Hierarchical ordered macro/mesoporous titania with a highly interconnected porous structure for efficient photocatalysis†

Tao Zhao, a Yuan Ren, b Jianping Yang, a Lianjun Wang, a Wan Jiang, a Ahmed A. Elzatahry, e Abdulaziz Alghamdi, f Yonghui Deng, bd Dongyuan Zhao b and Wei Luo* a c

In this study, a 3-dimensional interconnected hierarchical ordered macro/mesoporous titania (HOPT) with thin walls, crystalline framework, large cavities (~420 nm), uniform mesopores (3.7 nm) and high surface area (177 m² g⁻¹) was synthesized through a facile bi-template interface-directed deposition method using poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide) (Pluronic P123) triblock polymer as a soft template and structure directing agent, titanium isopropoxide (TIPO) as a titania source and 3-dimensional ordered macroporous carbon (3DOMC) as the hard template and the nanoreactor. This was followed with a two-step thermal treatment in nitrogen and air. Under simulated sunlight irradiation at room temperature, the HOPT shows an ultrahigh photocatalytic activity for the degradation of Rhodamine B (RhB) with a fast reaction rate that is three times higher than commercial titania nanoparticles (P25).

Introduction

Over the past decades, titanium dioxide (TiO₂) materials have received extensive research interest among researchers because of their unique electronic and optical properties, such as strong oxidizing power, favorable band gap (3.2 eV), low cost, high chemical inertness and good photo-stability. 1-3 As a result, titania-based materials have shown promising applications in diverse fields including dye-sensitized solar cells, 4,5 photocatalysis, 6-8 and gas sensing. 9-14 Therefore, tremendous effort has been made towards the design and fabrication of various nanostructures of TiO₂ to enhance their application performances including films, 15,16 nanohelixes, 9 nanorods, 17 hollow microspheres, 18 spherical particles, 19,20 nanotubes, 21 micro-boxes, 22 and porous structures. 23-27 Among them, photocatalysis based on porous titania has proven to be a promising method for the purification and treatment of contaminated air and waste water. 18-30 The pollutant degradation performance of titania-based materials is highly reliant on their nanostructures, crystal structures, surface states, crystallinity as well as specific surface area. 2 As an important kind of nanstructured materials, porous titania materials have attracted considerable attention owing to their distinctive properties such as high surface areas, uniform pore size, abundant porous structure and large pore volumes. These merits not only provide regularly aligned pathways for molecules to diffuse throughout the porous structure, but also offer plenty of active sites in the pore wall for interaction with guest molecules. 21,32 Additionally, hierarchically ordered porous titania materials with well-defined macropores and interconnecting mesopores have attracted much attention because they combine the excellent performance of mass transport from macropores and the advantages of high surface areas from mesopores. 4,31 Actually, hierarchically porous structures are ubiquitous in nature (e.g., diatoms, lumbar vertebra and lungs), which provide efficient transport of fluids and gases. 32,34-36 Therefore, considerable effort has been made to synthesize hierarchical porous titania and other metal oxides through a template-assisted strategy, which has been considered to be the most versatile and straightforward strategy towards hierarchical porous titania. The templates used mainly refer to polymer or silica colloidal crystals, biological hard templates, biomolecules and soft 

---

*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China. E-mail: whuo@dhbu.edu.cn

†Department of Chemistry, State Key Laboratory of Molecular Engineering of Polymers, iChEM, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China

‡State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

§State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, P. R. China

∥Materials Science and Technology Program, College of Arts and Sciences, Qatar University, PO Box 2713, Doha, Qatar

¶Qatar Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

††Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ta06849a
templates. The general route for templated synthesis of hierarchical porous TiO₂ includes the following steps as shown in Scheme 1A. In the first step, the hard template, based on colloidal crystals of organic polymer microspheres of polystyrene (PS) or poly(methyl methacrylate colloids) (PMMA), are impregnated in an ethanol solution containing titania precursor and surfactants (e.g. P123). In the second step, after evaporation of ethanol and aging, the composite is calcined, resulting in hierarchical porous TiO₂ materials. However, the hard template of PMMA or PS can be easily decomposed (at 300–350 °C) together with the soft template P123 during calcination, which causes the collapse of both the macroporous and mesoporous structure due to the lack of a rigid support during the crystallization of titania at higher temperature (usually about 450 °C). To date, it is still a great challenge to fabricate ordered hierarchical macro/mesoporous titania with an interconnected and periodic pores arrangement, high crystallinity and large accessible surface areas.

