

Supplementary Information

Visible light photocatalysis of pristine anatase TiO₂ mesocrystals induced by largely-exposed and stepped (001) surface

Jin Chen,^{a,c} Xiaofan Li,^a Bingyu Lei,^a Lei Zhou^{*a,b} and Shenqi Wang^{a,b}

^a Department of Biomedical Engineering, School of Life Science and Technology, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China

^b Advanced Biomaterials and Tissue Engineering Center, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China

^c Key Laboratory of Biology and Medical Engineering, Guizhou Medical University, Guiyang, 550025, P. R. China

AUTHOR INFORMATION

Corresponding Author

* lei.zhou.public@gmail.com

Experimental Section

Synthesis of NH_4TiOF_3 particles: All chemicals used in this work are analytical grade without further purification. 0.5 g CTAB was added to a freshly prepared 50 ml of solution containing $(\text{NH}_4)_2\text{TiF}_6$ (0.3 M) and H_3BO_3 (0.2 M). Stirring was stopped after the CTAB was completely dispersed. The solution was kept at 35 °C for 12 h. The collected white precipitates were cleaned and washed by consecutive centrifuging, decanting, and redispersion, in water (three times) and then in ethanol (three times).

Synthesis of TiO_2 with stepped structures: There are two steps to prepare TiO_2 with stepped structures. Firstly, the prepared NH_4TiOF_3 powders were sintered at 500 °C for 30 min in air to form the less crystallized TiO_2 mesocrystals. Secondly, the less crystallized TiO_2 mesocrystals were sintered at 900 °C for 2 ~ 6 h in air.

Photocatalytic experiments: The photocatalytic activity was evaluated by the photodegradation of methylene blue (MB) in a deionized water solution with an initial concentration of 6 mg L⁻¹. Photocatalytic experiments were carried out at 20 °C in a glass container containing 100 mg catalyst and 60 ml MB solution. The suspension solution was stirred in the dark for 1 h first in order to reach adsorption-desorption equilibrium. For visible light photocatalysis, a 300 W Xe lamp (159.2 mW cm⁻²) with a 420 nm cut-off filter to remove the light below 420 nm wavelengths was used as the light source. For UV light photocatalysis, an 8 W UV lamp ($\lambda = 365$ nm, 12.7 mW cm⁻²) was used as the light source. For full wavelength light photocatalysis, a 300 W Xe lamp (159.2 mW cm⁻²) was used as the light source. For indoor light photocatalysis, a 30 W household white LED lamp (23.8 mW cm⁻²) was used as the light source. At the given time intervals, a small amount of the suspension was sampled and centrifuged to remove catalyst and obtain the filtrate. The concentration of MB solution was analyzed using a UV-visible-near infrared spectrophotometer (UV-1700, Macy, China).

Characterization: Scanning electron micrographs (SEM) and Energy dispersive X-ray analysis (EDX) were obtained using a FEI Nova Nano SEM 450 equipped with EDX analyzer. Powder X-ray diffraction (XRD) studies were performed using a PANalytical X'Pert PRO diffractometer. The average crystallite sizes were calculated using the Scherrer Equation. Atomic Force Microscope (AFM) studies were performed using a Bruker MultiMode 8. Transmission electron micrographs (TEM) were obtained using a FEI Tecnai G2 F30. Brunauer-Emmett-Teller (BET) studies were analyzed by nitrogen adsorption in a Micromeritics ASAP 2460 nitrogen adsorption apparatus. X-ray photoelectron spectra (XPS) measurements were performed using a Kratos Axis Ultra DLD. All binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. UV-Vis absorption spectra were obtained using a PerkinElmer Lambda 35 equipped with an integrating sphere. ICP-OES analyses were performed using an Agilent ICPOES730. Carbon content was measured by infrared carbon sulfur analyzer using a LECO CS230. Nitrogen content was measured by oxygen-nitrogen analyzer using a LECO TC330. Bromine content was measured by ion chromatography using a Metrohm 881 Compact IC pro.

