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Full Length Article

Enhancing the photoresponse and photocatalytic properties of TiO_2 by controllably tuning defects across {101} facets

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ABSTRACT

Introducing defects into semiconductors with well-controlled exposed facets offers an effective route for the development of photocatalytic materials with greatly improved properties. Here, we report a facile ethylene glycol reduction procedure to make anatase titanium dioxide (TiO_2) with different concentrations of exposed {001} and {101} facets, leading to different surficial defects. TiO_2 with increased concentrations of {101} facets shows a 5-fold improvement in photocurrent generation as well as improved photocatalytic activity towards water splitting under visible light irradiation. The improved activity is ascribed to the oxygen vacancies as well as the variable surface chemical states, which collectively induce a slower recombination rate of photo-induced electron-hole pairs. This work also highlights a feasible strategy to obtain the defective TiO_2 and explore the synergistic effect of surface defects and different concentrations of exposed {001} and {101} facets for photocurrent and photocatalytic properties under visible light irradiation.

1. Introduction

Nanomaterials based on titanium dioxide (TiO_2) have been widely studied as semiconductor photocatalysts for hydrogen production [1], CO_2 reduction [2], and the removal of environmental pollution [3]. However, the band gaps of anatase and rutile TiO_2 are 3.2 and 3.0 eV, respectively, largely confining the application of TiO_2 to energy-intense ultraviolet (UV) light. Ideal semiconductor-based photocatalytic materials should function under visible light, since visible light accounts for nearly 45% of solar spectrum while UV light accounts for only 5% [4]. Thus, much research effort has focused on engineering the band gap of TiO_2 to extend its absorption range towards visible light, including doping with non-metals (i.e. S, N, C) [5–7], doping with noble metals (i.e. Ag, Au, Pt) [8,9], introducing crystal defects (i.e. Ti^{3+}, oxygen vacancies (V_o)) [10–12], altering the surface chemical environment [13], and simultaneously using doping and semiconductors coupling [14–16]. Despite these successful demonstrations of tuning the band gap of TiO_2, achieving pure TiO_2 without chemical doping and a favorable absorption to visible light has presented great challenges.

Engineering the crystal facets of semiconductor-based photocatalysts has been shown as a novel method for extending the photoresponse towards visible light with enhanced photocatalytic activity. Tuning the percentage of the {001} and {101} facets and optimizing the concentration of surface defects in TiO_2 offer a viable method for tuning the band gap [2,17,18], yet the influence of different percentages of exposed {001} facets to the generation of defective TiO_2 is rarely reported. Several approaches were previously explored to generate surface defects on TiO_2, including low-temperature vacuum treatment [19], thermal annealing under hydrogen [20], chemical reduction [21], and methods based on electrochemical and photo-assisted reduction [22,23].

Herein, we elucidate the influence of {001} facets and defects on the photoresponse and photocatalytic properties of TiO_2 by

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controllably tuning the concentration of percentages of {001} and {101} facets. The difference in binding energy and surface chemical states across {001} and {101} facets results in improved photocurrent generation under visible light and enhanced photocatalytic activity toward water splitting, demonstrating the potential applications of the newly synthesized defective TiO_2.

2. Experimental details

2.1. Preparation of TiO_2 nanoparticles

All chemical reagents used in this work were of analytical grade and were used as received. Anatase TiO_2 nanoparticles were synthesized through a hydrothermal method analogous to those in previous reports [2,24]. In short, four separate reactions were prepared by mixing 25 mL of tetrabutyl titanate with 3.0, 1.5, 0.5 or 0.0 mL of an aqueous HF solution (40 wt%), followed by the addition 0.0, 1.5, 2.5 or 3.0 mL of distilled water, respectively. The four mixtures were stirred for 30 min and transferred to separate 100 mL Teflon-lined stainless autoclaves. The autoclaves were sealed and heated at 180 °C for 24 h. After cooling to room temperature, the resulting white precipitates were collected and washed several times with ethanol and distilled water. The samples were then dried in an oven at 70 °C for 6 h. Then the dried mass were calcined at 400 °C for 3 h in air atmosphere to remove the fluorine ions adsorbed on the surface. The as-prepared samples are referred to as T1, T2, T3, and T4, respectively.