Herein, we report a novel controlled synthesis of hierarchical macro/mesoporous titania (denoted as HOPT) with thin macropore walls. The synthesis was accomplished through a facile bi-template interface-directed deposition method in a rigid 3-D ordered macroporous carbon (3DOMC) template. Commercial amphiphilic triblock copolymer P123 was used as the structure directing agent, titanium isopropoxide (TiPO) as the titania source and ethanol as the solvent. After a two-step thermal treatment in nitrogen and air, respectively, the obtained HOPT possessed large macro-cavities (420 nm), uniform mesopores (3.7 nm), large accessible surface areas (178 m² g⁻¹), high pore volumes (0.44 cm³ g⁻¹) and an anatase frameworks with high crystallinity. Moreover, the morphology of the HOPT materials could be tuned to mesoporous titania hollow microsphere arrays by controlling the amount of Ti-precursor soaked in the sacrificial 3DOMC. The hierarchical porous structure results in a high surface to volume ratio, which provides numerous active sites and substantial interfacial areas for heterogeneous photocatalysis, while the interconnected macropores and ordered mesopores favor guest molecule transportation. The HOPT shows excellent photocatalysis performance for degradation of Rhodamine B (RhB) under simulated sunlight irradiation at room temperature. The photocatalytic decomposition of RhB (10⁻⁵ mol L⁻¹) could be completed in 8 min under a simulated sunlight irradiation (200 < λ < 800 nm), and the degradation reaction rate was three times higher than that of commercial titania nanoparticles (P25).

### Experimental section

#### Chemicals

Pluronic block copolymers poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide) (P123, Mₘ = 5800, EO₂₀PO₇₀EO₂₀) was purchased from Aldrich Corp. TiPO was purchased from Acros. Ethanol, tetraethyl orthosilicate (TEOS), concentrated ammonia solution (28 wt%), hydrochloric acid, hydrofluoric acid, sodium hydroxide, nitric acid and concentrated sulfuric acid, were purchased from China Medicines Corp. Resol, a soluble phenolic resin with low molecular weight (∼500 g mol⁻¹), was prepared according to a previous report and dissolved in ethanol to form a solution with a resol concentration of 20 wt%.

#### Synthesis of 3-D ordered macroporous carbon (3DOMC)

This process can be divided into two steps. In the first step, monodisperse uniform silica microspheres were synthesized by using Stöber’s method. After washing three times with absolute ethanol and water, respectively, the silica microspheres were re-dispersed in ethanol to form a homogeneous suspension (15 wt%) for sedimentation for 6 days. Then, the super-natant liquor was removed and the sediments were further dried at 25 °C for 24 h and 100 °C for 12 h. In the second step, an ethanolic solution of resol precursor was cast on small plates of the colloidal crystals. After evaporation of ethanol, the plates were dried at 30 °C for 12 h and 100 °C for 6 h to achieve a full thermal polymerization of resol into phenolic formaldehyde (PF) resin. The obtained silica/PF composite was carbonized at 600 °C for 3 h with a heating rate of 3 °C min under N₂. After that, the obtained sample was etched in aqueous HF solution.
branches of the isotherms. The total pore volumes (V) were evaluated according to the amount adsorbed at a relative pressure P/Pc of 0.995. Small-angle X-ray scattering (SAXS) patterns were collected on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) employing Cu Ka radiation (40 kV, 35 mA). The d-spacing values were calculated using the formula \[ d = 2\pi/q \]. X-ray photoelectron spectroscopy (XPS) was recorded on an AXIS ULTRA DLD XPS System with MONO Al source (Shimadzu Corp.). The UV-vis spectra were recorded using a Shimadzu UV-2450 spectrophotometer from 200 to 800 nm using BaSO₄ as a baseline reference. Thermogravimetry analysis was carried out on a Mettler Toledo TGA/SDTA851 analyzer (Switzerland) from 30 to 800 °C in an air flow of 80 mL min⁻¹ at a heating rate of 10 °C min⁻¹. The Fourier-transform infrared (FTIR) spectrum was measured using an infrared spectrometer (Nicolet IS10) by pressing the mixture with IR grade KBr and the product powders into a pellet with a mass ratio of 100 : 1.

