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# A simple way to fabricate pure anatase 2D TiO<sub>2</sub> IO monolayer: structure, color control and its application in electrochromism†

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Pure anatase two dimensional (2D) TiO<sub>2</sub> inverse opal (IO) films, consisting of a highly ordered hexagonal-patterned structure, are synthesized from various sized polystyrene spheres (PS) as colloidal template simply coupled with TiOSO<sub>4</sub> aqueous solution as TiO<sub>2</sub> precursor using a "dynamic-hard-template infiltration" strategy. Herein, the TiOSO<sub>4</sub> solution is directly infiltrated into the interstices of the 2D self-assembled PS opal template at an air/water interface resulting in a TiOSO<sub>4</sub>/PS opal composite film floating on the surface of water which was further deposited onto ITO or silicon substrates. Calcination of the obtained opal composite films at temperatures ranging from 300 to 550 °C resulted in 2D TiO<sub>2</sub> IO films with various pore sizes having an inverse moth's eye structure. Based on EDS measurements, sulfur ions S<sup>6+</sup> were detected in the IO films calcined up to 550 °C. In order to eliminate these S<sup>6+</sup> ions and obtain pure anatase 2D TiO<sub>2</sub> IO, aqueous immersion was performed after calcination without disturbance of the IO ordered structure. Surface morphology, crystal phase and optical transmittance of the TiO<sub>2</sub> IO films, were concurrently investigated by SEM, Raman and UV-vis-NIR. Owing to their precisely adjustable structure, the obtained TiO<sub>2</sub> 2D IO films exhibited structural colors varying from pale purple, to blue, to polychrome as the array period increases. The films obtained on ITO substrates were successfully used as active electrodes in the fabrication of electrochromic (EC) devices.

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## Introduction

As one of the most promising semiconductors, titanium dioxide (TiO<sub>2</sub>) has been studied for a long time, due to its extensive applications in photocatalysis,<sup>1–3</sup> energy conversion and storage,<sup>4</sup> sensors,<sup>5,6</sup> and so on. Nanostructured TiO<sub>2</sub> films consisting of nanorods,<sup>7</sup> nanotubes,<sup>8</sup> hollow spheres<sup>9</sup> and inverse opal (IO)<sup>10</sup> have been particularly focused on due to their convenience for the fabrication of various devices. Among them, inverse opal or ordered macroporous structures have been widely popular candidates in optoelectronic applications because of their enhanced molecular diffusion kinetics due to increased surface area as well as their outstanding light capture ability and higher solar energy conversion from the increased path length of light (slow photons).<sup>11–14</sup>

To obtain TiO<sub>2</sub> inverse opal, various methods have been attempted, such as atomic layer deposition (ALD) or chemical vapour deposition (CVD),<sup>15,16</sup> doctor blade,<sup>17</sup> electrodeposition<sup>18</sup> and so on. The general fabrication scheme of IOs starts from

primary formation of an opal template, afterwards, infiltration of guest material, followed by its conversion and inversion into the aimed material.<sup>19,20</sup> Usually, for the synthesis of TiO<sub>2</sub> IO films, guest materials such as titanium alkoxides (reactive infiltration) or titania nanoparticles (non-reactive infiltration) were infiltrated into the interstices of the opal template by capillary action, in the form of fluid (liquid or vapour). When titania nanoparticles were directly introduced into the opal template, the stabilization of the TiO<sub>2</sub> colloidal sol was important, but also difficult to attain due to the low intrinsic surface charge of titania.<sup>21</sup> Although it was solved under the assistance of certain surfactant,<sup>10,22</sup> such as tetramethylammonium hydroxide (TMAH), the use of surfactant destroys the array of the opal template to some extent since it accordingly changes the surface tension of the opal films. In that case, a careful control of the infiltration is always needed, which process is difficult to replicate in the perspective of practical application. Therefore, most researchers chose reactive infiltration route by using precursors instead of titania nanoparticles followed by chemical conversion. Typical titania precursors are titanium alkoxides (for example, tetra-*n*-butyltitanate (TBT)<sup>9,23,24</sup>) and titanium halide salt.<sup>25,26</sup> The former TBT was often infiltrated by immersion or dip-coating, frequently resulting in low filling fraction and poor ordering, partly due to the high shrinkage during conversion and low interaction between opal template and substrate during dipping.<sup>9,24</sup> As for titanium halide salt, it is

