## Supporting Information

## Precursor-directed synthesis of well-facetted brookite TiO<sub>2</sub> single crystals for efficient photocatalytic performances

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In this work, titanium-glycolate and titanium-lactate complexes were utilized as the precursors to synthesize pure-phase brookite nanocrystals with various morphologies and enclosed facets. The formation reaction of these brookite precursors could be represented by the following equations:

$$TiOSO_4 + 5H_2O \rightarrow [Ti(OH)_4(OH_2)_2]^0 + 2H^+ + SO_4^{2-}$$
 (1)

$$[Ti(OH)_4(OH_2)_2]^0 + 3C_2H_2O_3^{2-} \rightarrow [Ti(C_2H_2O_3)_3]^{2-} + 4OH^- + 2H_2O$$
(2)

$$TiCl_4 + 6H_2O \rightarrow [Ti(OH)_2(OH_2)_4]^{2+} + 2H^+ + 4Cl^-$$
 (3)

$$[Ti(OH)_2(OH_2)_4]^{2+} + 3C_3H_4O_3^{2-} \rightarrow [Ti(C_3H_4O_3)_3]^{2-} + 2OH^- + 4H_2O$$
(4)

Soluble  $[Ti(OH)_4(OH_2)_2]^0$  was resulted first by hydrolysis of  $TiOSO_4$  as described by Equation (1).<sup>[1]</sup> When glycolate ligand was used as the chelating agent, a hydrosoluble titanium-glycolate complex  $[Ti(C_2H_2O_3)_3]^{2-}$  was generated (Equation

3).<sup>[2]</sup> On the other hand, a water-soluble titanium-lactate complex  $[Ti(C_3H_4O_3)_3]^2$  was evolved, following the complexing of  $[Ti(OH)_2(OH_2)_4]^{2+}$  by another bidentate lactate ligand in TiCl<sub>4</sub> decompounded solution (Equations 3 and 4).<sup>[3,4]</sup>



Fig. S1 XRD patterns of the synthesized brookite  $TiO_2$  QO nanocrystals, WT and ET nanorods.



**Fig. S2** Typical Raman spectra of pure-phase brookite TiO<sub>2</sub> with different shapes: (a) ET nanorods, (b) WT nanorods, and (c) QO nanocrystals.

In addition to the X-ray diffraction, phase purity of these powders was further confirmed by Raman spectroscopy. It is well documented <sup>[5,6]</sup> that brookite has 36  $(9A_{1g} + 9B_{1g} + 9B_{2g} + 9B_{3g})$  Raman active modes, while anatase has 6  $(3E_g + 2B_{1g} + A_{1g})$ , and rutile only exhibits 4  $(A_{1g} + B_{1g} + B_{2g} + E_g)$ . It should be noticed that the locations of vibration bands are the same for all these three shapes as described in Fig. S2. Moreover, a series of characteristic Raman signals at 126.4, 152.6, 171.2, 194.3, 213.5, 246.6, 287.1, 321.5, 365.8, 395.3, 412.1, 453.6, 462.3, 501.5, 546.3, 585.2, and 636.7 cm<sup>-1</sup> were clearly revealed to be extremely coincided with those of brookite TiO<sub>2</sub>.<sup>[5, 7]</sup> On the other hand, the absence of 144 (E<sub>g</sub>), 397 (B<sub>1g</sub>), 516 (A<sub>1g</sub>), and 639 (E<sub>g</sub>) cm<sup>-1</sup> for anatase and 143 (B<sub>1g</sub>), 449 (E<sub>g</sub>), and 610 (A<sub>1g</sub>) cm<sup>-1</sup> for rutile demonstrates a high purity of the as-prepared brookite nanocrystals.<sup>[5,6]</sup>



**Fig. S3.** TEM and HRTEM images of brookite in the shape of (A) QO nancrystals; (B,C) ET nanorods, and (D-F) WT nanorods, F and the insets in A and C are the SAED patterns of brookite nanocrystals.

The representative morphology and uncovered crystal facets of brookite ET nanorods were investigated in Fig. S3(B,C). One can recognize that the lattice fringes terminate clearly at (210), (0), (10) and (20) edges. On the other hand, the tip parts of the nanorods were carefully examined to be an ellipsoid shape bared with no specific facets, the diffraction rings existent in the strong diffraction spots in the insert of Fig. S3C demonstrate that ET nanorods are complex of single crystal and ploycrystal. The exposed crystal facets of brookite WT nanorods are shown in Fig. S3E. It can be found that two {101} and two {201} facets shape the tip surface of one WT nanorod. In addition, when the incident beam was in the [21] direction (Fig. S3E), nanorods were found to be enclosed by facets parallel to the clearly terminated (210) and (0) borders. As a consequence, these two {210} edges produce facets on the nanorods surface. Therefore, WT nanorods are surrounded by four equivalent {210}, two {101}, and two {201} facets.