Results and discussion

The HOPT materials were synthesized through a bi-template interface directed deposition approach, in which the macro-/mesopores of 3DOMC were immersed in a mixed solution containing TiO₂, P123, HCl, H₂SO₄, and ethanol. The titania precursor can assemble with the P123 templating agent to form a composite coating with ordered mesostructure due to the evaporation of ethanol. The porous titania negative replica was obtained by thermal treatment to remove the carbon scaffold and P123. The synthesis strategy is described in Scheme 1B. Monodisperse silica microspheres were fabricated through the well-understood Stöber method and dispersed in ethanol to form monolithic colloidal crystals in one week by gravity sedimentation, followed by thermal treatment in an oven at 100 °C for 24 h to stabilize the structure. The FE-SEM image (Fig. S1a†) displayed that the silica microspheres possess a uniform diameter size of 500 nm with a deviation less than 5%, and the SiO₂ spheres can self-assemble into a close-packed arrangement after sedimentation. The obtained colloidal crystals possessed the typically ordered hexagonal array, corresponding to the (111) plane of an fcc structure. Subsequently, the silica colloidal crystals were impregnated with resol solution (Scheme 1B, step 1). As shown in Fig. S1b†, polymer species have been employed to sufficiently fill the interstitial voids between the silica microspheres. Resol can further transform into carbon after thermosetting treatment at 100 °C and carbonization at 600 °C in a nitrogen atmosphere, and 3DOMC can be obtained after the removal of silica with HF as an etchant (Scheme 1B, step 2). The FE-SEM image (Fig. S1c†) shows that 3DOMC consisted of uniform macro-cavities roughly 450 nm in diameter, which were connected by the “windows” on the macropore walls. This morphology was consistent with that typically observed for an inverse opal structure, indicating a faithful replication of the ordered structure of silica colloidal crystals. The “windows” on the macropore walls of the 3DOMC, derived from the contact points of closed contacted silica spheres, were around 60 nm in diameter (Fig. S1d†), which was favorable for the diffusion and transportation of guest species in the interconnected porous framework. In order to introduce precursors and templates into
the 3DOMC materials, the monolithic 3DOMC plates (1 cm × 0.5 cm × 0.5 cm) were partially immersed in precursor solution composed of TiO₂, P123, HCl, H₂SO₄ and ethanol (Scheme 1B, step 3), followed by the evaporation of ethanol to induce the co-assembly of Ti species and template molecules. The infiltration of precursor solutions in the macropores of 3DOMC led to the formation of a periodic TiO₂–P123–C composite. After air for 24 h, the sample was carbonized in N₂ atmosphere at 350 °C to carbonize P123 templates with the assistance of H₂SO₄. This generated rigid carbonaceous layers on the surface of channels of mesoporous TiO₂ since the H₂SO₄ molecules were located around the PEO blocks during the co-assembly process. The rigid carbon can support the TiO₂ frameworks during the further calcination and crystallization process. Once the highly crystalline anatase frameworks were formed at high temperatures, the ordered mesostructure was thermally stable and could be well-retained when the sample was calcined at 450 °C in air to burn out the carbonaceous support from 3DOMC and residual carbon from P123 (Scheme 1B, step 4). At last, HOPT with uniform macro-cavities, highly ordered mesostructures and high crystallinity frameworks were obtained.

