Brookite TiO_2 nanoflowers

Bin Zhao, Feng Chen, Qiwei Huang and Jinlong Zhang*

Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China.

*Corresponding author. E-mail: Fengchen@ecust.edu.cn. Tel & Fax: +86-21-64252062.

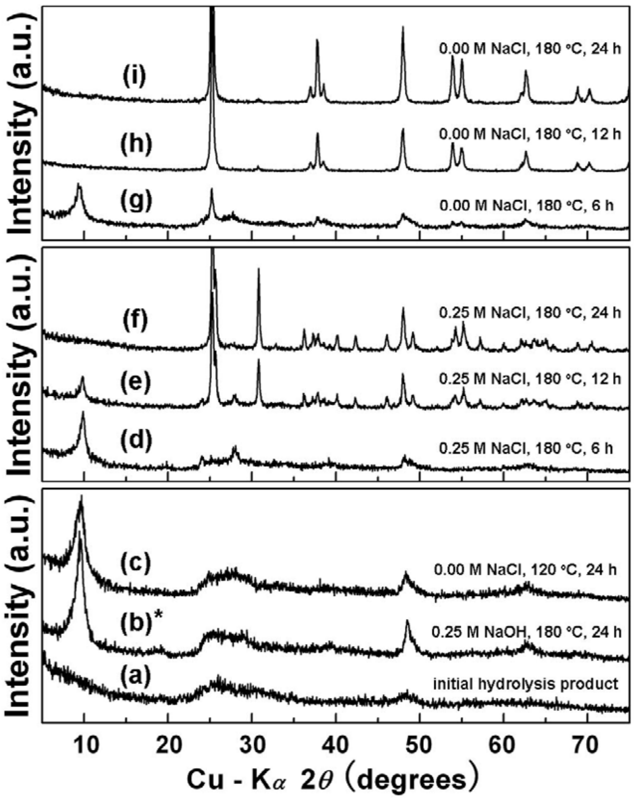

Fig. S1. XRD patterns of (a) the initial hydrolysis product of TBOT; the product synthesized (b) in 0.25 M NaOH aqueous solution at 180 ^{o}C for 24 h; (c) in aqueous ammonia at 120 ^{o}C for 24 h; (d-f) in 0.25 M NaCl ammonia solution at 180 ^{o}C for 6 h, 12 h and 24 h; (g-i) in aqueous ammonia at 180 ^{o}C for 6 h, 12 h and 24 h. *: the product (b) synthesized in NaOH aqueous solution.

Fig. S1a showed that the initial hydrolysis product of TBOT was amorphous. When TBOT was directly hydrolyzed in 0.25 M NaOH aqueous solution at 180 ^{o}C for 24 h (b), or in aqueous ammonia ($NH_3 \cdot H_2O$) at 120 ^{o}C for 24 h (c), pure hydrogen titanate $H_2Ti_2O_5 \cdot H_2O$ was obtained after hydrothermal treatment. When the concentration of NaCl was about 0.25M in aqueous ammonia ($NH_3 \cdot H_2O$), the products obtained at 180 ^{o}C for 6h, 12h and 24h (d-f) were layered titanate, brookite/titanate mixture, and pure brookite, respectively. When TBOT was directly hydrolyzed in aqueous ammonia ($NH_3 \cdot H_2O$) and hydrothermal treated at 180 ^{o}C for 6h, 12h and 24h, the products (g-i) were titanate/anatase mixture, smaller anatase particles and larger anatase particles, respectively. What has been mentioned above demonstrated that layered titanate should be formed by the intercalation of NH_4^+ ions and / or Na^+ ions in the initial period of hydrothermal treatment.