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often applied in various vapour phase deposition routes, especially atomic layer deposition (ALD).<sup>25</sup> The latter makes it possible to deposit precursor onto complex-shaped substrates with a controllable layer thickness<sup>27,28</sup> while relatively expensive equipment hinders its practical use.

Many authors have used  $\text{TiOSO}_4$  to obtain  $\text{TiO}_2$  nanoparticles (in powder form), mainly for photocatalytic applications. Moreover, the synthesis methods used are more or less complex, using additives, depending on the goal of the research.<sup>29–34</sup> However, papers on fabrication of  $\text{TiO}_2$  thin films using  $\text{TiOSO}_4$  as precursor are scarce. For instance Ge *et al.* synthesized anatase  $\text{TiO}_2$  sols by peptization of the hydrolysed titanyl sulfate in hydrogen peroxide solution with subsequent reflux.  $\text{TiO}_2$  thin film were deposited on glass slides at room temperature from the as prepared  $\text{TiO}_2$  sol by dip-coating without further thermal treatment to eliminate organics or to induce crystallization.<sup>35</sup> Bavykin *et al.* produced  $\text{TiO}_2$  thin films on different substrates placed in a solution containing  $\text{TiOSO}_4$  and  $\text{H}_2\text{SO}_4$  at various concentrations and heated at 80 °C to study the kinetics of film growth.<sup>36</sup> Yamabi *et al.* obtained films with mixed rutile and anatase phases by heterogeneous nucleation in aqueous solutions with titanyl sulfate at near room temperature. The phase of the  $\text{TiO}_2$  films was essentially determined by the initial pH value and the Ti concentration of the precursor solutions.<sup>37</sup> In these three cited works, no mention is made of the possible presence of sulfur ions in the obtained films.

Here, we propose  $\text{TiOSO}_4$  as an alternative to fabricate 2D  $\text{TiO}_2$  IO films under our newly developed route, the “dynamic hard template infiltration” strategy.<sup>38</sup> Unlike titanium alkoxides, which usually requires organic solvent,  $\text{TiOSO}_4$  is an inorganic salt which easily dissolves in water. Moreover,  $\text{TiO}_2$  in the anatase phase can be obtained solely from hydrolysis of an aqueous solution of  $\text{TiOSO}_4$  followed by calcination, without using any other additive or method to enhance crystallisation. Apart from the usage of  $\text{TiOSO}_4$ , the “dynamic hard template infiltration” strategy assures the maximum filling fraction since the polystyrene spheres, floating on the surface of water in the form of opal film, are loosely connected with each other, having more freedom to move in comparison to a hard PS opal template already deposited on a substrate in the conventional “hard template” method. The high filling fraction obtained in “dynamic hard template infiltration” strategy also avoids a repeated infiltration which happens in most situations of immersion route. To attain pure anatase 2D  $\text{TiO}_2$  IO films, the  $\text{SO}_4^{2-}$  ions were eliminated by aqueous immersion after calcination of the films.

## Experimental

### Materials

The non-cross-linked monodispersed carboxyl polystyrene (PS) sphere aqueous suspensions (PS particles, 5.0% w/v) were purchased from SpheroTech Inc. Before using, they were diluted into 0.5% w/v (for 200 nm PS sphere, 0.25 %w/v is used) with equal volumes of ethanol and water. Prior to use, the ITO coated glass substrates or silicon chips were ultrasonically treated for

15 min successively in water, acetone, ethanol and deionized water.  $\text{TiOSO}_4$ , sodium dodecylsulfate (SDS) and ethanol of reagent grade were purchased from Sigma-Aldrich. All the aqueous solutions were prepared with Millipore water (resistance = 18.2 M $\Omega$  cm<sup>−1</sup>). The glass substrates were cleaned in a piranha solution (30%  $\text{H}_2\text{O}_2$ : concentrated  $\text{H}_2\text{SO}_4$  = 3 : 7 v/v) at 100 °C for 15 min, and then washed with Millipore water.