The FE-SEM image of HOPT exhibited uniform macropores and a periodic macropores arrangement (Fig. 1a). The large-magnification FE-SEM image (Fig. 1b) also clearly indicated that the HOPT possesses ultrathin macroporous walls and large cavities. Moreover, the large cavities were connected by “windows”, diameter of 80 nm, which can facilitate dye molecules diffusion among the porous framework in photocatalytic applications. The diameter of the HOPT’s macro-cavity was measured from FESEM and TEM images to be around 420 nm (Fig. 1b–d), smaller than that of the 3DOMC, which was attributed to the shrinkage of the titania frameworks during the high temperature treatment. TEM observations (Fig. 1c and S2†) further confirmed that the obtained HOPT possessed uniform macro-cavities and ordered macroporous architecture, in good agreement with the SEM images (Fig. 1a and b). Large-magnification TEM image (Fig. 1d) revealed the presence of curved cylindrical mesopores. Interestingly, the packing cavities between ordered macropores were also observed in SEM and TEM images (Fig. 1b and d), indicating that the current macrostructure was related to the packing of hollow microspheres. The thickness of the HOPT macroporous wall was around 20 nm, as estimated from SEM and TEM images (Fig. 1b and d). A HR-TEM image of nanocrystals in the macroporous walls further showed the lattice fringes of titania with d-spacing of 0.35 nm, corresponding to the (101) planes and indicating that the porous framework consisted of titania nanocrystals (Fig. 1e). Selected-area electron diffraction (SAED), recorded on HOPT showed well-resolved diffraction rings corresponding with the (200), (105) and (101) crystal planes of anatase TiO₂ (Fig. 1f), further confirming that HOPT had a highly crystallized anatase scaffold.

The WA-XRD pattern (Fig. 2a) of HOPT showed well-resolved and broad diffraction peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.1° and 62.7°, which can be indexed to anatase titania composed of nanocrystals (JCPDS no. 21-1272; space group I₄₁/amd). No diffraction peaks from other crystalline impurities were detected in the XRD pattern, suggesting that HOPT was comprised predominantly of pure crystalline anatase. The broadening of the diffraction peaks can be ascribed to the small particle size of the TiO₂ nanocrystals. According to the Scherrer formula, the average crystallite size was calculated to be approximately 10 nm. Nitrogen adsorption–desorption isotherms of HOPT (Fig. 2b) exhibited type IV curves with large hysteresis loops. The hysteresis loop, located in the P/P₀ range of 0.6–0.9, was typical for 2D hexagonal mesoporous materials with uniform pore sizes. As displayed in the pore size distributions (Fig. 2b inset) derived from the adsorption branch of the isotherms using the BJH model, the pore size was around 3.7 nm due to the removal of the triblock copolymer P123 template. The specific surface area and pore volume of HOPT were calculated to be as high as 177 m² g⁻¹ and 0.44 cm³ g⁻¹, respectively, which attributed to

![Fig. 1](image-url) SEM (a) and FE-SEM (b) images of HOPT with uniform cavities of ~420 nm. TEM (c, d) and HRTEM (e) images of the obtained HOPT with high crystallization framework. The SAED pattern (f) taken from the cylindrical pore bundles region.

![Fig. 2](image-url) WA-XRD pattern (a). Nitrogen adsorption–desorption isotherms (b) and the pore diameter distribution calculated by the BJH method (inset).
the dual-mode pores and thin walls of the macro-cavities. Such a hierarchically porous structure was beneficial for the diffusion and adsorption of large guest molecules. Moreover, the small-angle X-ray scattering (SAXS) pattern (Fig. S3†) of HOPT exhibits a single broad scattering peak at ~0.427 nm⁻¹, indicating that HOPT possessed a periodic mesostructure, corresponding to a d-spacing of about 14.7 nm for the (100) plane.

The valence states of O and Ti in the surface region of HOPT were studied by XPS spectroscopy. Fig. S4a† shows that the O 1s profile displays the two asymmetric chemical states of oxygen. The sharp peak at 530.7 eV was assigned to the O–Ti bonds of the HOPT, indicating the main lattice oxygen atoms. The other peak at 532.6 eV was assigned to O–H absorbed on the HOPT, indicating that the HOPT contained numerous hydroxyl groups. Fig. S4b† presents the XPS spectra of Ti 2p. The peak positions of Ti 2p³/2 and Ti 2p½ are located at 462.6 eV (Ti 2p½) and 456.9 eV (Ti 2p½), respectively. Based on these results, it could be concluded that the Ti element was in the state of Ti⁴⁺, implying a similar co-assembly process of P123 and Ti-species in the macro pores of the 3DOMC scaffold. TEM observation (Fig. 3c) revealed the TiO₂ hollow microspheres arrays also possessed a large-domain of ordered mesostructure with circular mesochannels and uniform pore size of about 4.0 nm, analogous to the result of HOPT above mentioned. As a result, it is without doubt that HOPT can be easily controlled by simply varying the synthesis parameters of 3DOMC immersed in a precursor solution, leading to tunable shell thickness or different morphologies.

