# **Electronic Supplementary Information for:**

# Hexagonal microrods of anatase tetragonal TiO<sub>2</sub>: Self-directed growth and superior photocatalytic performance

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## 1 1. Preparation of HMATT

2 The hierarchical TNTs stratification layer with porous structure, the precursor, 3 was firstly synthesized by voltage-regulated anodization [25]. A 0.30-mm Ti foil was burnished and immersed in polishing solution (HF:HNO<sub>3</sub>:H<sub>2</sub>O = 1:1:2, vol.%) to 4 5 remove oxide layer and blot, then cleaned with soap, acetone and isopropanol. The 6 electrolyte was 0.09 M NH<sub>4</sub>F dissolved in 8 ml de-ionized water and 72 ml ethylene glycol. The anodization was conducted by applying a potential scanning from the 7 open-circuit potential first to 90 V for 2 min, then to 80 V for 2 min, 70 V for 2 min, 8 9 60 V for 2 min and 50 V for 2 min, then repeated this process for 2 times and finally 10 to 40 V for 120 min. Secondly, the prepared TNTs stratification layer was directly 11 calcinated (without washing) under atmosphere conditions at 500°C for 3 h in muffle 12 furnace, with a ramping rate of 3°C/min. Finally, a white color particle layer was 13 prepared and then rinsed with distilled water until the filtrate pH reached 7.0, and 14 dried in a vacuum oven at 60°C for 5 h.

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# 16 2. Characterization of HMATT

17 The morphology and structure were characterized by field-emission scanning SIRION200, 18 electron microscope (FE-SEM, FEI Co., the Netherlands). 19 high-resolution transmission electron microscope and selected-area electron 20 diffraction (HRTEM/SAED, JEM-2100, JEOL Co., Japan). The surface area was 21 measured by the Brunauer-Emmett-Teller (BET) method with a Builder 4200

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22	instrument (Tristar II 3020M, Micromeritics Co., USA). The chemical compositions
23	were characterized by energy dispersive X-ray analyzer (EDX, GENESIS, EDAX Co.,
24	USA) fitted to the SEM chamber and X-ray photoelectron spectroscopy (XPS, PHI
25	5600, Perkin-Elmer Inc., USA). X-ray diffraction (XRD, X'Pert, PANalytical BV, the
26	Netherlands) was used to analyze the structure. The diffuse reflectance spectroscopy
27	(DRS) was investigated using a UV-Vis spectrophotometer (UV 2550, Shimadzu Co.,
28	Japan).

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# 30 3. Determination of photocatalytic performance of HMATT

31 The photocatalytic properties of HMATT were evaluated by short-circuit photocurrent in a conventional three-electrode system, amount of generated ·OH and 32 BPA (10 mg L<sup>-1</sup>) degradation under UV irradiation (200-400 nm). The tests were 33 34 conducted in a home-made photoreactor with an effective volume of 60 ml. The light 35 source was a 500 W Xe arc lamp (PLS-SXE500, Beijing Trusttech Co., China), with a 10 cm infrared water filter and a Pyrex filter ( $\lambda > 200$  nm). For each test, 50 ml 36 37 solution was used. Fluorescence spectra were regularly recorded using a spectrofluorophotometer (RF-5301PC, Shimadzu Co., Japan). The BPA concentration 38 39 was determined by high-performance liquid chromatography (HPLC-1100, Agilent 40 Inc., USA) with a Hypersil-ODS reversed-phase column and detected at 254 nm using 41 a VWD detector. The mobile phase was a mixture of water and methanol (30:70)

42 delivered at a flow rate of 1 mL min<sup>-1</sup>. Mineralization efficiency was estimated
43 according to the TOC removal (Vario, Elementar Co., Germany).

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# 45 **4.** XPS analysis of HMATT

The XPS spectrum of F1s at 684.4 eV is a typical value for fluorated TiO<sub>2</sub> systems and could be ascribed to F<sup>-</sup> ions physically adsorbed on the TiO<sub>2</sub> surface (such as the surface Ti-F species formed by ligand exchange between F<sup>-</sup> and surface hydroxyl groups,  $\equiv$ Ti-OH + F<sup>-</sup>  $\rightarrow \equiv$ Ti-F + OH<sup>-</sup>). The formation of Ti-F bond can significantly lower the surface free energy of {001} facets and reversely make them more stable than {101} facets, ultimately enables the formation of anatase TiO<sub>2</sub> single crystals with a large percentage of reactive {001} facets.

