

Supporting information

Facile Construction of Hierarchical Ellipsoid-shaped TiO₂ Porous Nanostructure with Enhanced Photocatalytic Activity

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Table of Contents

1. Experimental section

1.1 Chemicals.....	S3
1.2 Instrument and characterization.....	S3
1.3 Preparation of ellipsoid-shaped TiO ₂ with hierarchically porous nanostructure.....	S4
1.4 Photocatalytic measurement.....	S5

2. Figures

Fig. S1 Evolution of XRD patterns of ellipsoid-shaped TiO ₂	S6
Fig. S2 UV-Vis spectra of MB with ellipsoid-shaped TiO ₂ nanoparticles in the dark.....	S6
Fig. S3 UV-vis absorbance spectra of MB with P25 in the dark.....	S7
Fig. S4 UV-vis absorbance spectra of MB with P25 under ultraviolet light irradiation at different light irradiation times.....	S8
Fig. S5 UV-Vis spectra of MB with ellipsoid-shaped TiO ₂ nanoparticles under ultraviolet light irradiation at different light irradiation times.....	S8
Fig. S6 UV-vis spectra of MB with ellipsoid-shaped TiO ₂ nanoparticles in the dark and under simulated sunlight irradiation at different light irradiation times.....	S9
Fig. S7 The pure sample and the sample treated with HCl.....	S9

Experimental section

Chemicals

Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, chemical purity) and Sodium sulphate (Na_2SO_4 , analytical grade) was purchased from Sinopharm Group Chemical Reagent Co., LTD. Hydrogen peroxide 30 % (H_2O_2 30 %, analytical grade) and absolute ethanol (C_2H_6O , analytical grade) were purchased from Tianjin Deen Chemical Reagent Co., LTD. Ammonium carbonate ($(NH_4)_2CO_3$, analytical grade) was purchased from Shanghai Reagent Fourth Factory. Ammonia solution ($NH_3 \cdot H_2O$, analytical grade) and hydrochloric acid (HCl) was purchased from Luoyang Chemical Reagent Factory. Methylene blue ($C_{18}H_{18}N_3SCl_3 \cdot H_2O$) was purchased from Beijing Chemical Factory. Ultrapure water was used in the experiment.

Instrument and characterization

The crystalline structures of the prepared products were investigated by the powder X-ray diffraction (XRD) on a Bruker D8 & Advance X-ray powder diffractometer with graphite monochromatized $CuK\alpha$ ($\lambda=0.15406$ nm). X-ray photoelectron spectroscopy (XPS) was also used to investigate the chemical composition of as-prepared products. The morphologies were observed by means of a SU8010 Field emission electron microscope (FE-SEM) and Transmission electron microscope (TEM) analyses were performed using a JEM-2100 transmission electron microscope equipped with a selected-area electron diffraction (SAED), which was used to investigate the particle size and the presence of

pore structures. And samples were prepared by mounting an ethanol dispersed samples onto the carbon-coated copper grids. N₂ absorption/desorption isotherms were generated at 77 K and the Brunauer-Emmett-Teller (BET) surface area and pore size distribution were evaluated on a ASAP 2010 analyzer. The samples were firstly degassed at 300 °C for 6 h before analysis. The specific surface areas were calculated utilizing the Brunauer-Emmett-Teller (BET) model. Pore size distribution was derived from the desorption branch of the isotherms using the Barret-Joyner-Halenda (BJH) model. The total pore volume was estimated from the amounts of N₂ adsorbed at a relative pressure (P/P_0) of 0.99. Ultraviolet-visible (UV-vis) spectra were measured by Lambda 950. The photoluminescence (PL) emission spectra were obtained from a FLS980 fluorescence spectrophotometer. The photocurrent density of photocatalyst loaded on glassy carbon electrode as working electrode were measured on AOT87353 electrochemical station under 300 w xenon lamp with turning off and on every 2 minutes.