According to the above-mentioned results, we proposed a bi-template interface-directed deposition mechanism for the formation of the hierarchical macro/mesoporous titania. This approach combines the advantages of both soft structure-directing assembly and a hard-template to control the synthesis of HOPT with periodic macro-cavities, highly ordered mesostructures and high crystallinity. When the monolithic 3DOMC hard template is partially immersed in the precursor solution containing TIPO, ethanol, P123 and acidic aqueous solution, the solution can be quickly adsorbed into the 3DOMC scaffold through the “windows” derived by capillary force. However, if the 3DOMCs were entirely immersed in the precursor solution, the air, locked in the macropores of 3DOMCs, would hamper the impregnation process. This would make it difficult for the precursor solution to enter the macropores by capillary adsorption. Therefore, the 3DOMCs were partially immersed in the precursor solution on purpose, which could facilitate the injection of precursor solution into cavities. And after adsorption for 1 h, the macropore walls of 3DOMC were covered with a liquid film of the precursor solution. With the evaporation of ethanol, Ti-species oligomers formed by the hydrolysis and condensation of TIPO could associate with P123 molecules via hydrogen bonding and van der Waals’ forces, then further cooperatively assemble into rod-like composite micelles that gradually deposit on the macropore walls. Due to the confinement of the macropores, the composite rod-like micelles adjust to a curved morphology and grow into ordered mesostructures in the same direction along the inner surface of macroporous walls. After the evaporation of ethanol, mesostructured P123/TiO₂ composites were uniformly coated around the spherical inner walls of the macroporous carbon scaffold. Finally, after calcination in nitrogen and then air, HOPT materials with ordered macro/ mesoporous frameworks and high crystallinity were obtained. The thermogravimetry (TG) curve of HOPT with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C conducted in air showed a weight loss of about 2.46% (Fig. S5†), which could be attributed to the dehydration and removal of hydroxyl groups (–OH) on the macro/mesoporous TiO₂ shells, confirming that the carbon species and P123 have been burned out in the final sample after calcination treatment. The formation of arrays of mesoporous titania hollow microspheres was quite similar to the above mentioned mechanism, except that the prolonged soaking time (3 h) for 3DOMC in precursors solution introduced more Ti–P123 nanocomposite coatings onto the surface of the macropore walls, leading to a layer of mesoporous titania with a larger thickness.
The ordered and interconnected macro/mesoporous structures, as well as ultrahigh surface areas of the obtained hierarchically porous titania, enabled it to be an ideal candidate for loading and degrading organic dye molecules. Before light irradiation, HOPT performed very fast adsorption to RhB, and it took only about 40 min to essentially attain adsorption-desorption equilibrium with a maximum adsorption capacity of 24% due to the high specific surface area, high porosity, well connected porous channels and abundant hydroxyl groups of HOPT. To evaluate the photocatalytic capability of HOPT, we examined the decomposition of RhB dye in solutions under simulated sunlight irradiation with an intensity of 180 mW cm$^{-2}$. The photocatalytic decomposition of RhB (10$^{-5}$ mol L$^{-1}$), catalyzed by HOPT, could be completed in 8 min under simulated sunlight irradiation (200 < $\lambda$ < 800 nm). The concentrations of RhB solutions were measured by ultraviolet-visible (UV-vis) spectroscopy, and the characteristic absorption peak at $\lambda$ = 554 nm was found to drop sharply with the extension of exposure time. It completely disappears after about 8 min (Fig. 4a), which was also reflected by the corresponding color change of the RhB solution (Fig. 4a inset). No new absorption band appeared in either the visible or ultraviolet region, which indicated the complete photodegradation of RhB. For comparison, we also carried out decomposition of RhB in solution over the mesoporous TiO$_2$ hollow microsphere arrays and commercial P25. As shown in Fig. 4b, mesoporous TiO$_2$ hollow microspheres and P25 took about 12 and 20 min to decompose RhB completely, respectively, indicating that the HOPT exhibited higher photoactivities. Fig. 4e showed that the logarithms of the normalized frequency changes during the photodegradation were linear with respect to light irradiation time, indicating that the photodegradation of RhB followed pseudo-first-order kinetics.$^{15}$