### Fabrication of $\text{TiO}_2$ IO films

The 2D  $\text{TiOSO}_4$ /PS opal composite monolayer building blocks were synthesized by “dynamic hard template infiltration” strategy as developed in our previous work.<sup>10,20,38</sup> Initially, a PS opal floating on surface of water was synthesized by gas–liquid–solid interface self-assembly method, as follows: a clean functionalized glass slide was placed on the bottom of a Petri dish. Then, Millipore water was added until it nearly submerged the slide. Afterwards, diluted PS suspension was added drop-by-drop onto the glass slide, to get a self-assembled monolayer of PS spheres on the water surface. Then a few drops of 2 wt%, SDS solution were added into the water to closely pack the PS monolayer, resulting in a 2D PS opal template floating over water.

After the formation of the PS opal monolayer, 12 ml  $\text{TiOSO}_4$  aqueous solution (0.43 mol L<sup>−1</sup>) was injected into the water underneath the PS spheres opal template. After around 20 minutes, a 2D  $\text{TiOSO}_4$ /PS opal composite monolayer was self-assembled on the water surface. Next, the water was slowly sucked out to sink the opal composite monolayer film onto ITO or silicon substrate.

To obtain the 2D  $\text{TiO}_2$  IO films, the PS spheres template was removed from the opal composite by calcination for 1.5 h at various temperatures ranging from 300 to 550 °C.

After calcination, some chosen samples were further immersed into water for 3 days.

The samples were named using letters and three digits in the following way: PS, TP and T, refers to PS spheres opal template, titania precursor/PS spheres opal composite, and  $\text{TiO}_2$  inverse opal, respectively, while the three succeeding digits used refer to the PS spheres diameter in nm. The calcination temperatures were indicated by adding a dash symbol (“—”) followed by the calcination temperature in °C. Finally, when immersion took place “im” was added at the end of the sample name. For instance, sample T530-550im is a 2D  $\text{TiO}_2$  IO templated from 530 nm PS spheres, calcined at 550 °C, followed by immersion in water for 3 days.

### Synthesis of the ion conducting solution

For the synthesis of the ion conducting (IC) solution, hybrid ORMOSIL was first prepared by an acylation reaction between poly(propylene glycol)bis(2-aminopropyl ether) (2-APPG) and isocyanatopropyltriethoxysilane (ICS) in tetrahydrofuran (THF) in a volume ratio of 1 : 0.1 : 1, refluxed for 6 hours at 65 °C. Then, THF was evaporated resulting in a transparent, thick solution. An alcoholic solution of LiI (Aldrich powder, 99.9%) +  $\text{I}_2$  (BDH, 99.8%, AR) was added into this hybrid ORMOSIL, to



obtain the IC solution. Final solution was viscous with a yellow/brown color.<sup>38</sup>

### Fabrication of an EC device

An EC device was fabricated using sample T530-550im. First, an ion conducting layer (ICL) was coated by doctor blade technique on top of the 2D TiO<sub>2</sub> IO film deposited on an ITO substrate. Then, another ITO substrate was gently pressed against the ICL coating to ensure a uniform distribution of the ICL. This assembly resulted in an asymmetric EC device with the following configuration: ITO/TiO<sub>2</sub> IO/ICL/ITO. The area of the EC device was  $\sim 2.5 \times 4 \text{ cm}^2$ .