Preparation of ellipsoid-shaped TiO₂ with hierarchically porous nanostructure

Firstly, 0.01 mol tetrabut titanate (C₁₆H₃₆O₄Ti) was dissolved in 2.50 mL absolute ethanol. And 2.50 mL ammonia solution and 7.50 mL absolute ethanol were slowly added to the above mixed solution with constant stirring. Then white precipitates appeared and the stirring was continued for another 20 min. The resultant precipitate was collected by centrifuge and washed 3 times with de-ionized water. Then, 35 mL 0.2 mM ammonium carbonate solutions was added to the resultant precipitate with constant stirring. Next, 1.25 mL 30 % H₂O₂ was added into the above precursor solution and a light yellow clear solution can be obtained. The mixed solution was transferred into a 100 mL capacity

Teflon-lined stainless steel autoclave, which was heated to 180 °C and kept for 6 h. The white products obtained were washed respectively with deionized water and ethanol several times, and dried at 80 °C for 12 h.

Photocatalytic measurement

Methylene blue (MB) decomposition tests were carried out to study the photocatalytic activities of as-synthesized products. Typically, 50 mg samples were dispersed into 50 mL solution containing MB at a concentration of 10 mg/L. The mixture was stirred in dark environment for 60 min to reach adsorption equilibrium of MB, and then exposed to a 250 W high-pressure mercury lamp and 300W Xenon lamp at room temperature. At different time intervals, about 4 mL of the mixture was taken out and centrifuged, and the MB concentration of supernatant was monitored using a UV-vis spectrophotometer. Compared to the commercial P25 under the identical condition, the ellipsoid-shaped TiO₂ showed significantly enhanced photocatalytic activity for MB degradation. In addition, the adsorption ability of ellipsoid-shaped TiO₂ for MB removal in the dark was weak.

The photocatalytic degradation kinetic of MB was investigated by using Langmuir-Hinshelwood first-order reaction kinetic as expressed in the following equation:

$$\ln C/C_0 = -k_{app}t \quad (1)$$

The apparent rate constant, k_{app} is used to evaluate the photocatalytic activity of photocatalyst. The linear relations of $\ln(C/C_0)$ versus the irradiation time for different samples are obtained. Compared with the commercial P25, the photocurrent density of ellipsoid-shaped TiO₂ cast on glassy carbon electrode as working electrode, showed

markedly enhanced photocurrent density. In which the electrolyte is 0.5 M Na₂SO₄ solution, under 300W xenon lamp.

