Supporting Information

Black Brookite Titania with High Solar Absorption and Excellent Photocatalytic Perfomance

Guilian Zhu,[a] Tianquan Lin,[a] HaoYin,[a] Xujie Lü,[a] Wei Zhao,[a] Zhanqiang Liu,[a] and Fuqiang Huang[a,b]*

[1] CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China;

[2] Beijing National Laboratory for Molecular Sciences and State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P.R. China;

Experimental Section

Preparation of brookite. The brookite was synthesized similarly to reference 8. 3g of $TiOSO_4 \cdot xH_2O$ was dissolved in 50 mL deionized water under magnetic stirring and a transparent solution was formed； 6.25 mL of 10 M NaOH solution was added into the solution under vigorously stirring to yield a white suspension with flocculent precipitates. The suspension was filtered and redispersed into 60mL deionized water, and NaOH solution was added into the resulting suspension to adjust pH to about 12.5. Lastly, the suspension was transferred into two 50ml autoclaves which were subsequently sealed and kept in an oven at 220 ºC for 48 h. After naturally cooling to room temperature, the pale yellow products were collected, rinsed with deionized water several times, and then dried in the oven at 80 ºC overnight.

Preparation of black brookite TiO_{2-x}. The black brookite TiO_{2-x} was prepared through reducing by melted Al. The Al powders and brookite TiO_2 were separately placed in a two-zone evacuated furnace of 800 °C (Al) and 300–600 ºC (brookite) for 4 h under a pressure of 0.5 Pa.

Photocatalytic methyl orange decomposition. The photocatalytic activities of the brookite samples were evaluated by measuring the decomposition of methyl orange (MO) in an aqueous solution under solar light irradiation with 400W iodine gallium lamp. The experiments were performed as follows: 100 mg of photocatalyst was added into 100 mL MO solution (10 mg/L), and the suspension was poured in to a 600 ml glass container that was cooled with circulating water. The suspension was magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium between the MO and the photocatalyst. Then, the mixture was irradiated and at given time intervals, about 5 ml of the suspension was withdrawn for the following analysis after centrifugation. The concentration of the MO was monitored by tracking the absorbance at 464 nm over time using a Hitachi U-3010 UV-vis spectrophotometer.

Photocatalytic Methylene blue decomposition. The visible photocatalytic activities of the TiO_2 samples were evaluated by monitoring the decomposition of methylene blue (10 mg/L) in an aqueous solution under visible light irradiation. After stirring for 30 min in dark to stabilize the black TiO_2 in water, the solution was illuminated by a Xe lamp (300 W) with a 420 nm filter to cut off the UV light and allow only visible light (>420 nm) to pass through. The concentration of the MB was monitored by tracking the absorbance at 664 nm over time using a Hitachi U-3010 UV-vis spectrophotometer.

Photocatalytic phenol decomposition. The photocatalytic activities of the TiO_2 samples were evaluated by monitoring the decomposition of phenol in an aqueous solution (30 mg/L) under visible light irradiation. The phenol photodegradation experiment was conducted under the same condition as MB decomposition, after stirring for 30 min in dark to stabilize the black TiO_2 in water, the phenol solution was illuminated by a Xe lamp (300 W) with a 420 nm filter to cut off the UV light and allow only visible light (>420 nm) to pass through. The concentration of the phenol was monitored by tracking the absorbance at 270 nm over time using a Hitachi U-3010 UV-vis spectrophotometer.

Sample characterizations. TEM and SEM were inspected separately on a JEOL

JEM 2100F and a Hitachi S-4800. XRD patterns were obtained with a Bruker D8 advance diffractometer operating with Cu Ka radiation. Raman spectra were collected on a Thermal Dispersive Spectrometer using a laser with an excitation wavelength of 532 nm at laser power of 10 mW. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV). EPR spectra were investigated using a Bruker EMX-8 spectrometer at 9.44 GHz at 300 K.

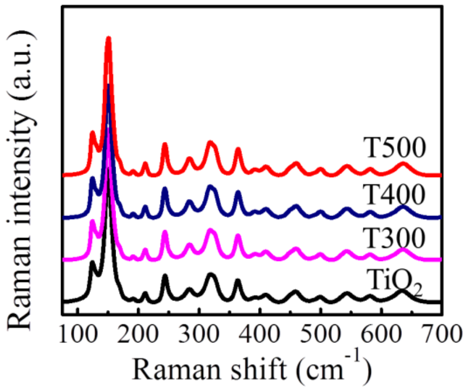

Fig. S1. Raman micrographs of the pristine TiO_2 and TiO_{2-x} after Al reduction at different temperatures for 4h.