$$\ln(C_0/C) = kt,$$

where $C_0$ is the initial dye concentration, $C$ is the concentration of RhB at time $t$ and $k$ is the apparent first-order rate constant. The photocatalytic activity of the TiO$_2$ materials can be quantitatively evaluated by comparing the apparent reaction rate constants (denoted as $k$), as illustrated in histograms of Fig. S6.$^{\dagger}$ A direct comparison of the reaction rate constants, HOPT ($k = 0.46$ min$^{-1}$) was markedly improved when compared to P25 ($k = 0.12$ min$^{-1}$) and hollow microspheres ($k = 0.25$ min$^{-1}$) due to the higher surface area and well-connected porous framework. In addition to efficiency, stability and recyclability of photocatalysts are also important for applications. After the degradation reaction, HOPT was illuminated under simulated sunlight irradiation for another 1 h in water solution to ensure that the adsorbed RhB molecules were completely degraded. Then, the HOPT was washed with water and ethanol, collected and recycled by centrifugation. The in situ FTIR spectroscopy analysis of HOPT after photocatalysis was also performed, and no characteristic absorption peaks of organic compounds was detected, indicating a complete decomposition of RhB (Fig. S7$^{\dagger}$). Moreover, the photograph of HOPT after photocatalysis and washing shows that the HOPT retained the original morphology and appearance, suggesting that HOPT was left intact without pollution from dye molecules (Fig. S8$^{\dagger}$). The photocatalytic reusability test shows that the HOPT can be reused more than 10 times as an efficient photocatalyst without any loss of catalytic activities (Fig. 4d), confirming a reliable catalytic performance of the hierarchical macro-/meso porous TiO$_2$. Furthermore, the HOPT materials maintained an ordered porous structure after degradation of RhB (Fig. S9$^{\dagger}$), indicating a good structural stability of HOPT. The UV-vis absorption spectra (Fig. S10$^{\dagger}$) revealed that HOPT had significantly enhanced light absorption over the entire tested wavelength range compared to Degussa P25. Moreover, various representative titania-based porous photocatalysts (e.g. mesoporous TiO$_2$ films, hierarchical porous TiO$_2$ prepared by a traditional method, doped TiO$_2$ materials) were listed and compared with our HOPT materials in terms of their catalytic performance and porosities (Table 1). It is clearly seen that HOPT delivers much better photocatalytic performance compared to other previously reported TiO$_2$ nanomaterials. The outstanding photocatalytic performance of the as-prepared HOPT as photocatalysts for degradation of RhB can be understood from several aspects. Firstly, the highly accessible large mesopores and macro-cavities, high surface areas and crystalline anatase frameworks of HOPT could not only boost the adsorptive capacity for dye molecules, but also provide a huge amount of active sites. Secondly, both macropores and mesopores of hierarchical HOPT could act as light-scattering centers under the illumination, giving rise to enhance utilization levels for light.