Results

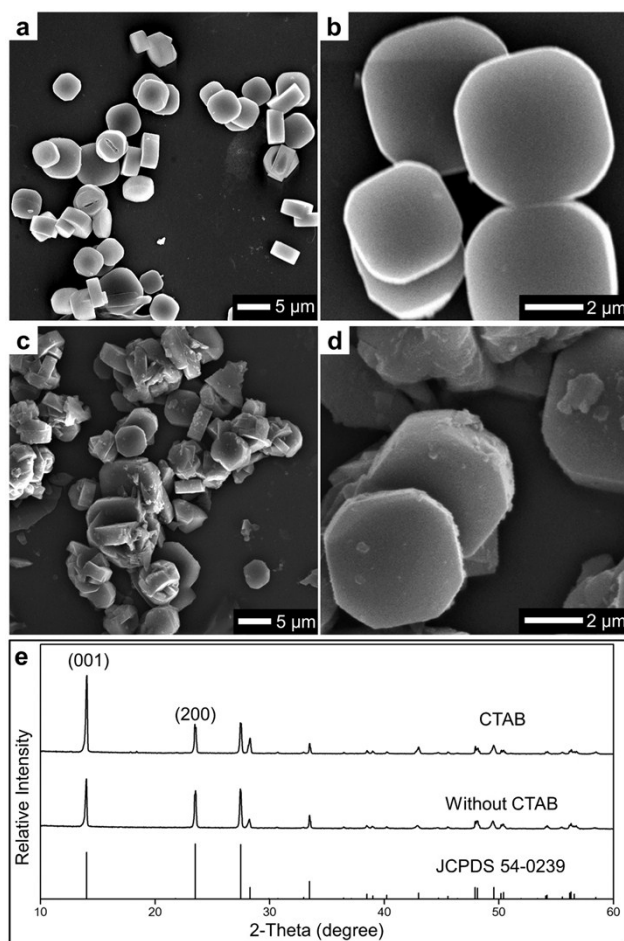


Fig. S1 SEM images of the NH_4TiOF_3 particles prepared with CTAB (a and b), and without CTAB (c and d). (e) XRD patterns of the two samples.

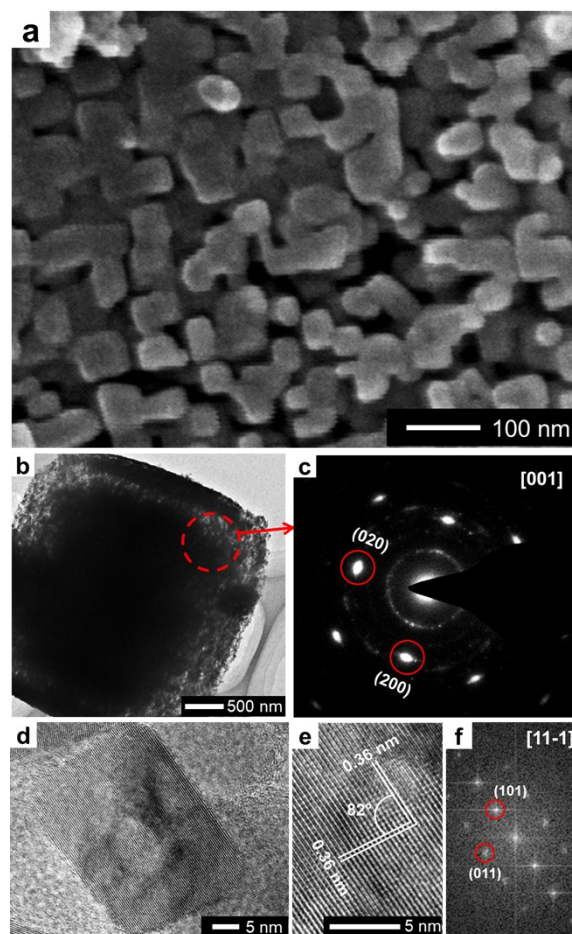


Fig. S2 (a) Large magnification SEM image of the less crystallized TiO_2 mesocrystal particles. (b and c) TEM analysis of a less crystallized TiO_2 mesocrystal particle: (b) TEM image; (c) SAED pattern. (d-f) TEM analysis of a typical nanoparticle (building block) in the less crystallized TiO_2 mesocrystal particle: (d) TEM image; (e) HRTEM image; (f) FFT pattern.

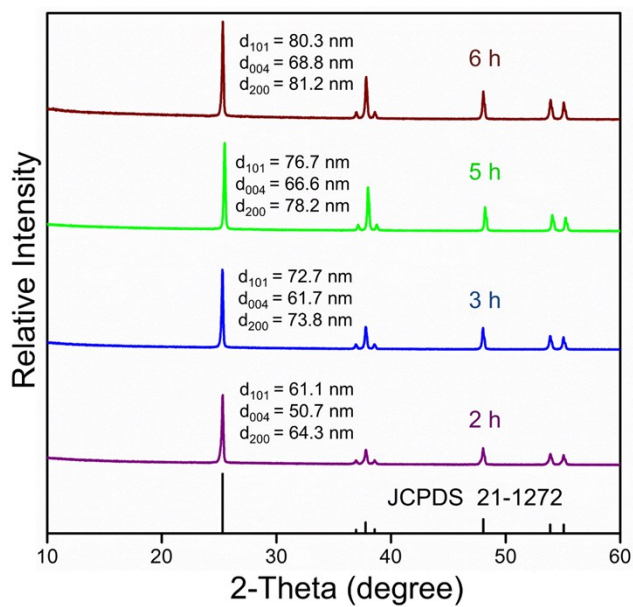


Fig. S3 XRD patterns of the samples prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for different hours.

