Electronic Supplementary Information for:

Hexagonal microrods of anatase tetragonal TiO$_2$: Self-directed growth and superior photocatalytic performance

Ai-Yong Zhang, Lu-Lu Long, Wen-Wei Li, Wei-Kang Wang, Han-Qing Yu*
Department of Chemistry, University of Science & Technology of China, Hefei, 230026, China
1. Preparation of HMATT

The hierarchical TNTs stratification layer with porous structure, the precursor, was firstly synthesized by voltage-regulated anodization [25]. A 0.30-mm Ti foil was burnished and immersed in polishing solution (HF:HNO₃:H₂O = 1:1:2, vol.%) to remove oxide layer and blot, then cleaned with soap, acetone and isopropanol. The electrolyte was 0.09 M NH₄F dissolved in 8 ml de-ionized water and 72 ml ethylene glycol. The anodization was conducted by applying a potential scanning from the open-circuit potential first to 90 V for 2 min, then to 80 V for 2 min, 70 V for 2 min, 60 V for 2 min and 50 V for 2 min, then repeated this process for 2 times and finally to 40 V for 120 min. Secondly, the prepared TNTs stratification layer was directly calcinated (without washing) under atmosphere conditions at 500°C for 3 h in muffle furnace, with a ramping rate of 3°C/min. Finally, a white color particle layer was prepared and then rinsed with distilled water until the filtrate pH reached 7.0, and dried in a vacuum oven at 60°C for 5 h.

2. Characterization of HMATT

The morphology and structure were characterized by field-emission scanning electron microscope (FE-SEM, SIRION200, FEI Co., the Netherlands), high-resolution transmission electron microscope and selected-area electron diffraction (HRTEM/SAED, JEM-2100, JEOL Co., Japan). The surface area was measured by the Brunauer-Emmett-Teller (BET) method with a Builder 4200
instrument (Tristar II 3020M, Micromeritics Co., USA). The chemical compositions were characterized by energy dispersive X-ray analyzer (EDX, GENESIS, EDAX Co., USA) fitted to the SEM chamber and X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin-Elmer Inc., USA). X-ray diffraction (XRD, X’Pert, PANalytical BV, the Netherlands) was used to analyze the structure. The diffuse reflectance spectroscopy (DRS) was investigated using a UV-Vis spectrophotometer (UV 2550, Shimadzu Co., Japan).

3. Determination of photocatalytic performance of HMATT

The photocatalytic properties of HMATT were evaluated by short-circuit photocurrent in a conventional three-electrode system, amount of generated ·OH and BPA (10 mg L⁻¹) degradation under UV irradiation (200-400 nm). The tests were conducted in a home-made photoreactor with an effective volume of 60 ml. The light 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 (λ > 200 nm). For each test, 50 ml solution was used. Fluorescence spectra were regularly recorded using a spectrofluorophotometer (RF-5301PC, Shimadzu Co., Japan). The BPA concentration was determined by high-performance liquid chromatography (HPLC-1100, Agilent Inc., USA) with a Hypersil-ODS reversed-phase column and detected at 254 nm using a VWD detector. The mobile phase was a mixture of water and methanol (30:70)
delivered at a flow rate of 1 mL min\(^{-1}\). Mineralization efficiency was estimated according to the TOC removal (Vario, Elementar Co., Germany).

4. **XPS analysis of HMATT**

The XPS spectrum of F1s at 684.4 eV is a typical value for fluorated TiO\(_2\) systems and could be ascribed to F\(^-\) ions physically adsorbed on the TiO\(_2\) surface (such as the surface Ti-F species formed by ligand exchange between F\(^-\) and surface hydroxyl groups, \(\equiv\text{Ti-OH} + \text{F} \rightarrow \equiv\text{Ti-F} + \text{OH}\)). 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\(_2\) single crystals with a large percentage of reactive \{001\} facets.

5. **Formation of HMATT**

With the mechanisms of “dissolution-recrystallization” and “self-organization” (Fig. 1), the formation could be divided into two stages (Figs. S2 and 3): 1) TiO\(_2\) scaffolds (shell) formation from the hierarchical TNTs layer; and 2) HMATT (core) 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.\(^{1-3}\) In this work, the solvothermal alcoholysis included the dissolution, attenuation and fracture of the hierarchical TNTs stratification layer via a
classical alcoholysis, nucleation and crystal growth, by a simple calcination of the precursor (Fig. S2A). The TNTs became more and more thinner and shorter due to the gradual dissolution by F⁻ to form [TiF₆]²⁻ (Reaction 1), some of them were fractured or even completely dissolved (Fig. S2B-D). When the F⁻ concentration decreased sufficiently, [TiF₆]²⁻ was transformed into TiO₂ clusters through an alcohololytic reaction (Reactions 2 and 3) (Fig. S2B-D): the adsorbed ethylene glycol (HO-CH₂CH₂-OH) tended to heterolytically dissociate to form two alkoxy groups (O-CH₂CH₂-O⁻) and then bound to the {001} and {101} facets.