The low symmetry and large unit cell of brookite result in a diagnostically complex Raman spectrum compared to the other two polymorphs (anatase and rutile), thus Raman spectroscopy has been widely used to detect the presence of the brookite phase in TiO_2 containing materials.[1-4] Therefore we measure the Raman spectra of the samples before and after aluminium reduction to further confirm the phase composition. As Fig. S2 indicates, the pristine brookite TiO_2 and the Al-reduced TiO_{2-x} both display the typical Raman spectra of brookite, and 16 bands were identified in total, including seven A1g (124, 151, 192, 244, 410, 544, 636 cm^{-1}), four B1g (211, 318, 415, 500 cm^{-1}), four B2g (365, 393, 460, 581 cm^{-1}), and B3g (287 cm^{-1}) while the characteristic Raman signals at 399 cm^{-1} and 519 cm^{-1} for anatase or at 447 cm^{-1} and 612 cm^{-1} for rutile were not observed. This further proves the high phase purity of brookite for the pristine and the Al-reduced samples.

During the preparation of brookite, the stirring time when the precursor redispersed into deionized water is critical and would make a great difference in morphologies of the products, intensive and lengthy stirring favored both nucleation and growth of the platelike brookite; in comparison, mild and short stirring contributes to producing flowerlike samples. The flower-like sample is also pure brookite according to the XRD patterns and remains the brookite phase during aluminium reduction (Fig. S2 b); the particles are averagely ~5 μm and mainly made up of irregularly faceted nanocrystals of nonuniform sizes, as shown in Fig. S2 a.

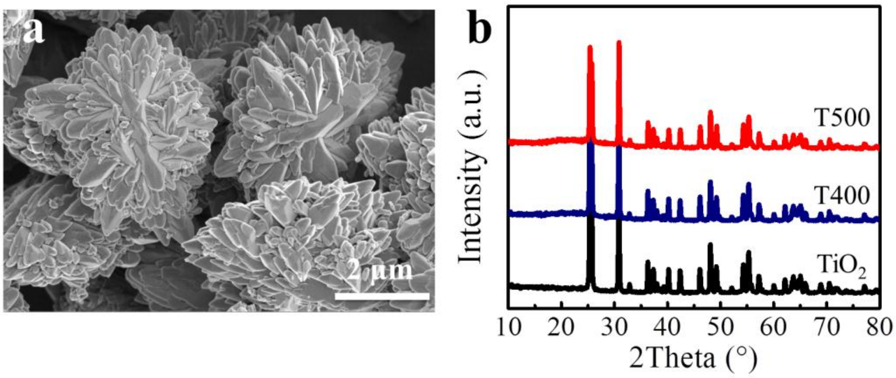

Fig. S2. (a) SEM micrographs of the flowerlike brookite. (b) XRD patterns of the pristine brookite TiO_2 and Al-reduced $TiO_{2\text{-}x}$.

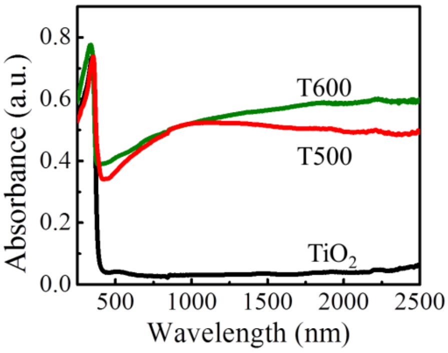

Fig. S3. UV-VIS-NIR diffuse reflectance spectra of TiO_2, T500 and T600 samples.

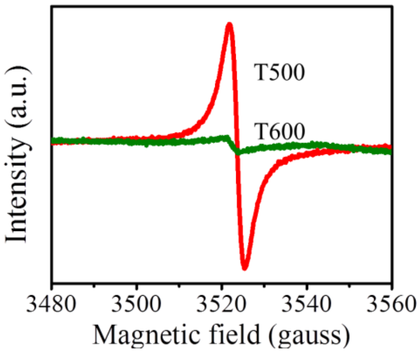

Fig. S4. EPR spectra of T500 and T600 samples.

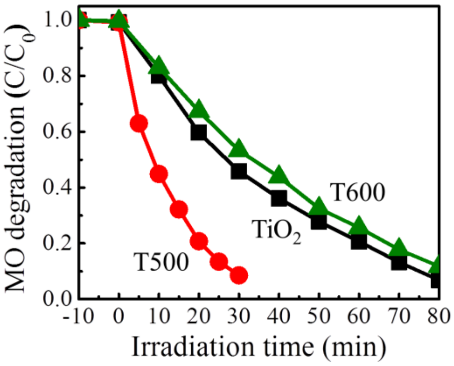

Fig. S5. Solar-light driven photocatalytic decomposition of MO over TiO_2, T500 and T600 samples.

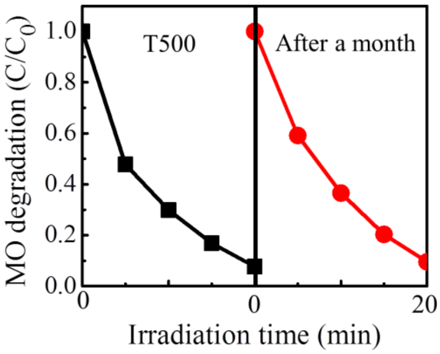

Fig. S6. Solar-light driven photocatalytic decomposition of MO over T500 samples before and after placing in air over a month.