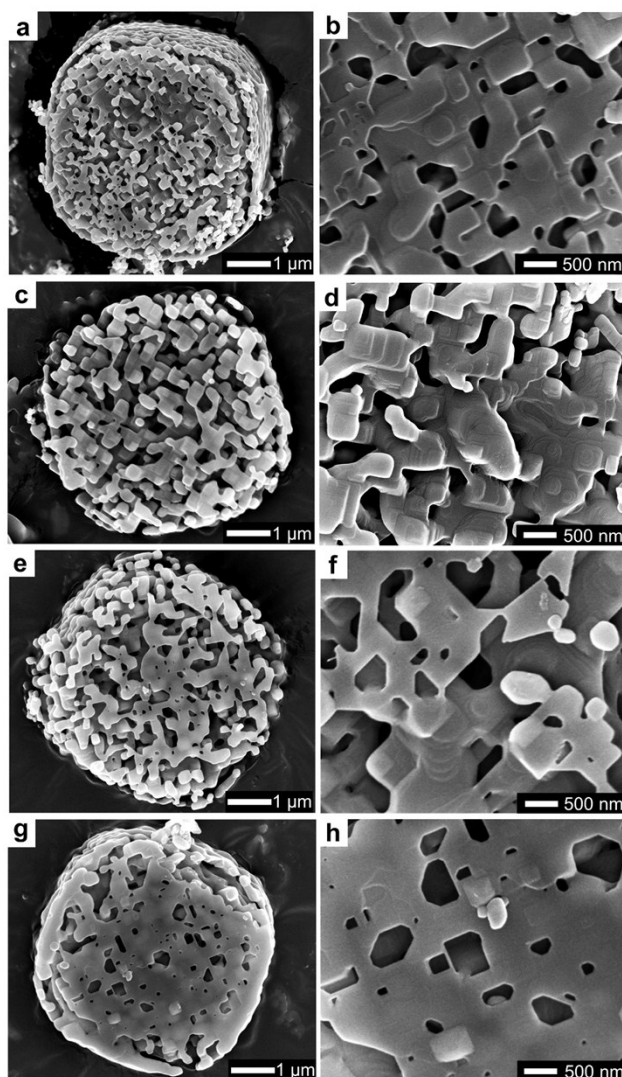


Fig. S4 SEM images of the samples prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for different hours: (a and b) 2 h; (c and d) 3 h; (e and f) 5 h; (g and h) 6 h.

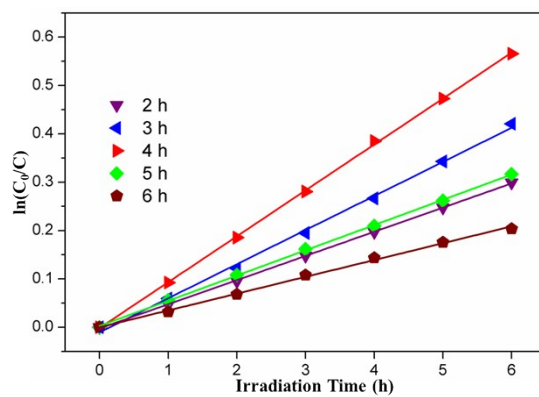


Fig. S5 The plot of $\ln C_0/C$ vs. time for the samples obtained by sintering the less crystallized TiO_2 mesocrystals at $900\text{ }^\circ\text{C}$ for various times. It indicates that the kinetic studies follow the first-order reaction.