Fig. S4 TEM and HRTEM photos of PbO<sub>2</sub>-Pt-TiO<sub>2</sub>.

Photoinduced depositions of Pt and PbO2 onto the facets of brookite quasioctahedral nanocrystals exposed with {210}, {101}, and {201} facets were carried out to identify the redox sites. For Pt deposition, H<sub>2</sub>PtCl<sub>6</sub> and 2-propanol were employed as the precursor and hole scavenger, respectively. With regard to PbO<sub>2</sub> deposition, the procedure was performed using Pb(NO<sub>3</sub>)<sub>2</sub> as the precursor and water as electron acceptors. The deposited species were resolved by TEM, HRTEM, EDX, and XPS measurements. It can be found from TEM and HRTEM graphs (Fig. S4) that the interplanar spacing is about 0.231 nm (Fig. S4C), which can be attributed to the (111) plane of cubic Pt. XPS signal of Pt 4f core level reflects that the deposited Pt grains on the brookite quasi-octahedral nanocrystal were primarily in the metallic state (Fig. S5b). On the other hand, under UV irradiation, lead oxide aggregates were mainly formed on the {201} facets of brookite quasi-octahedral nanocrystal (Fig. S4D-F). On the basis of HRTEM image displayed in Fig. S4F, the planar space of 0.223 nm was demonstrated, which corresponds to the (112) plane of orthorhombic PbO<sub>2</sub>. The presence of Pb<sup>4+</sup> ions<sup>[8,9]</sup> was confirmed by XPS signals of Pb 4f core level (Fig. S5). Therefore,  $Pb^{2+}$  ions were photo-oxidized onto the brookite {201} planes,

while  $PtCl_6^{2-}$  species were photo-reduced on the {210} and {101} facets. These results suggest that the photogenerated holes prefer to accumulate on the {201} surfaces for oxidation reactions. On the contrary, photoproduced electrons tend to be trapped by the {210} and {101} facets responsible for reduction reactions. Namely, brookite {201} serves as the oxidative facets, and therefore brookite {210} and {101} facets function as the reductive sites. The redox reactions in relation to  $PtCl_6^{2-}$  and  $Pb^{2+}$  ions stimulated by the photoinduced electrons and holes could be expressed as belows:



**Fig. S5** EDX data and Pt 4f and Pb 4f spectra of (a, b) Pt-TiO<sub>2</sub> and (c, d) PbO<sub>2</sub>-Pt-TiO<sub>2</sub>.



**Fig. S6** Photocurrent responses as a function of time for brookite nanocrystals with varied percentages of crystal facets. The relevant data for Degussa P25 is given for comparison.



Fig. S7  $N_2$  adsorption-desorption isotherms of the synthesized brookite nanocrystals with different shapes.



**Fig. S8** XPS valence band spectra of brookite with given shapes: (a) WT nanorods and (b) QO nanocrystals.



**Fig. S9** Ti 2p and O 1s XPS spectra of brookite  $TiO_2$  with given shapes: (a,b) WT nanorods and (c,d) QO nanocrystals, (e,f) Ti 2p and S 2p XPS spectra of ET nanorods.

The XPS spectra of brookite ET and WT nanorods and quasi-octahedral nanocrystals were studied. We can identify from Fig. S9, Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  peaks at ~458.3 eV and ~464.1 eV are related to the Ti<sup>4+</sup> ions;<sup>[10]</sup> on the other hand, O 1s spectra could be resolved into two signals around 529.5 eV and 531.2 eV, which are assigned to the lattice oxygen and surface hydroxyl oxygen, respectively.<sup>[11]</sup> The percentage of surface hydroxyl oxygen for WT nanorods is estimated to be 14 %, which is much lower than that of 28 % for quasi-octahedral nanocrystal. What's more, the absence of Ti<sup>3+</sup> and Ti<sup>2+</sup> ions<sup>[12,13]</sup> were confirmed by Ti 2p spectra, indicating that the defects in the as-prepared brookite nanocrystals might be ignored. The S 2p XPS spectrum

(Fig.S9e) in ET nanorods is negligible while compared to Ti (Fig.S9f), which demonstrates that surface of our prepared  $TiO_2$  crystals are clean. We infer that the defects and the ellipsoid tipped shape feature of ET  $TiO_2$  are formed by the introduced  $SO_4^{2-}$  in the process of hydrothermal condition, but the absorbed  $SO_4^{2-}$  can be removed out by carefully washed with deionized water and ethanol.



**Fig. S10** Fluorescence emission spectra of TAOH produced in the presence of brookite with different shapes: (a) ET nanorods, (b) WT nanorods, and (c) QO nanocrystals under UV irradiation for given period of time.

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