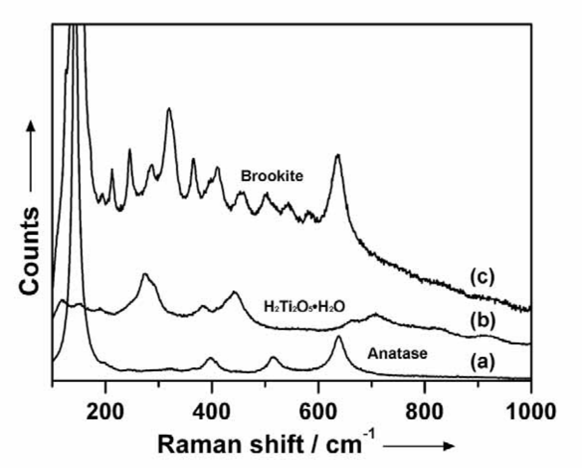

Fig. S2. Raman spectra for the samples of (a) anatase, (b) hydrogen titanate $H_2Ti_2O_5{\cdot}H_2O$ and (c) pure brookite.

Samples of anatase, pure brookite and hydrogen titanate shown in XRD patterns were further characterized by Raman spectroscopy in Fig. S2. The synthesized brookite shows strong Raman peaks at about 156 (A_{1g}), 245 (A_{1g}), 287 (B_{3g}), 320 (B_{1g}), 365 (B_{2g}) and 637 cm^{-1} (A_{1g}), [1] and the synthesized anatase exhibits characteristic scatterings at 144 (E_g), 397 (B_{1g}), 517 (A_{1g}) and 639 cm^{-1} (E_g). [2, 3] The Raman spectra of hydrogen titanate $H_2Ti_2O_5{\cdot}H_2O$ was seldom reported so that the key peaks should be used for detecting the presence of layered hydrogen titanate. [4, 5] Fig. S2b exhibited the unique Raman spectra of synthetic hydrogen titanate $H_2Ti_2O_5{\cdot}H_2O$, which could be dominated by broad and medium intensity peaks at about 275, 382, 441 and 708 cm^{-1}.[4] All three samples showed pure Raman bands without contamination.

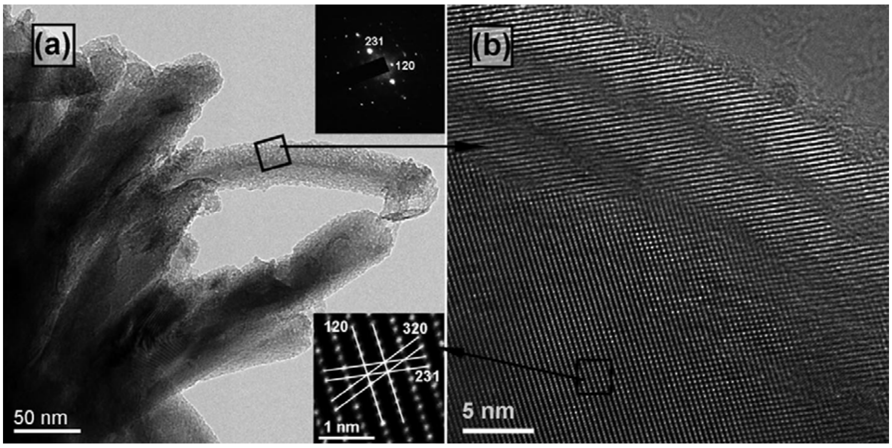

Fig. S3. Supplementary HRTEM images of brookite TiO_2 nanoflowers.

Fig. S3b is a magnified image of the marked region in Fig. S3a, which indicates the high crystallinity of brookite TiO_2. HRTEM image in the bottom right inset of Fig. S3a is a further magnified image of the marked region in Fig. S3b, which exhibits the ultra clear lattice planes of brookite TiO_2 nanoflowers.