Dissolution: \[ \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \] (1)

Recrystallization: \[ \equiv\text{Ti-F} + \text{R-OH} \rightarrow \equiv\text{Ti-OR} + \text{HF} \] (2)

\[ \text{Ti(OR)}_n + \text{TiF}_n \rightarrow 2\text{TiO}_{n/2} + n\text{RF} \] (3)

Then, the as-formed TiO₂ clusters further grew along the {001} and {101} directions. The residual ethylene glycol electrolyte not only provide the reaction medium for the solvothermal alcoholysis, but also act as a synergistic capping agent to stabilize the fluorin adsorption on the exposed facets and synthesize the TiO₂ nanocrystals with a high fraction of {001} facets.² ⁴ ⁵ Compared to {101} surfaces, the higher density of 5-fold Ti on {001} have more selective adhesion of ethylene glycol and modified the adsorption energy of fluorin to more preferable state, thus the growth of TiO₂ nanocrystals along {001} direction was retarded.⁶ At this stage, the {001}-exposed primary nanocrystals of ca. 10 nm were formed due to the synergistic effects of ethylene glycol and fluorin in residual electrolyte (Fig. 2F).⁷ ⁸
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 packing arrangement of nanocrystals governed the unit-cell parameters of superstructure.\(^9\) Thus, the nanocrystals as building blocks then underwent a mesoscale oriented self-assembly along \{001\} directions and ultimately formed the intermediate iso-oriented mesocrystalline scaffolds (Figs. S2E, F and S3A), in which ethylene glycol might preferentially attach onto the nanocrystal surfaces and thus lead to strongly anisotropic mutual interactions between them.

Once the intermediate scaffolds were secondly formed (inset of Fig. S2F), formation of mesocrystalline microrods via self-directed self-assembly of primary nanocrystals as building blocks were observed to commence. As illustrated by the sawtooth-shape aggregations and filling (marked by red lines in inset of Fig. S2F), the primary nanocrystals site-selectively self-assembled within the TiO\(_2\) scaffolds under their self-guiding effects, gradually grew into the quadrangular and then into the 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$_2$ scaffolds (shell in Fig. S2H), the typical non-classical and particle-mediated growth mechanism could be well described.\(^9\) 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.

6. *Influences of TNTs precursors and calcination environment*

To further investigate the influence of TNTs precursor and calcination environment on HMATT formation, several control experiments were carried out comparatively. For common solid TNTs monolayer prepared by usual voltage-stabilized anodization, TiO$_2$ nanocrystals with well-defined size and narrow size distribution were formed after calcinating under the same conditions as for HMATT (Fig. S4A-1 and A-2). The nanocrystal properties are consistent with the literature;\(^{10}\) For solid TNTs stratification layer prepared according to Ref. 5 with minor modifications, some poor-defined HMATT with unregular shape were formed after calcinating under the same conditions as for HMATT (Fig. S4B-1 and B-2). Compared to solid TNTs stratification layer, the porous analogue might be more advantageous to collect and capture the fluoride, ethylene glycol and “dissolute-recrystallize” amorphous TNTs precursor, and finally form HMATT with more synergistic effects of thermodynamic and kinetic factors that govern crystal nucleation, growth and the final self-directed self-assembly within the intermediate...
scaffolds (Fig. S2). For porous TNTs stratification layer prepared in this study, only some poor-defined TiO$_2$ single crystals with sizes of several hundred nanometers were formed after calcinating under less F and EG environments than that for HMATT, and most of the TNTs stratification layer were remained and fractured (Fig. S4C-1 and C-2). This might be due to an insufficient “dissolution-recrystallization” of the titanium precursor; Moreover, the nanotubular architecture of the titanium precursor remained intrinsically unchanged and were not destroyed by high-temperature calcination under no F and EG environments (Fig. S4D-1 and D-2). This might be due to the absence of “dissolution-recrystallization” of the titanium precursor by F and EG, and as a consequence only a transformation process from amorphous to anatase phase taken place under the common calcinating conditions of air atmosphere.

Notes and references


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 evolitional 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 environments on crystal products.
Fig. S5  BPA degradation kinetic constants in photolysis (A) and photocatalysis on P25 (B) and on HMATT (C).