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# 54 5. Formation of HMATT

55 With the mechanisms of "dissolution-recrystallization" and "self-organization" 56 (Fig. 1), the formation could be divided into two stages (Figs. S2 and 3): 1) TiO<sub>2</sub> 57 scaffolds (*shell*) formation from the hierarchical TNTs layer; and 2) HMATT (*core*) 58 self-directed formation under the guidance of *shell*.

It is well documented that  $TiO_2$  crystallization and growth could be accelerated by fluoride ions under acidic conditions, attributed to the rapid in-situ dissolution-recrystallization.<sup>1-3</sup> In this work, the solvothermal alcoholysis included the dissolution, attenuation and fracture of the hierarchical TNTs stratification layer via a

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63 classical alcoholysis, nucleation and crystal growth, by a simple calcination of the precursor (Fig. S2A). The TNTs became more and more thiner and shorter due to the 64 gradual dissolution by  $F^{-}$  to form  $[TiF_6]^{2-}$  (Reaction 1), some of them were fractured 65 or even completely dissolved (Fig. S2B-D). When the F<sup>-</sup> concentration decreased 66 sufficiently,  $[TiF_6]^{2}$  was transformed into TiO<sub>2</sub> clusters through an alcoholytic 67 reaction (Reactions 2 and 3) (Fig. S2B-D): the adsorbed ethylene glycol 68 (HO-CH<sub>2</sub>CH<sub>2</sub>-OH) tended to heterolytically dissociate to form two alkoxy groups 69 70  $(^{\circ}O-CH_2CH_2-O^{\circ})$  and then bound to the {001} and {101} facets.

71 Dissolution: 
$$\operatorname{TiO}_2 + 6F^{-} + 4H^{+} \rightarrow [\operatorname{TiF}_6]^{2^{-}} + 2H_2O$$
 (1)

72 Recrystallization:  $\equiv Ti-F + R-OH \rightarrow \equiv Ti-OR + HF$  (2)

$$Ti(OR)_n + TiF_n \rightarrow 2TiO_{n/2} + nRF$$
 (3)

74 Then, the as-formed  $TiO_2$  clusters further grew along the {001} and {101} 75 directions. The residual ethylene glycol electrolyte not only provide the reaction 76 medium for the solvothermal alcoholysis, but also act as a synergistic capping agent to 77 stabilize the fluorin adsorption on the exposed facets and synthesize the TiO<sub>2</sub> nanocrystals with a high fraction of  $\{001\}$  facets.<sup>2,4,5</sup> Compared to  $\{101\}$  surfaces, the 78 79 higher density of 5-fold Ti on {001} have more selective adhesion of ethylene glycol 80 and modified the adsorption energy of fluorin to more preferable state, thus the growth of TiO<sub>2</sub> nanocrystals along  $\{001\}$  direction was retarded.<sup>6</sup> At this stage, the 81 {001}-exposed primary nanocrystals of ca. 10 nm were formed due to the synergistic 82 effects of ethylene glycol and fluorin in residual electrolyte (Fig. 2F).<sup>7,8</sup> 83

84 After primary nanocrystals were firstly formed, these crystals with uniform size and shape could take the places of atoms in conventional crystalline solids, and the 85 86 packing arrangement of nanocrystals governed the unit-cell parameters of superstructure.<sup>9</sup> Thus, the nanocrystals as building blocks then underwent a mesoscale 87 88 oriented self-assembly along {001} directions and ultimately formed the intermediate 89 iso-oriented mesocrystalline scaffolds (Figs. S2E, F and S3A), in which ethylene 90 glycol might preferentially attach onto the nanocrystal surfaces and thus lead to 91 strongly anisotropic mutual interactions between them.