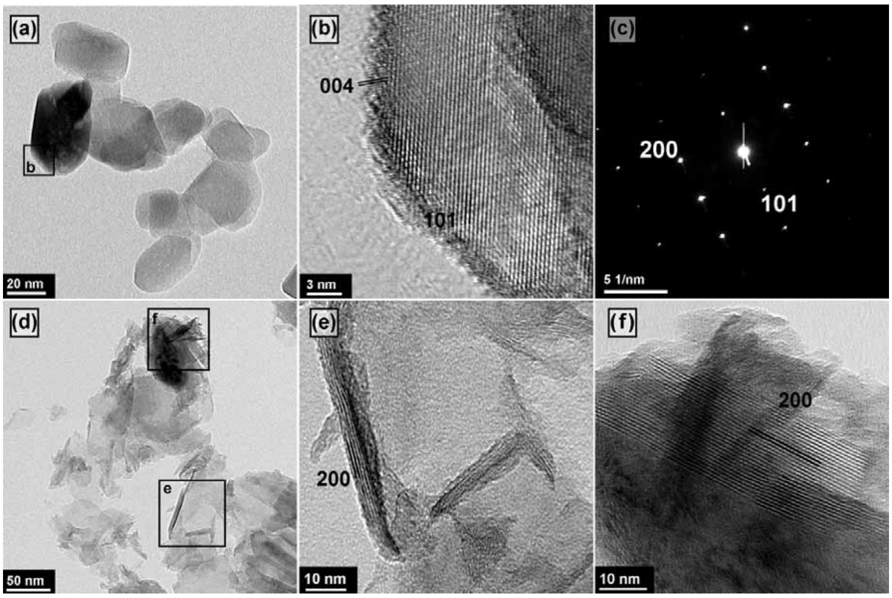

Fig. S4. TEM and HRTEM images of anatase nanoparticles (a-b) and layered hydrogen titanate nanosheets (d-f) synthesized by adjusting the concentration of NaCl under hydrothermal conditions. The SAED pattern located in Fig. S4c indicates the single crystalline nanoparticles of anatase TiO_2.