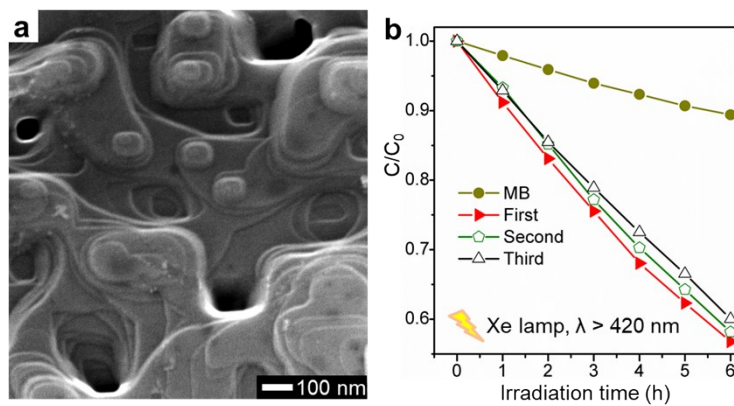


Fig. S6 The sample prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for 4 h. (a) SEM image of the sample after 6 hours of the visible light photocatalytic reaction. (b) Three cycles of visible light photocatalytic reaction of the sample.

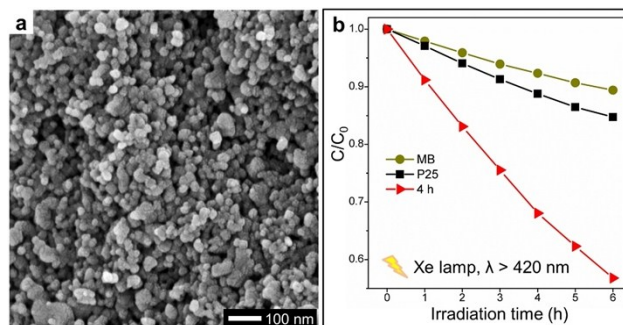


Fig. S7 (a) SEM image of P25 powders. (b) Visible light photocatalytic activities ($\lambda > 420$ nm) of P25 and the sample prepared by sintering the less crystallized TiO_2 mesocrystals at 900 °C for 4 h.

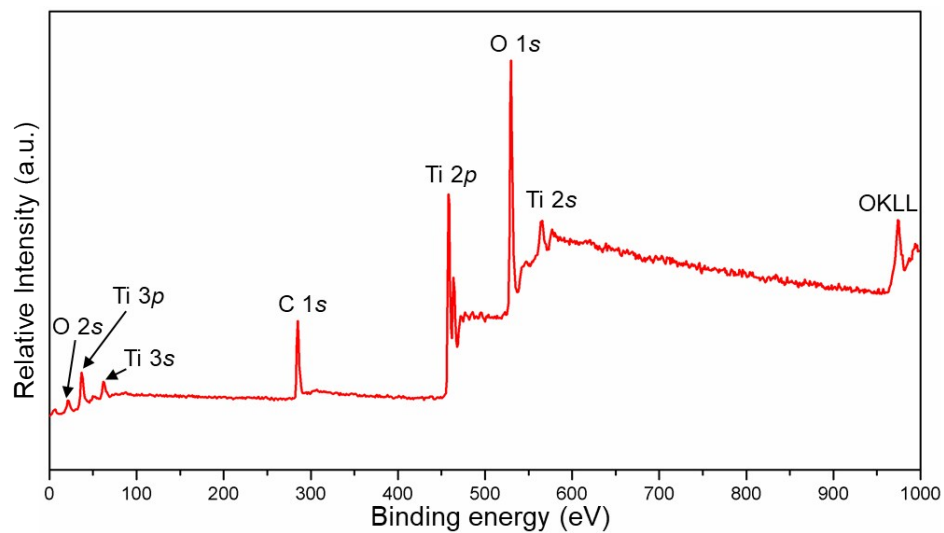


Fig. S8 The XPS full spectrum of the sample obtained by sintering the less crystallized TiO₂ mesocrystals at 900 °C for 4 h.

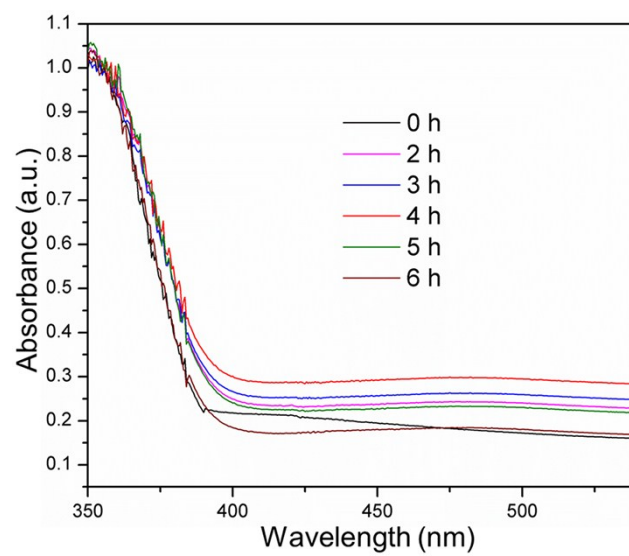


Fig. S9 UV-Vis absorption spectra of samples obtained by sintering the less crystallized TiO₂ mesocrystals at 900 °C for various hours.