0.5 g of each as-prepared TiO_2 sample (T1, T2, T3, or T4) was added into 20 mL of ethylene glycol and the mixture was sonicated for 10 min. The solution was then heated to 180 °C for 90 min under continuous stirring. After cooling to room temperature, the obtained solid masses were collected by filtration, washed several times with ethanol and distilled water, and dried in an oven at 70 °C for 6 h to obtain powdered samples. After ethylene glycol reduction, the as-prepared samples are referred to as T1-EG, T2-EG, T3-EG, and T4-EG, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a PANalytical Empyrean x-ray diffractometer using Cu Kα irradiation (λ=1.5418 Å). Scanning electron microscopy (SEM) images were collected on a field emission SEM (JEOL JSM-7800F). Ultraviolet visible diffuse reflectance spectrum (UV-vis DRS) was measured from 240 nm to 800 nm using a Shimadzu UV-2100 UV–vis spectrophotometer, where $BaSO_4$ served as a reference material. Chemical compositions and oxidation states were analyzed using X-ray photoelectron spectroscopy (XPS) (Thermo Scientific Escalab 250Xi). All binding energies were referenced to the C 1 s peak (284.8 eV) arising from the adventitious carbon. Raman measurements were carried out using a Raman spectroscopy (HORIBA Jobin Yvon LabRAM HR Evolution, France) with the laser excitation at 532 nm. Electron paramagnetic resonance (EPR) spectra were collected on a JEOL JES-FA200 X-band spectrometer at 100 kHz magnetic field modulation. The photoelectric tests were carried out using CHI 600E electrochemical workstation equipped with a constructed three electrode system. A $0.5 \times 0.5\,cm^2$ platinum plate was used as a counter electrode, saturated calomel electrode as a reference electrode. The working electrode was prepared by depositing a 10 mg sample on ITO conducting glass. In the photoelectric tests, 0.1 moL/L Na_2SO_4 solution was utilized as electrolyte and a 500 W Xe lamp was employed as the simulative solar source. The electrochemical impedance spectroscopy (EIS) measurements were evaluated with potential amplitude of 5 mV in the frequency range from 0.1 Hz to 100 kHz.

Table 1
BET surface areas of T1/-EG and T4/-EG.

Sample	Surface area ($m^2\,g^{-1}$)
TiO_2–H_2O (T4)	98.95
TiO_2–H_2O–EG (T4–EG)	89.49
TiO_2–HF (T1)	33.90
TiO_2–HF-EG (T1–EG)	30.56

2.3. Photocatalytic H_2 generation

The photocatalytic hydrogen evolution reaction (HER) was carried out in a Pyrex reaction vessel connected to a gas circulation system. A 300 W Xenon (Newport Corportion) was used as the light source with a 400 nm cut-off filter to provide visible light irradiation. All experiments were performed at ambient temperature (25 °C) using a water jacket around the photocatalytic cell. In a typical photocatalytic reaction, 50 mg of the photocatalyst was dispersed in an aqueous solution of 40 mL of deionized water and 10 mL of methanol used as the sacrificial reagent. Before illumination, the suspension was degassed with nitrogen gas for 30 min to remove any dissolved oxygen. Then, the solution was exposed to visible light irradiation under magnetic stirring. The amount of hydrogen produced was quantified by gas chromatography (HP 6890 with TCD FID, Argon carrier).

3. Results and discussion

Tuning the synthetic conditions of anatase TiO_2 leads to truncated octahedral bipyramids comprising of eight {101} facets on sides and two {001} facets [2,25]. SEM images (Fig. 1a–d) were collected for TiO_2 nanocrystals, displaying that the morphology and microstructure changes with a decreasing ratio of HF to H_2O added to the reactions. As illustrated in the SEM images (Fig. 1a–d), T1 displays distinct nanosheet-like morphology (T1, Fig. 1a). When the ratio of HF to H_2O was decreased, the overall size of the TiO_2 nanocrystal decreases. When no HF was added to the reaction, the size of as-prepared TiO_2 (T4, Fig. 1d) remarkably decreases. The overall particle size of TiO_2 samples (T1, T2, T3, T4) were about 51.3, 24.5, 20.8, 14.2 nm, respectively. This shape transformation is summarized in the morphology diagram presented in Fig. 1e according to the SEM images. To clearly observe the morphology of the anatase TiO_2 nanocrystals, STEM images of T1 (Fig. 1f) and T4 (Fig. 1g) were collected. STEM images further display the change of shape and size and testify the validity of Fig. 1e. We calculated the percentage of {101} and {001} facets of T1 and T4 to be 45.3% and 87.2%, respectively (see ESI for specific computing details). These results suggest that TiO_2 prepared with different concentrations of HF have a clear trend in the percentage of the exposed {001} and {101} facets, which is similar to that reported by Maitani et al. [26] The product of the reactions were evaluated by X-ray diffraction (XRD), and the patterns show that all samples were pure anatase (JCPDS No. 21-1272, space group: *I41/amd* (141)) with different percentages of {001} and {101} facets (Fig. 1h). There was no obvious phase change of TiO_2 after EG reduction, as shown in the XRD patterns (Fig. S1). It is noteworthy that the full width at half maximum of the XRD peaks become wider, indicating the diminution of TiO_2 particle size with decreasing volume of HF added to the reactions. The BET surface areas for T4 and T4-EG are ~3 times larger than those of T1 and T1-EG because of the small size. It is also worth noting that the difference in surface areas of TiO_2 before and after EG reduction is negligible (Table 1).

Fig. 2a shows the UV–vis diffuse reflectance spectra (DRS) and images of the TiO_2 powder samples. We can see that the samples undergo an obvious color change from white to blue for T1 with ~45.3% (101) facets and white to yellow for T4 with ~87.2% (101)