Figures

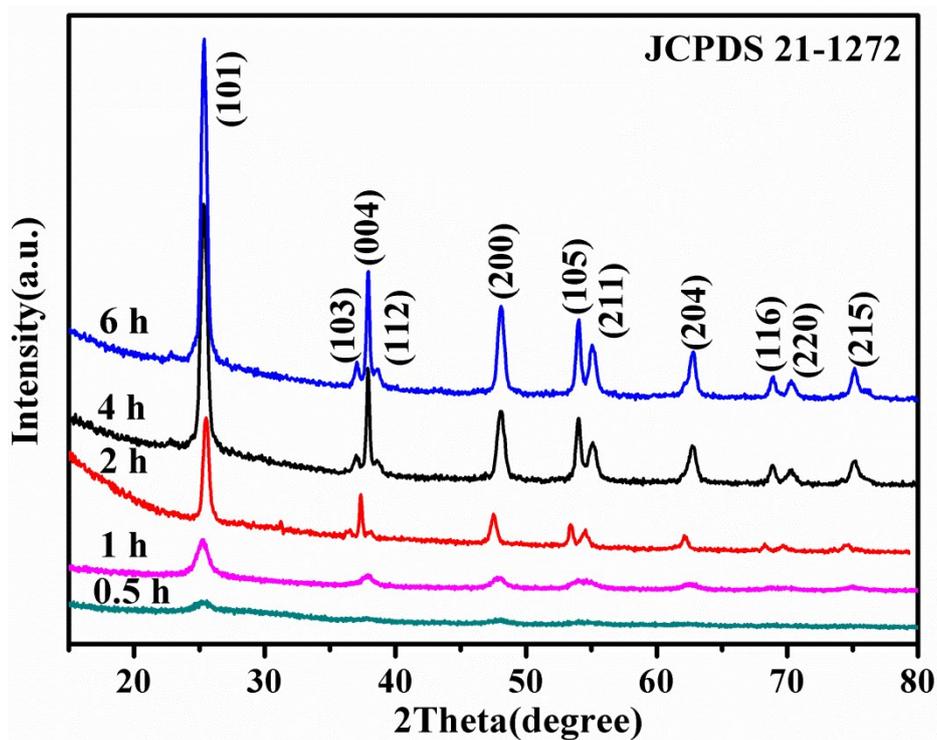


Fig. S1 Evolution of XRD patterns of ellipsoid-shaped TiO₂ during hydrothermal reaction process.

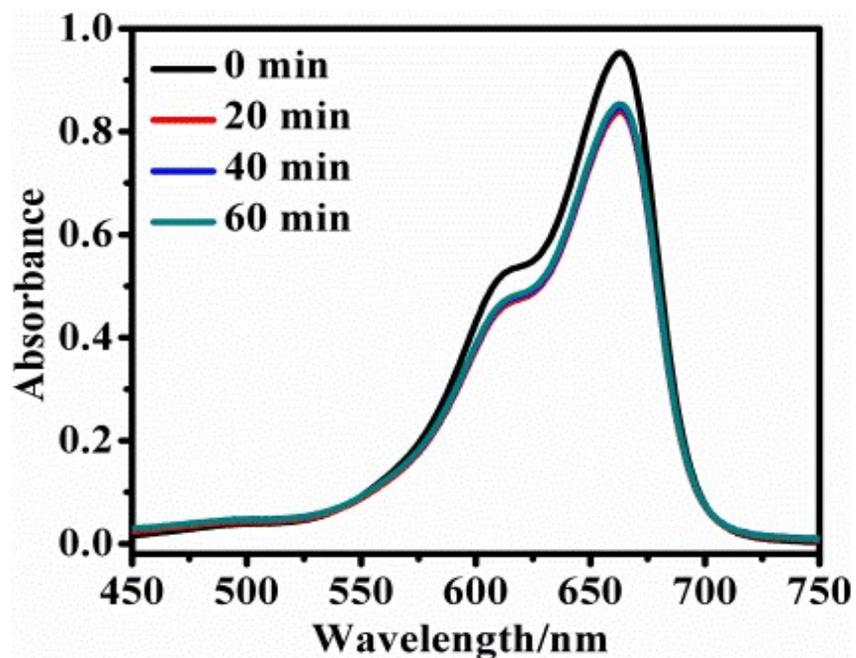


Fig. S2 UV-vis absorbance spectra of MB with ellipsoid-shaped TiO₂ nanoparticles in the dark.