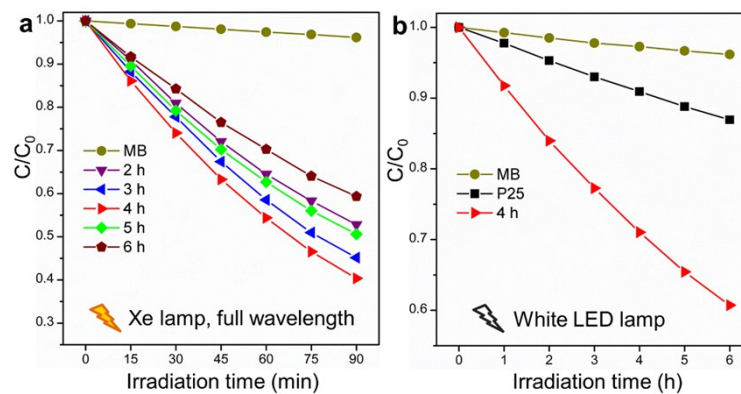


Fig. S10 (a) Full wavelength light photocatalytic activities of the samples prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for different hours. (b) White LED light photocatalytic activities of P25 and the sample prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for 4 h.

| Sample | S_{BET} ($\text{m}^2 \text{g}^{-1}$) |
|--------|---|
| P25 | 53.6 ± 2.1 |
| 2 h | 7.8 ± 0.7 |
| 3 h | 7.6 ± 0.5 |
| 4 h | 7.3 ± 0.7 |
| 5 h | 7.3 ± 0.6 |
| 6 h | 7.3 ± 0.4 |

Table S1 Specific surface areas (S_{BET}) of P25 and the samples obtained by sintering the less crystallized TiO_2 mesocrystals at 900 °C for different hours, S_{BET} were calculated using BET results.

| Sample | F (at%) | N (at%) |
|--------|---------|---------|
| 700 °C | 0.28 | 0.11 |
| 800 °C | 0.15 | 0.07 |
| 900 °C | < 0.01 | < 0.01 |

Table S2 F and N atomic concentration of the samples prepared by sintering the less crystallized TiO₂ mesocrystals at 700 °C, 800 °C and 900 °C for 2 h. Atomic concentrations were calculated using XPS spectra.

| Sample | F (wt%) | N (wt%) | C (wt%) | B (wt%) | Br (wt%) |
|--------|---------|---------|---------|---------|----------|
| 0 h | 1.55 | 1.21 | 1.37 | 0.00 | 0.00 |
| 2 h | 0.00 | 0.00 | 1.25 | 0.00 | 0.00 |
| 3 h | 0.00 | 0.00 | 1.15 | 0.00 | 0.00 |
| 4 h | 0.00 | 0.00 | 1.16 | 0.00 | 0.00 |
| 5 h | 0.00 | 0.00 | 1.33 | 0.00 | 0.00 |
| 6 h | 0.00 | 0.00 | 1.12 | 0.00 | 0.00 |

Table S3 Element concentrations of the samples prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for different hours, element concentrations were calculated using EDX results.

| Sample | N (wt%) | C (wt%) | B (wt%) | Br (wt%) |
|--------|----------------------|---------|-----------------------|----------|
| 0 h | 0.129 | 0.065 | 1.01×10^{-3} | < 0.001 |
| 2 h | 4.2×10^{-3} | 0.057 | 0.93×10^{-3} | < 0.001 |
| 3 h | 3.4×10^{-3} | 0.058 | 1.05×10^{-3} | < 0.001 |
| 4 h | 2.9×10^{-3} | 0.049 | 0.84×10^{-3} | < 0.001 |
| 5 h | 2.7×10^{-3} | 0.044 | 0.78×10^{-3} | < 0.001 |
| 6 h | 3.1×10^{-3} | 0.048 | 0.86×10^{-3} | < 0.001 |

Table S4 Results of element analysis of the samples prepared by sintering the less crystallized TiO₂ mesocrystals at 900 °C for different hours. N content was measured by oxygen-nitrogen analyzer. C content was measured by Infrared Carbon Sulfur Analyzer. B contents was measured by ICP-OES. Br content was measured by ion chromatography.