92 Once the intermediate scaffolds were secondly formed (inset of Fig. S2F), 93 formation of mesocrystalline microrods via self-directed self-assembly of primary 94 nanocrystals as building blocks were observed to commence. As illustrated by the 95 sawtooth-shape aggregations and filling (marked by red lines in inset of Fig. S2F), the 96 primary nanocrystals site-selectively self-assembled within the TiO<sub>2</sub> scaffolds under 97 their self-guiding effects, gradually grew into the quadrangular and then into the 98 hexagonal mesocrystalline microrods within the scaffolds (Fig. S2G and H).

Finally, the chain-like scaffolds were formed via oriented self-assembly of several secondary micro-sized crystallites along {101} directions (approximately 0.2  $\mu$ m, Fig. S3B, D and F). These secondary micro-sized crystallites were formed upon crystallographical fusion of the primary nano-sized crystallites due to the high lattice energy (approximately 10 nm, Fig. S3A, C and E). After further ripening to the well-defined single crystals, the self-assembled scaffolds became fragmented and detached from the *core* to form the free-standing HMATT (Fig. S2I). Therefore, for
the TiO<sub>2</sub> scaffolds (*shell* in Fig. S2H), the typical non-classical and particle-mediated
growth mechanism could be well described.<sup>9</sup> Comparatively, for HMATT, the
primary nanosized crystallites did not undertake crystallographical fusion (Fig. S2G,
H and I), which might be attributed to the crystalline confinement to the scaffolds.

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#### 111 6. Influences of TNTs precursors and calcination environmentions

112 To further investigate the influence of TNTs precursor and calcination 113 environment on HMATT formation, several control experiments were carried out 114 comparatively. For common solid TNTs monolayer prepared by usual voltage-stabilized anodization, TiO<sub>2</sub> nanocrystals with well-defined size and narrow 115 116 size distribution were formed after calcinating under the same conditions as for 117 HMATT (Fig. S4A-1 and A-2). The nanocrystal properties are consistent with the literature;<sup>10</sup> For solid TNTs stratification layer prepared according to Ref. 5 with 118 119 minor modifications, some poor-defined HMATT with unregular shape were formed 120 after calcinating under the same conditions as for HMATT (Fig. S4B-1 and B-2). 121 Compared to solid TNTs stratification layer, the porous analogue might be more 122 advantageous to collect and capture the fluoride, ethylene glycol and 123 "dissolute-recrystallize" amorphous TNTs precursor, and finally form HMATT with 124 more synergistic effects of thermodynamic and kinetic factors that govern crystal 125 nucleation, growth and the final self-directed self-assembly within the intermediate

scaffolds (Fig. S2).<sup>11</sup> For porous TNTs stratification layer prepared in this study, only 126 127 some poor-defined TiO<sub>2</sub> single crystals with sizes of several hundred nanometers 128 were formed after calcinating under less F and EG environments than that for 129 HMATT, and most of the TNTs stratification layer were remained and fractured (Fig. 130 S4C-1 and C-2). This might be due to an insufficient "dissolution-recrystallization" of 131 the titanium precursor; Moreover, the nanotubular architecture of the titanium 132 precursor remained intrinsically unchanged and were not destroyed by 133 high-temperature calcination under no F and EG environments (Fig. S4D-1 and D-2). 134 This might be due to the absence of "dissolution-recrystallization" of the titanium 135 precursor by F and EG, and as a consequence only a transformation process from 136 amorphous to anatase phase taken place under the common calcinating conditions of 137 air atmosphere.

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**Fig. S1** XPS survey spectra (A) and high-resolution XPS spectra (B, C and D) for HMATT after calcinating at 450°C for 3 h.



**Fig. S2** Morphological and self-directed evolution process of the HMATT after calcination at different times: (A) 0 min; (B) 5 min; (C) 10 min; (D) 30 min; (E) 60 min; (F) 90 min; (G) 120 min; (H) 150 min; and (I) 180 min.



**Fig. S3** Typical SEM, TEM and HRTEM images of the evolutional  $TiO_2$  scaffolds at different stages: 90 min (A, C and E) and 150 min (B, D and F). The insets show the SAED patterns of  $TiO_2$  scaffolds at different stages.



**Fig. S4** Influences of TNTs precursors and calcination environmentions on crystal products.



**Fig. S5** BPA degradation kinetic constants in photolysis (A) and photocatalysis on P25 (B) and on HMATT (C).