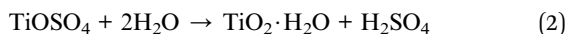
### Characterization

SEM studies were performed using a S4800 FESEM system from Hitachi at a working distance of 3.2 mm. Energy Dispersive Spectroscopy (EDS) analysis were performed using Oxford Instruments X-Max and an INCA software. Micro-Raman spectra were recorded at room temperature with a Jobin-Yvon Labram HR micro analytical spectrometer. The spectra were generated with 17 mW, 632.8 nm, He-Ne laser excitation. 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.

## Results and discussion

### Formation process of 2D TiO<sub>2</sub> IOs

TiOSO<sub>4</sub> is usually used to prepare TiO<sub>2</sub> particles in pigment industry. It has obvious advantages over most of other Ti<sup>4+</sup> containing precursors (such as titanium alkoxides) like low cost, aqueous solubility, and relative stability in aqueous solution. When dissolved in water, TiOSO<sub>4</sub> is partly hydrolyzed into H<sub>2</sub>TiO<sub>3</sub> or TiO<sub>2</sub>·H<sub>2</sub>O (eqn (1) & (2)) and further converts into TiO<sub>2</sub> particles depending on the reaction conditions.<sup>39</sup>



Such formed H<sub>2</sub>TiO<sub>3</sub> (TiO<sub>2</sub>·H<sub>2</sub>O) exist in the form of stable aqueous colloid when its concentration is lower than a certain value, rendering it practical for the preparation of 2D TiO<sub>2</sub> IO films under “dynamic hard template infiltration” strategy. Here the maximum concentration was 0.43 mol L<sup>-1</sup>.

After the formation of PS spheres opal templates obtained from 220 to 920 nm diameter PS spheres floating on the surface of water, H<sub>2</sub>TiO<sub>3</sub> (TiO<sub>2</sub>·H<sub>2</sub>O) precursor sol was injected underneath the PS opal crystal. Under the influence of capillary forces, the H<sub>2</sub>TiO<sub>3</sub> precursor sol infiltrated the interstitial spaces between the PS spheres of the opal film. During this process, the PS spheres interstitial spaces enlarge to some extent, but the relative position of the spheres is kept unchanged due to the dominant capillary action, *i.e.*, the opal structure is retained. Apart from this, since the PS spheres are floating onto the liquid–air interface, they have freedom to

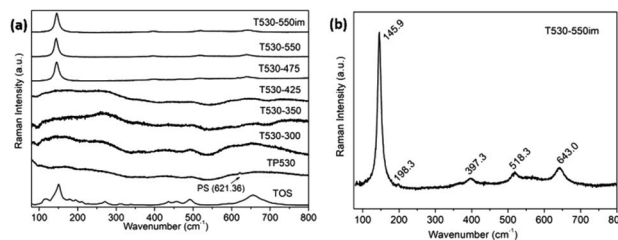
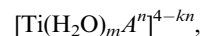


Fig. 1 Raman spectra of: (a) TiOSO<sub>4</sub> (TOS) and of TiO<sub>2</sub> IOs templated from 530 nm diameter PS spheres and calcined at different temperatures, including sample T530-550 after immersion; (b) Raman spectrum of sample T530-550im alone, exhibiting the peaks of anatase TiO<sub>2</sub>.

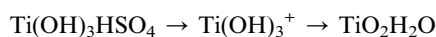
accommodate guest materials in their interstitial spaces and therefore higher filling fraction is achieved in contrast to infiltration conducted under a “static hard template” with the opal template stuck onto the substrate.<sup>10,38</sup> After a homogenizing period of around 20 minutes, an ITO or silicon substrate was inserted into the solution, underneath the floating 2D TiOSO<sub>4</sub>/PS opal composite film. The final TiO<sub>2</sub> IO film was obtained by sucking out the solution to deposit the opal composite film onto the substrate, followed by drying at 50 °C and calcination at temperatures ranging from 300 to 550 °C.

