In-Situ Preparation of Oxygen-Deficient TiO₂ Microsphere with Modified {001} Facet for Enhanced Photocatalytic

Activity

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Supplementary Materials

Material preparation.

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. in analytical grade purity and used in the experiments without further purification.

Preparation of microsphere consists of TiO₂ with etched {001} facet. Hydrochloric acid (1.5 M) was used to adjust the pH of deionized water to around 2.1. Titanium tetrafluoride (TiF₄, Aldrich Chemical) was then dissolved in this solution to a concentration of 0.04 M, which changed the pH to 1.8. In a typical experimental procedure, 14.5 mL of 0.04M TiF4 aqueous solution and 13.38 mL of isopropyl alcohol (IPA) were mixed in a 50 ml of beaker by magnetic stirring for 30 min, and then 0.5 ml hydrofluoric acid solution (5 wt%) were mixed in the above mixed solution and stirring for another 30 min, and the mixture solution then transferred into a dried Teflon-liner stainless steel autoclave with a volume of 100 mL. The autoclave was kept at 180 °C for 6 h in an electric oven. After reaction and being cooled to room temperature, the white powder was harvested by high speed centrifugation and washed with ethanol and distilled water for several times. For comparison, the hydrothermal reaction time was varying from 1 h to 12 h to obtain TiO₂ microsphere with different morphology. The prepared TiO₂ micro-sphere denoted as TS-X h, which X presents the hydrothermal reaction time.

Preparation of intact- and etched-TiO₂.

The detail preparation method is reported elsewhere.¹

Fluorine removal from the surface of anatase TiO_2 single crystals. Typically, the powder samples of as-prepared anatase TiO_2 single crystals were heat treated in static air in a Muffle

furnace at 600 °C for 120 min with a ramping rate of 5 °C min⁻¹. The samples were then cooled to room temperature in the Muffle furnace for further characterization.

Materials characterization. Crystallographic information of prepared samples was identified by X-ray diffraction analysis (XRD, Rigaku RINT-2000 using Cu K α radiation at 40 keV and 40 mA. Scanning electron microscope (SEM) images were taken using a field-emission scanning electron microscope (JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (JEM1200EX, JEOL) at an acceleration voltage of 100 kV. The Brunauer–Emmett–Teller (BET) specific surface area (SBET) was determined by a multipoint BET method by using the adsorption data within the relative pressure (P/P₀) range 0.05–0.3.

Photocatalytic properties of hydrogen production. The photocatalytic hydrogen production were examined in a Pyrex top-irradiation type reaction vessel connected to a closed gas circulation system. Before irradiation, the reaction system was evacuated to ensure complete air removal, and then irradiated from the top side using a 300 W xenon lamp. A flow of cooling water was used to keep the reaction suspension at room temperature. Photocatalyst, 0.1 g, was dispersed in 100 mL of aqueous solution containing 90 mL of deionized water, 10 mL of absolute methanol (as the sacrificial reagents) and 0.5 ml 1 wt% chloroplatinic acid aqueous solution. Before irradiation, the photocatalysts were completely dispersed by sonication treatment for 30 s. Gas chromatography (Agilent; GC-7890A, MS-5A column, TCD, Ar carrier) was used to analyse the evolved gases.

Measurement of hydroxyl radical (OH)

The photocatalytic activities of the photocatalysts were further studied by detecting hydroxyl radicals (OH) using terephthalic acid as a probe molecule under light illumination.^{2,3} Typically, 10 mg of photocatalyst was added into 50 ml of 1×10^3 M terephthalic acid aqueous solution with a concentration of 0.5×10^2 M NaOH. The mixed solution was stirred incessantly, and after every 15 min, 3 ml solutions were extracted to test the generation of OH, which was evaluated by measuring the change of FL intensity emitted from 2- hydroxyterephthalic acid at 425 nm excited by 315 nm light on afluorescence spectrophotometer (F-7000, HITACHI, Japan).

Calculating the exposed percentage of {001} facets: According to the literature reported elsewhere^{4,5}, the percentage of {001} facets can be calculated using follows equation:

$$=\frac{\cos\theta}{\cos\theta + \left(\frac{a}{b}\right)^{-2} - 1}$$
(1)

Here θ is the theoretical value (68.3°) for the angle between the [001] and [101] facets of anatase TiO₂, b and a denote lengths of the side of the bipyramid and the side of the square {001} 'truncation' facets, respectively. According to our careful measurement, the measured average b and a value of the truncated bipyramid building blocks of microsphere are 1.108 and 0.996 µm respectively. Based on the equation presented above, the percentage of exposured {001} facet is calculated to be 60.69%.



Figurea S1. A) TEM and B) the interior and C) exterior HR-TEM images of TS-2h.



Figurea S2. A) TEM and B) the exterior HR-TEM images of TS-6H.



Figurea S3. A) TEM and B) the interior and C) exterior HR-TEM images of TS-12H.



Figure S4. XRD patterns of the photocatalysts, together with the standard diffraction peaks for anatase TiO₂ and TiOF₂, respectively.



Figure S5. XRD patterns (A) and UV-Vis diffuse reflectance spectra (DRS) (B) of as prepared microspherical TiO₂ single crystal (the inset of B is the plot of $(\alpha hv)^2$ vs hv for as prepared TS samples).



Figurea S6. Defluorination study using as prepared TiO_2 microspheres.(A)XPS spectra of F 1s for the initial anatase single crystals (take the sample of TS-6H for example) and (B) the F1s spectra of TS-1, -2, -4, -6, -9, -12H after heated at 600°C for 120 min.



Figure S7. Nitrogen-adsorption/desorption isotherms (A) and its corresponding poresize-distribution plots of as prepared TiO_2 samples (B).



Figure S8. SEM images of anatase TiO₂ single crystals with (A) intact and (B) etched-TiO₂



Figure S9. (A) Fluorescence spectra of the UV-vis irradiated TS-6H; (B) Comparison of fluorescence spectra of prepared TiO₂ microspheres under UV-vis light irradiation.



Figure S10. High-resolution XPS spectra for A) Ti 2p and B) O 1s of as prepared TS samples under different hydrothermal reaction time.

Table	S1.	The	structural	parameters	and	pore	structure	information	of
differe	ent T	'S sar	nples.						

	BET surface	Pore volume	Average	HERs
Sample	Area [m ² g ⁻¹	$\int cm^{-3}q^{-1}$	pore size [
]		nm]	
TS-1H	13.698	0.081435	28.324	68.65
TS-2H	15.7479	0.095861	27.5159	92.95
TS-4H	19.7635	0.095914	20.0048	112.14
TS-6H	14.5639	0.087269	26.676	255
TS-9H	16.7586	0.095277	23.342	164.75
TS-12H	13.2965	0.083502	25.246	136.66

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