following configuration: ITO/TiO$_2$-WO$_3$-N719 dye/ICL.

Characterization:
Morphologies of the films were characterized using a field-emission scanning electron microscope (SEM, Hitachi S-570). HRTEM characterization was achieved using JEM-2010(HR). The optical transmittance spectra of the films and of the devices in their colored states were obtained using a PERSEETU-1810PC UV-vis-NIR spectrophotometer. ALRS-5 Micro-Raman Spectrometer was used to record the Raman Spectra at room temperature. The N$_2$ sorption isotherms were measured using a BeiShiDe 3H-2000PM2 porosimeter. Powder XRD patterns were recorded by using a Rigaku D/Max2200PC diffractometer with CuKa radiation (40 kV and 40 mA) with a scanning rate of 10 °min$^{-1}$.

**Figures**

**Figure S1** Micro-Raman spectra for hierarchically porous anatase TiO$_2$-coated-WO$_3$ 2D IO bilayer (red line) and WO$_3$ IO on SiO$_2$ coated ITO substrate (black line), calcined at 400 °C for 4 h and using SDS assistant route [s4].

**Figure S2** SEM image of hierarchically porous anatase TiO$_2$-coated-WO$_3$ 2D IO composite bilayer templated from 750 nm PS spheres.
Figure S3 $\text{N}_2$ sorption isotherms of the TiO$_2$ used for coating, with pore distribution in inset.

Figure S4 TiO$_2$ coating covering the WO$_3$ 2D IO macropores when low withdrawing speed was used.
Figure S5 Cross-sectional view of TiO$_2$ coated -WO$_3$ 2D IO bilayer film templated from 500 nm PS spheres (left) and corresponding EDS analysis (right).

Figure S6 XRD patterns of the TiO$_2$ -WO$_3$ powder obtained by carefully scraping from the substrate the film templated from 500 nm PS spheres (WT500 powder); TiO$_2$ coated-WO$_3$2D IO composite bilayer films templated from 500 nm PS spheres (WT500 film) and 750 nm PS spheres (WT750 film). The tungsten oxide peaks are identified as monoclinic-WO$_3$ (pdf # 43-1035, vertical solid bars). TiO$_2$ in the anatase form is also present (dotted vertical bars, pdf # 21-1272).
Table S1 Lattice constants, crystalline phases, and particle sizes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constants (nm)</th>
<th>Crystalline phase</th>
<th>Crystal size (nm)</th>
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<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
</tr>
<tr>
<td>WT750 film</td>
<td>0.7304 ± 0.0006</td>
<td>0.7547 ± 0.0006</td>
<td>0.7688 ± 0.0005</td>
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<tr>
<td>WT500 film</td>
<td>0.7351 ± 0.0004</td>
<td>0.7580 ± 0.0004</td>
<td>0.7713 ± 0.0004</td>
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<tr>
<td>WT500 powder</td>
<td>0.7317 ± 0.0003</td>
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<td>0.7686 ± 0.0003</td>
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<tr>
<td></td>
<td>0.3794 ± 0.004</td>
<td>0.3794 ± 0.004</td>
<td>0.946 ± 0.003</td>
</tr>
</tbody>
</table>

Figure S7 Micro-Raman spectra of the TiO$_2$-coated-WO$_3$ 2D IO composite bilayer films templated from 750 nm (WT750 film) and 500 nm PS spheres (WT500 film). All labeled peaks are from monoclinic WO$_3$ except the one at 148.6 cm$^{-1}$ which belongs to TiO$_2$ in the anatase form.
Figure S8 (a) HRTEM pattern of the TiO$_2$-WO$_3$ powder obtained by carefully scraping down the film template using 750 nm PS spheres. The plane spacing $d = 0.39$ nm corresponds to the 002 lattice planes of m-WO$_3$ (pdf#43-1035). (b) HRTEM image taken from another area. The plane spacing $d = 0.35$ nm and 0.19 nm correspond respectively to the 101 and 200 lattice planes of anatase TiO$_2$ (pdf#21-1272). The TiO$_2$ nanoparticles are found to be from 5 to 10 nm in size. The inset in (b) shows the area, revealing WO$_3$ particles of around 20 nm in size.