After hydrolyzation, TiOSO<sub>4</sub> became amorphous with sulfate ions complexed with Ti<sup>4+</sup> forming some ligand:



“A” refers to anions with chemical valence of (−*k*), such as SO<sub>4</sub><sup>2−</sup> while “*m*” is from 1 to 6 and *n* = 6 *m*, typical complex, as {[TiO(OH)<sub>*k*</sub>]<sub>*n*</sub><sup>*n*(−2−*k*+4)</sup>SO<sub>4</sub>]<sub>*n*</sub><sup>*n*(−2−*k*+4)−2</sup>}.<sup>39</sup> Upon calcination, this situation persisted until 425 °C was reached. Crystallization of TiO<sub>2</sub> occurs when the calcination temperature reaches 475 °C as shown in the Raman spectra of Fig. 1(a).

Generally, the reaction could be presented as follows:



The Raman results from Fig. 1 were combined to the corresponding EDS test results to produce Table 1. It is observed for sample T530-300, T530-350 and T530-425, whose phases are amorphous, that the ratios of S<sup>6+</sup> to Ti<sup>4+</sup> are all above 1.5,

Table 1 Effect of calcination on phase and S<sup>6+</sup>/Ti<sup>4+</sup> ratio

Sample name	Calcination temperature (°C)	Raman result	S <sup>6+</sup> /Ti <sup>4+</sup>
T530-300	300	Amorphous	1.65
T530-350	350	Amorphous	3.1
T530-425	425	Amorphous	3.52
T530-475	475	Crystallized	0.28
T530-550	550	Crystallized	0.75
T530-475im	475	Crystallized	0–0.03
T530-550im	550	Crystallized	0



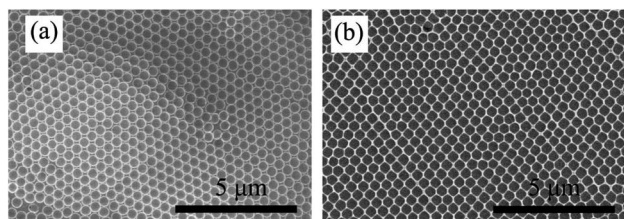


Fig. 2 SEM images for sample T530-550 before (a) and after (b) aqueous immersion.

indicating that sulfate was still complexed firmly with  $\text{Ti}^{4+}$ , without full decomposition. When calcination temperature is higher than  $425^\circ\text{C}$ , the ratio of  $\text{S}^{6+}$  to  $\text{Ti}^{4+}$  is quickly lowered below 1.0 (sample T530-475 & T530-550). Unfortunately, it is hard to get rid of  $\text{S}^{6+}$  thoroughly simply through calcination. In order to obtain pure anatase  $\text{TiO}_2$  from calcination and considering that the remaining sulfate in our samples exists in the form of soluble ions ( $\text{SO}_4^{2-}$ ), further washing was attempted by immersing the films into distilled water for 3 days (T530-475im & T530-550im). After this immersion, the  $\text{S}^{6+}$  to  $\text{Ti}^{4+}$  ratios for both samples were greatly reduced, especially for sample T530-550im whose ratio became 0, indicating that the  $\text{S}^{6+}$  has been removed thoroughly. Further SEM observation demonstrates that the sample calcined at  $550^\circ\text{C}$  kept the same good ordered structure before and after aqueous immersion (Fig. 2).