---

**Fig. 4** Changes in the UV-vis absorption of RhB aqueous solutions in the presence of HOPT under light irradiation (a). The inset is a photograph showing the corresponding color changes of the RhB solution. Photocatalytic activities for HOPT, mesoporous TiO$_2$ hollow sphere arrays and P25 were evaluated by degradation of a RhB solution under simulated sunlight irradiation (b). $\ln(C_0/C)$ as a function of UV irradiation time in the presence of TiO$_2$ photocatalysts (c). The performance of the recycled HOPT catalyst for degradation of RhB after using 10 times in 8 minutes (d).
Table 1  The physicochemical property and photocatalytic performance of representative porous titania materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Irradiation light</th>
<th>Organic dye and concentration</th>
<th>Illumination time</th>
<th>Degradation efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPT</td>
<td>177</td>
<td>Simulated sunlight</td>
<td>Rhodamine B (RhB) (10⁻⁵ M)</td>
<td>8</td>
<td>97%</td>
<td>This work</td>
</tr>
<tr>
<td>Mesoporous hybrid TiO₂–SiO₂</td>
<td>141</td>
<td>UV</td>
<td>Methylene blue (MB) (10 mg L⁻¹)</td>
<td>90</td>
<td>&gt;95%</td>
<td>44</td>
</tr>
<tr>
<td>Mesoporous TiO₂ films</td>
<td>65</td>
<td>UV</td>
<td>MB (2 × 10⁻⁴ M)</td>
<td>110</td>
<td>&gt;95%</td>
<td>15</td>
</tr>
<tr>
<td>Nb-doped TiO₂ nanosheets</td>
<td>98</td>
<td>UV</td>
<td>RhB (20 ppm)</td>
<td>60</td>
<td>&gt;85%</td>
<td>45</td>
</tr>
<tr>
<td>V-Doped mesoporous TiO₂</td>
<td>135</td>
<td>Visible light</td>
<td>RhB (10⁻⁴ M)</td>
<td>120</td>
<td>&gt;95%</td>
<td>46</td>
</tr>
<tr>
<td>Hierarchical porous TiO₂ films</td>
<td>165.9</td>
<td>UV</td>
<td>RhB (10 mg L⁻¹)</td>
<td>80</td>
<td>&gt;95%</td>
<td>47</td>
</tr>
<tr>
<td>TiO₂ nanosheets</td>
<td>311</td>
<td>UV</td>
<td>RhB (10⁻⁵ M)</td>
<td>70</td>
<td>&gt;95%</td>
<td>18</td>
</tr>
<tr>
<td>Hollow TiO₂ mesoporous spheres</td>
<td>25</td>
<td>Visible light</td>
<td>RhB (10⁻³ M)</td>
<td>70</td>
<td>&gt;85%</td>
<td>25</td>
</tr>
<tr>
<td>Macroporous TiO₂ film modified by BiVO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

compared to P25, while the macropores and “windows” on the walls favor great transportation of dye molecules in the 3DOMT scaffold and promote separation efficiency after degradation in the host framework.

Conclusion

3-Dimensional interconnected hierarchical macro/mesoporous titania (HOPT) was synthesized by the bi-template interface-directed deposition strategy in a 3DOMC template using amphiphilic block copolymer P123 as a structure directing agent and TiPO as a titania source. The obtained HOPT possessed large macro-cavities (420 nm), uniform pore sizes (3.7 nm), high accessible surface areas (177 m² g⁻¹), large pore volumes (0.44 cm³ g⁻¹) and highly crystallized anatase frameworks. The morphology of HOPT can be easily tuned into ordered mesoporous titania hollow microsphere arrays through simply controlling the amount of P123/titania precursor deposited on the macropore wall of 3DOMC. Furthermore, HOPT shows excellent performance in the degradation of RhB dye under simulated sunlight irradiation in an aqueous solution at room temperature. It is expected that the new interface-directed co-assembly based on the 3DOMC nanoreactor opens up a new strategy to synthesize ordered hierarchical macro/mesopores materials with crystalline framework, inverse opal structure and much improved mass diffusion and transport for applications in catalysis, sensors, energy storage and energy conversion.

Acknowledgements

This work was supported by national natural science foundation of China (No. 51402049, 51422202, 51432004 and 51372041), the Shanghai committee of science and technology, China (No. 14ZR1400600), the programme of introducing talents of discipline to universities (No. 111-2-04), the fundamental research funds for the central universities (No. 2232015D3-06), the "Shu Guang" project (13SG02) of Shanghai municipal education commission, Qatar University grant # QUUG-CAS-DMST-15-16-18, the National Youth Top-notch Talent Support Program in China. The authors extend their sincere appreciations to the Deanship of Scientific Research at King Saud University for its funding this Prolific Research group (PRG-1437-32).

Notes and references

40 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, 2, 62–69.