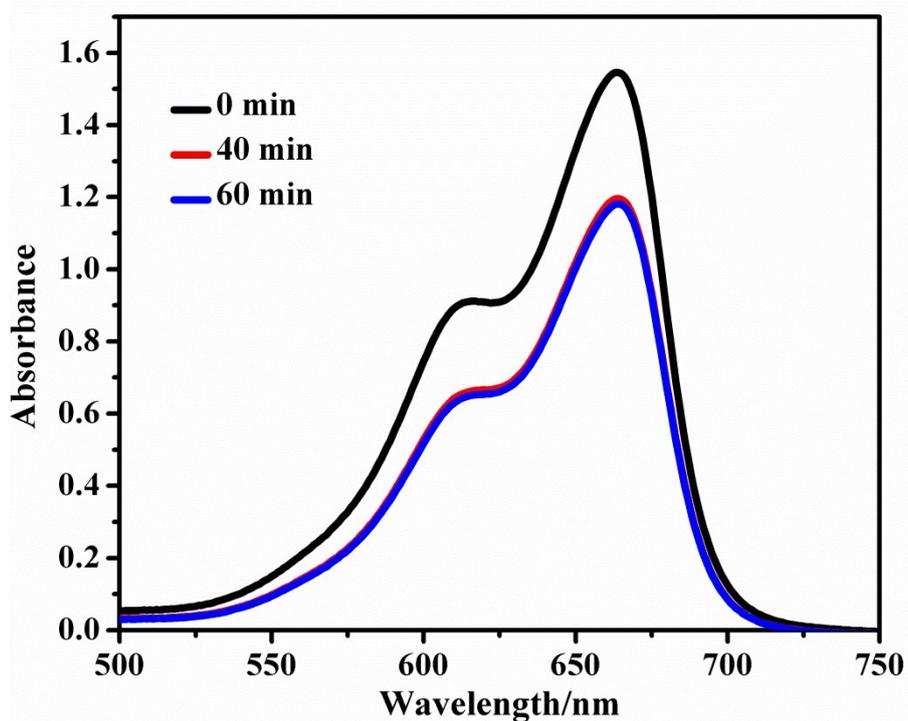


Fig. S3 UV-vis absorbance spectra of MB with P25 in the dark.

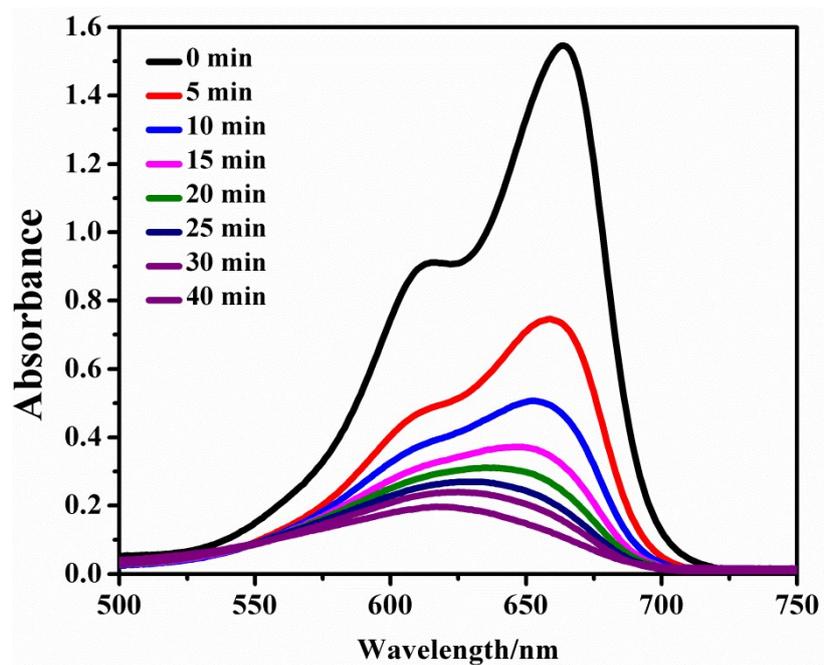


Fig. S4 UV-vis absorbance spectra of MB with P25 under ultraviolet light irradiation at different light irradiation times.