As seen in Fig. 1(b), the Raman spectrum of  $\text{TiO}_2$  IO sample T530-550im exhibits the typical modes of anatase  $\text{TiO}_2$ .<sup>40,41</sup> These are three  $\text{E}_g$  modes at  $145.9$ ,  $198.3$  and  $643.0\text{ cm}^{-1}$ , two  $\text{B}_{1g}$  modes at  $397.3$  and  $518.3\text{ cm}^{-1}$ . This last mode overlaps with an additional  $\text{A}_{1g}$  mode at  $518.9\text{ cm}^{-1}$ . The  $\text{E}_g$  mode is caused by symmetric stretching vibration and the  $\text{B}_{1g}$  by symmetric bending while the  $\text{A}_{1g}$  mode is caused by antisymmetric bending of O–Ti–O in  $\text{TiO}_2$ .<sup>40,41</sup> Both  $\text{E}_g$  (1) and  $\text{E}_g$  (2) modes at  $145.9$  and  $198.3\text{ cm}^{-1}$  are blue-shifted in the  $\text{TiO}_2$  IO in contrast to commercial anatase  $\text{TiO}_2$  powder ( $142.5\text{ cm}^{-1}$ ) while other Raman modes remain unchanged. The broadened ( $12.9\text{ cm}^{-1}$ ) and high-frequency shifts ( $145.9\text{ cm}^{-1}$ ) indicate that sample T530-550im is constituted of fully crystallized  $\text{TiO}_2$  nanoparticles. Furthermore, it was verified that PS and its calcination products were completely removed from the 2D  $\text{TiO}_2$  IO samples after calcination at  $550^\circ\text{C}$  (see Fig. S1†). A phonon confinement model, which establishes a relationship between the crystallite sizes and the FWHM of the main Raman peak of  $\text{TiO}_2$  (here  $12.1\text{ cm}^{-1}$ ), was used and the corresponding crystallite size was found to be  $\sim 11.5\text{ nm}$ .<sup>42,43</sup>

Recently Pillai *et al.* studied sulfur doped  $\text{TiO}_2$  ( $\text{S-TiO}_2$ ) nanoparticles for their enhanced photochemical activity.<sup>34</sup> In the Raman characterization of those nanoparticles they observed that  $\text{S-TiO}_2$  presents Raman scattering similar to that of  $\text{TiO}_2$ . However, by close examination of the main peak, they also noticed that the presence of sulfur shifted the main Raman peak towards lower frequencies. They attributed the shift to the Ti–S bond formation, possibly altering the force constant of the  $\text{E}_g$  vibration mode in contrast to the Ti–O bonds. In our work,

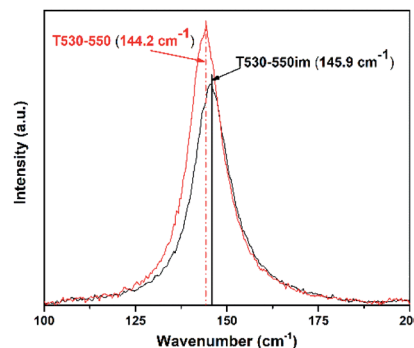


Fig. 3 Raman spectra of samples T530-550 and T530-550im illustrating the shift of the main  $\text{E}_g$  peak from the presence of sulphur ions.

similar shift of the main  $\text{TiO}_2$  Raman peak was observed. As mentioned above, EDS was used to assess the ratio of ions  $\text{S}^{6+}$  to  $\text{TiO}^{4+}$ . No sulfur was seen in the EDS results for sample T530-550im whereas sample T530-550 had a  $\text{S}^{6+}$  to  $\text{TiO}^{4+}$  atomic ratio of 0.75. In agreement with Vishnu's observations, the main Raman peak of sample T530-550 was shifted to  $144.2\text{ cm}^{-1}$  as compared to that of sample T530-550im ( $145.9\text{ cm}^{-1}$ ) as seen in Fig. 3.

Fig. 4(a) to (c) show the SEM images of the large-area highly ordered and uniform opal structures obtained from 530 nm PS spheres at each fabrication step, from PS opal (Fig. 4(a)), to  $\text{TiO}_2$  precursor/PS opal composite (Fig. 4(b)), to  $\text{TiO}_2$  IO (Fig. 4(c)). Infiltration of  $\text{TiO}_2$  precursor enlarged the interstitial spaces in the PS opal film from close contacted to around 27 nm. After removal of the PS spheres by calcination, one can recognize their traces left in the form of spherical air cavities. The opal periods of the samples were estimated from the SEM images using the ImageJ software. The results were 471, 498 and 469 nm for samples PS530, TP530 and T530-500im, respectively. These values are smaller than the 530 nm nominal value of the PS spheres diameter by 11%. The difference between nominal and actual (or measured) value of the PS spheres diameter had been noted in one of our earlier work.<sup>20</sup> From the cross-sectional SEM image Fig. 4(d) and using ImageJ software, the film sample