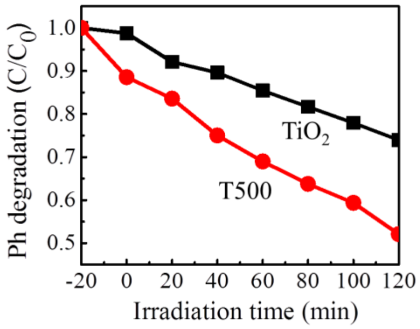

Fig. S7. Visible-light driven photocatalytic decomposition of phenol over TiO_2 and T500 samples

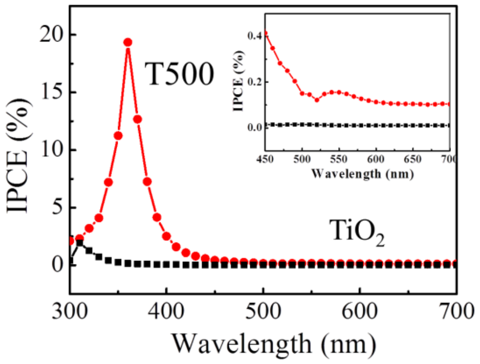

Fig. S8. IPCE spectra of the pristine and the 500°C-Al-reduced brookite. Inset: magnified IPCE spectra that highlighted in the dashed box, at the incident wavelength range from 450 to 700 nm at 0.65 V_{RHE}.

In order to understand quantum efficiency in photocatalytic reaction, the incident photon-to-current conversion efficiency (IPCE) measurements were conducted on pristine TiO_2 and Al-reduced black brookite TiO_{2-x} photoanodes at 0.65 V_{RHE} (Fig. S9). The working electrode were prepared by dip-coating of TiO_2 and TiO_{2-x} slurry (0.5g samples dispersed in 2.5ml ethanol) on FTO glass substrates; a Pt wire, and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. 1.0 M NaOH aqueous solution was used as the supporting electrolyte to maintain the stability of films. A solar simulator (AM 1.5) with a power of 100 mW/cm^2 was used as the illumination source.The IPCE can be expressed by the following equation,

$$\text{IPCE\%} = [1240\times \text{I (A/cm}^2)]/[\lambda \text{ (nm)} \times \text{J (W/cm}^2)]\times 100,$$

where I is the measured photocurrent density at a specific wavelength, λ is the wavelength of incident light, and J is the measured irradiance at a specific wavelength.

In comparison with pristine TiO_2, the IPCE values of TiO_{2-x} are greatly enhanced in the UV region. It indicates that the UV light was effectively used in the photocatalytic reaction and the separation and transportation of photoexcited charge carriers are more efficient in the TiO_{2-x} The recognizable photoactivity was also observed in the visible light region for the TiO_{2-x} sample, the IPCE value of TiO_{2-x} is ncreased to 0.1-0.4, in contrast to the negligible IPCE values for pristine TiO_2 in the same region (Figure R5, inset). It shows that Al-reduction not only highly enhances the efficiency of photoelectric conversion under UV light, but also extends the range of photo response into the visible-light. We hope that the revision is appropriate and provide the necessary information on the experimental setup.

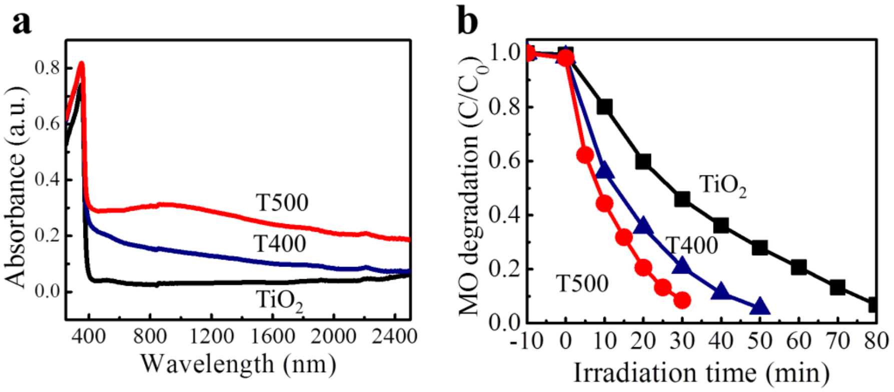

Fig. S9. (a) UV-VIS-NIR diffuse reflectance sperctra and (b) Solar-light driven photocatalytic decomposition of MO over the pristine flowerlike TiO_2, T500 and T600 samples.

References

1. H. Lin, L. Li, M. Zhao, X. Huang, X. Chen, G. Li and R. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 8328.
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