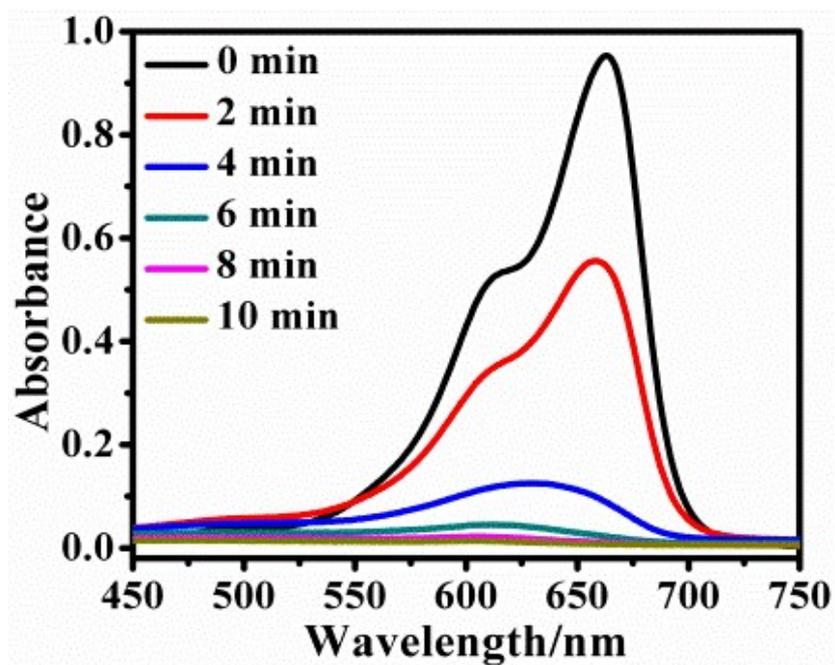


Fig. S5 UV-vis absorbance spectra of MB with ellipsoid-shaped TiO₂ nanoparticles under ultraviolet light irradiation at different light irradiation times.

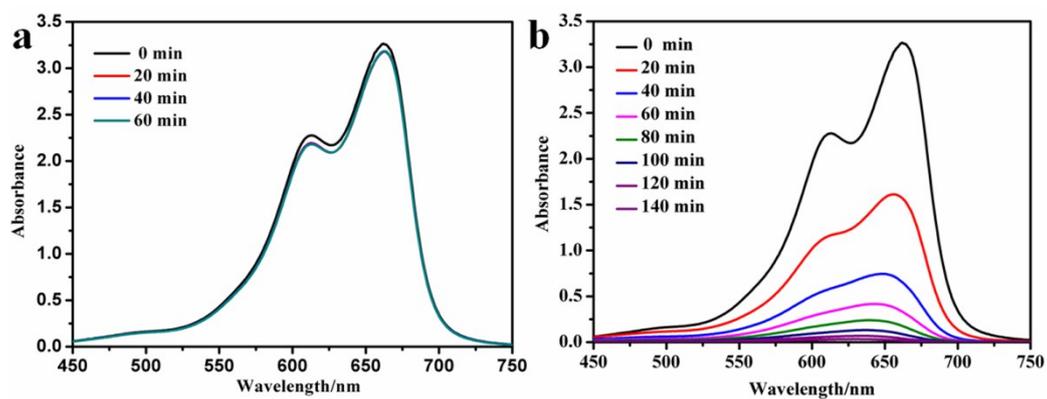


Fig. S6 UV-vis absorbance spectra of MB with ellipsoid-shaped TiO₂ nanoparticles in the dark and under simulated sunlight irradiation at different light irradiation times.

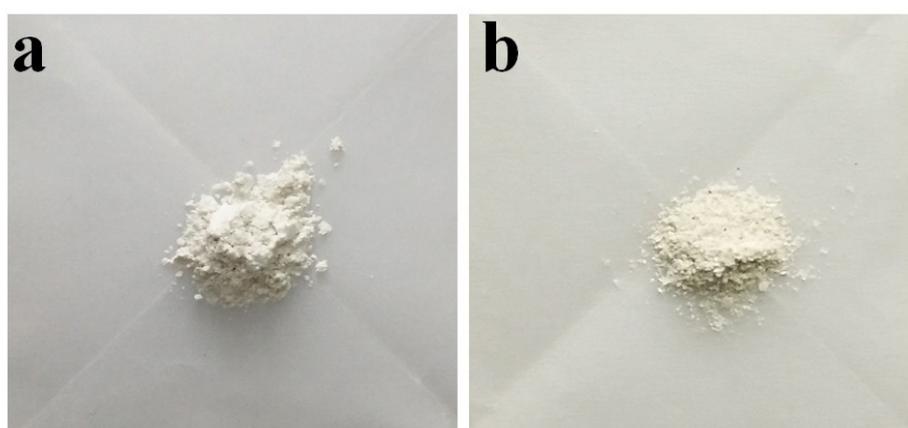


Fig. S7 The pure sample (a) and the sample treated with HCl after absorbed MB (b).