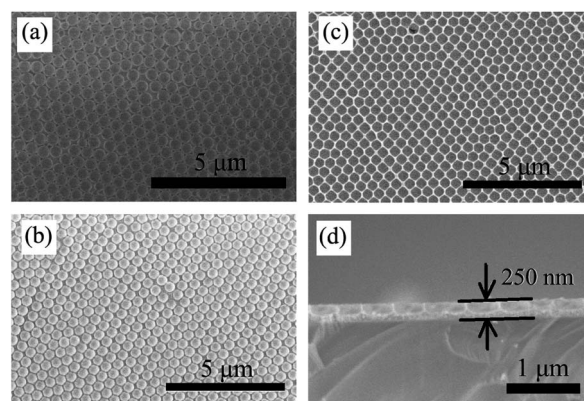


Fig. 4 SEM images of (a) PS530; (b) TP530; (c) T530-550im and its cross-sectional SEM image (d).



T530-500im, was estimated to be 250 nm thick. The resultant  $\text{TiO}_2$  IO shows some shrinkage in contrast to the 2D  $\text{TiOSO}_4/\text{PS}$  opal composite whose structural period is around 498 nm (Fig. 4(a)). Thus, the lateral shrinkage, calculated from the opal periods before and after calcination is estimated to be 5.8%.<sup>44</sup> This is attributed to mass loss and density increase during the transformation of the sample from 2D  $\text{TiOSO}_4/\text{PS}$  opal composite to anatase  $\text{TiO}_2$  IO.

Fig. 5(a) shows the UV-vis-NIR transmittance spectra of PS opal (PS530), 2D  $\text{TiOSO}_4/\text{PS}$  opal composite (TP530) and  $\text{TiO}_2$  IO (T530-550im) films templated from 530 nm PS spheres. All three samples show peaks in the range of 500 to 600 nm attributed to the blue-green range. The PS opal has a main peak situated at around 570 nm while the 2D  $\text{TiOSO}_4/\text{PS}$  opal composite film (TP530) has its main peak at 540 nm. The main peak for the  $\text{TiO}_2$  IO film (T530-550im) is situated at 580 nm. Similar to most of other photonic crystals (PCs),<sup>20</sup> both 2D  $\text{TiOSO}_4/\text{PS}$  opal composite film (TP530) and  $\text{TiO}_2$  IO film (T530-550im) show characteristic shining structural blue-green color (Fig. 5(b) to (e)), which is consistent with the results from UV-vis-NIR transmittance spectra, proof of a well-ordered array of pores. Also, different substrates render different glare effect due to their different refractive indices: films on ITO substrates (Fig. 5(b) and (c)) have lower glaring effect than those on silicon substrates (Fig. 5(d) and (e)) since ITO has a much lower refractive index (around 1.9) than silicon (3.42).

### Microstructural and color control of $\text{TiO}_2$ 2D IOs

Further exploration of color control by structure adjustment was conducted by using various sizes of PS sphere templates, from 200 to 920 nm, using the same process as for sample T530-