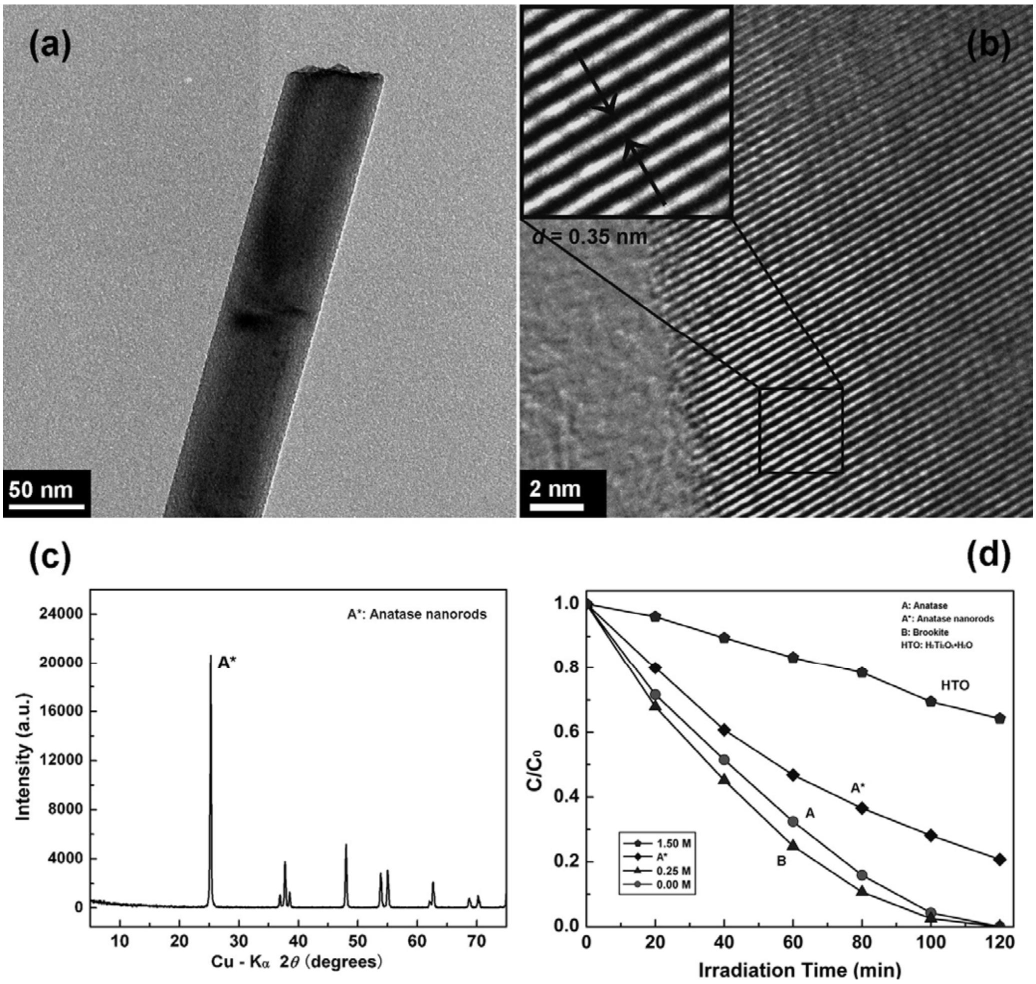

Fig. S5. TEM (a) and HRTEM (b) images of anatase nanorods synthesized in reference to the reported procedures; (c) XRD pattern of the anatase nanorods; (d) Photocatalytic activity of anatase nanorods compared with the pure brookite nanoflowers, anatase and titanate samples obtained in current work.

A comparative experiment was schemed to evaluate the photocatalytic activity of pure brookite nanoflowers. The pure anatase nanorods, which had a similar size to the pure brookite nanoflowers, were synthesized by hydrothermal and post-heat treatment in reference to the reported procedures. [6] Fig. S5d indicated the pure brookite nanoflowers exhibited much higher photocatalytic activity compared to the anatase nanorods.

Table S1. Specific surface areas of Samples

Sample[a]	0.00 M	0.12 M	0.25 M	0.50 M	0.75 M	1.00 M	1.50 M
Phases[b]	A	A + B	B	B + HTO	B + HTO	HTO + B	HTO
Specific surface area (S_{BET}, $m^2 \cdot g^{-1}$)	90.4	85.6	81.7	85.4	156.6	163.7	175.2

a: Catalysts were denoted by the concentration of NaCl in the synthetic media.

b: Anatase, Brookite and layered hydrogen titanate ($H_2Ti_2O_5 \cdot H_2O$) were denoted as A, B and HTO, respectively.

Specific surface areas were determined using an ASAP 2020 Micromeritics apparatus following the BET analysis. Adsorption and desorption of N_2 were performed at –196 ^oC. Samples had been previously outgassed by heating at 180 ^oC under vacuum.

References

[1] J. G. Li, T. Ishigaki and X.D. Sun, *J. Phys. Chem. C*, 2007, **111**, 4969 – 4976.

[2] G. A. Tompsett, G. A. Bowmaker, R. P. Cooney, J. B. Metson, K. A. Rogers and J. M. Seakins, *J. Raman Spectrosc.*, 1995, **26**, 57 – 62.

[3] T. Ohsaka, F. Izumi and Y. J. Fujiki, *Raman Spectrosc.*, 1978, **7**, 321 – 324.

[4] D. L. Morgan, H. Y. Zhu, R. L. Frost and E. R. Waclawik, *Chem. Mater.*, 2008**, 20***,* 3800 – 3802.

[5] X. M. Sun and Y. D. Li, *Chem. Eur. J.*, 2003, **9**, 2229 – 2238.

[6] R. Yoshida, Y. Suzuki and S. Yoshikawa, *J. Solid State Chem.*, 2005**, 178**, 2179 – 2185.