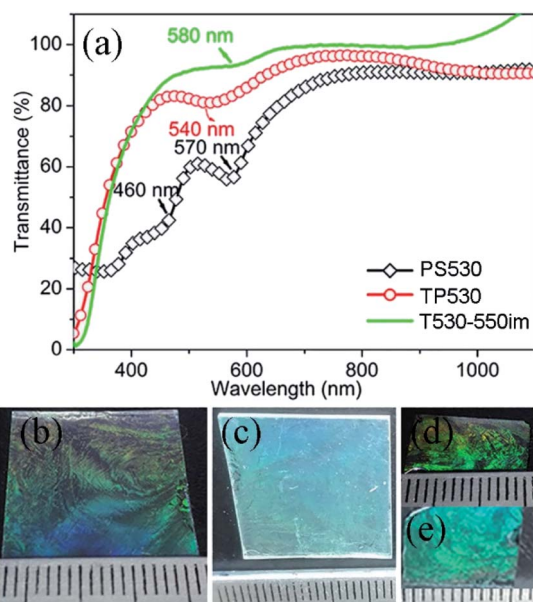


Fig. 5 UV-vis-NIR transmittance spectra of PS530 (black diamonds) (a), TP530 (red circles), T530-550im (green trace), and optical photos for samples TP530 supported on ITO (b) and silicon chips (d); T530-550im supported on ITO (c) and silicon chips (e).

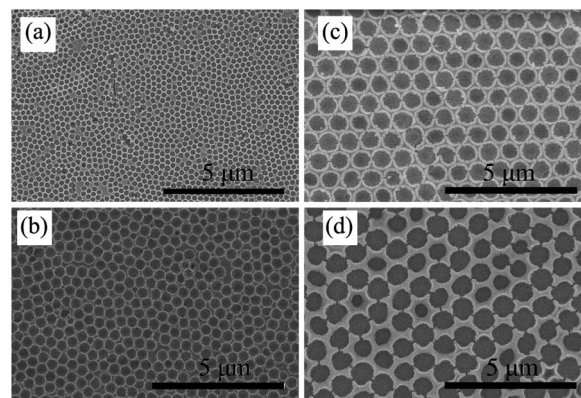


Fig. 6 SEM images of (a) T220; (b) T480; (c) T880 and (d) T920 templated from 220, 480, 880 and 920 nm PS spheres, respectively.

550im. In order to simplify the sample name, we used T220, T480, T880 and T920, 'T' referring to template and the digits to the nominal diameter of the PS spheres in nm: T220 refers a  $\text{TiO}_2$  IO film templated from 220 nm sized PS spheres. Those  $\text{TiO}_2$  IO films were also referred to as T series. As it is shown in Fig. 6, all these films show circular upper-end openings with honeycomb structures, indicating their hexagonal symmetry. Similar to crystal defects, some minor disorder could be attributed to sporadic presence of PS spheres of different diameters. The pore diameter at the film surface is smaller than that of the PS spheres due to the framework shrinkage as well as the filling height of the guest materials. From measurements on the SEM images of Fig. 6 using the imageJ software, the array periods of the T series IO samples were estimated to be 237, 435, 809 and 919 nm for samples T220, T480, T880 and T920, respectively. Fig. 7(a) shows the UV-vis-NIR transmittance spectra as well as corresponding optical reflection images (insets in Fig. 7(a)) for samples T220, T480, T880 and T920. One can see an obvious color change which depends on the wavelength absorbed by the photonic band gap as the sizes of PS templates change. A single color is distinct for T220 (dark purple) and T480 (blue), while T880 and T920 appeared as rainbow-like. The wavelength of the absorption maximum shows red shift as the array period increases from 435 nm (T480) to 809 nm (T880) to 919 nm (T920), while there is no absorption maximum observed in T220 partly due to its

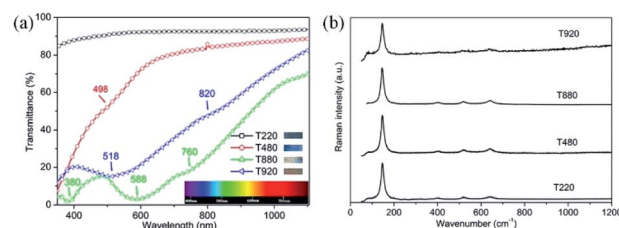


Fig. 7 (a) UV-vis-NIR transmittance spectra for samples T220 (black squares), T480 (red circles), T880 (green up-triangles) and T920 (blue left-triangles); (b) Raman spectra of the corresponding 2D  $\text{TiO}_2$  IO films. Inset in (a) show the film's optical reflection images.





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