



Engineering highly active TiO₂ photocatalysts via the surface-phase junction strategy employing a titanate nanotube precursor



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ABSTRACT

TiO₂ photocatalysts were synthesized by the hydrothermal treatment of titanate nanotube precursor at different HNO₃ concentrations. Their structures were characterized, and their photocatalytic activity in H₂ production from water was evaluated. The phase structure of TiO₂ photocatalysts is dependent on the HNO₃ concentration employed during the hydrothermal treatment and varies from pure anatase to pure rutile with increasing HNO₃ concentration, with the heterophase in-between. The heterophase TiO₂ photocatalysts exhibit large specific surface areas and intimately contacting anatase–brookite and anatase–rutile surface junctions. The presence of anatase–brookite and anatase–rutile-phase junctions on heterophase TiO₂ photocatalysts was found to efficiently suppress recombination of photoinduced charge carriers in TiO₂. The heterophase TiO₂ photocatalysts are photocatalytically active in H₂ production from water. TiO₂ photocatalysts consisting of 72.9 wt% anatase, 24.6 wt% brookite, and 2.5 wt% rutile exhibits a photocatalytic H₂ yield of 179 μmol h⁻¹ g⁻¹ under Xe lamp irradiation, about four times that of P25 (45.3 μmol h⁻¹ g⁻¹) under the same reaction conditions. These results demonstrate that the surface-phase junction strategy is very useful for engineering highly active TiO₂ photocatalysts, and there still exists plenty of space to explore.

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1. Introduction

Increasing environmental pollution and the shortage of fossil fuels stimulate the exploitation of clean and renewable energy. Hydrogen is recognized as an ideal candidate for the replacement of fossil fuels, and photocatalytic H₂ production utilizing solar light is one of the most promising strategies. Thus, extensive investigations and great efforts have been made on photocatalytic H₂ production over semiconductor catalysts [1–8], which generally involves three steps: initial photon absorption and creation of electron–hole pairs, separation and migration and also possible recombination of photogenerated charge carriers, and surface reaction for hydrogen and oxygen evolution. Among the semiconductor photocatalysts, TiO₂ appears to be the most suitable material, owing to its superior activity, chemical stability, low cost, and nontoxicity [9].

TiO₂ naturally exists in three crystalline polymorphs, anatase, brookite, and rutile, which are most commonly encountered. Its crystal phase is recognized as the most significant factor that influ-

ences its photocatalytic performance, and the formation of surface-phase junctions has been demonstrated as an effective strategy for greatly promoting the photocatalytic efficiency [10–15]. For instance, commercially available Degussa P25 TiO₂, composed of anatase and rutile, is often used as a benchmark model photocatalyst due to its high activity. Many efforts have been dedicated to the design and fabrication of biphasic TiO₂ based on anatase and rutile [13,14,16], anatase and brookite [17,18], or brookite and rutile [19,20], or even of TiO₂ with three mixed phases [10,21,22], to explore active TiO₂ photocatalysts. However, most previously reported heterophase TiO₂ photocatalysts were transformed from amorphous Ti-containing precursors or prepared by high-temperature calcination and thus suffered from low specific surface area. Meanwhile, the systematic correlation of TiO₂ surface phase and catalytic performance is still not well established, particularly concerning TiO₂ with three mixed phases of anatase, brookite, and rutile, due to the lack of preparation methods to finely control the phase structure of TiO₂.

Recently, hydrogen titanate (H-titanate) nanotubes and nanofibers have attracted much attention due to their special structural features, consisting of the same TiO₆ octahedron unit as TiO₂ [23–27]. The transition from H-titanates to TiO₂ polymorphs under relatively mild hydrothermal conditions by in situ rearrangement of the common structural unit has been employed to fabricate various TiO₂ nanostructures. The chemically reactive H-titanate

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precursors, particularly under acidic conditions [25], can be readily transformed into diverse TiO₂ crystalline forms by dehydrating and rearranging TiO₆ octahedra. The phase composition and morphology of the resulting TiO₂ were found to depend on the H-titanate precursors employed, acidic or alkaline environment, and hydrothermal conditions [28–32]. The soft chemical transformation could convert H-titanate into pure rutile TiO₂ crystalline in a concentrated acid solution (above 2.0 M) and into pure anatase TiO₂ in a diluted acid (below 0.10 M) or even neutral solution [24–26,33]. However, the transition from H-titanate to TiO₂ polymorphs in the intermediate-concentration acid solution between 0.10 and 2.0 M has not been well investigated, and the results remain diverse and unambiguous. For H-titanate nanotubes treated in an acidic solution of 0.10 M, the resulting TiO₂ was reported to exhibit predominant anatase with minor rutile [34], comparable anatase and rutile mixture [35], or even pure rutile [36]. At pH of 0.5, a mixture of rutile and brookite [37] or predominant rutile with minor anatase [34] was reported. Transformation from ammonium-exchanged and potassium titanate to TiO₂ with different shapes and phases has also been reported [30,38].

Since H-titanate and TiO₂ consist of the same TiO₆ octahedron unit, the transition from H-titanate offers a novel method of preparing TiO₂ samples with various types of surface-phase junctions. In this paper, we systematically investigated the phase structure of TiO₂ samples prepared by controlled phase transition from H-titanate nanotube precursors in various acidic environments of hydrothermal treatment and their photocatalytic activity in H₂ production from water. TiO₂ photocatalysts with large specific surface areas and various phase structures were successfully fabricated and active in photocatalytic splitting of water to H₂. The most active TiO₂ photocatalyst, consisting of 72.9 wt% anatase, 24.6 wt% brookite, and 2.5 wt% rutile, exhibits a photocatalytic H₂ yield of 179 μmol h⁻¹ g⁻¹, about four times that of P25 (45.3 μmol h⁻¹ g⁻¹) under the same reaction conditions. The enhanced photocatalytic activity is associated with the formation of smooth surface-phase junctions among different phases within TiO₂.

2. Experimental

2.1. Catalyst preparation

All chemical reagents used in this work were Analytical Reagent grade from Sinopharm, including anatase TiO₂ particles, NaOH pellets, HCl, and HNO₃. The hydrogen titanate was prepared via hydrothermal reaction of anatase TiO₂ in a concentrated NaOH solution and the following neutralization of the resultant sodium titanate in a diluted acid solution as in the previous reports [23,24,33,39]. In a typical synthesis, 6 g of anatase TiO₂ particles was mixed with 80 mL of a 10 M NaOH solution. The mixture of white suspension was sonicated in an ultrasonic bath for 30 min and then placed in a 100-mL Teflon-lined autoclave with an 80% filling factor, where it was subjected to hydrothermal treatment for 48 h at 150 °C. The precipitate after hydrothermal reaction was isolated by filtration and washed repeatedly with deionized water until the pH value was close to 7. The resultant sodium titanate was dried overnight at 80 °C and subsequently neutralized using 0.10 M HCl solution, which was washed repeatedly with deionized water until the neutral pH value and the negative Ag ions test. The obtained H-titanate was dried at 80 °C.

Nanostructured TiO₂ with mixed crystalline phases was fabricated by a controllable phase transition from the H-titanate nanotubes via another one-step hydrothermal treatment in different acidic environments. Typically, 0.8 g of the resulting H-titanate was dispersed in 80 mL of deionized water or HNO₃ solution with concentration from 0.03 to 2.65 M. The mixture of white suspen-

sion was also placed in a 100-mL Teflon-lined autoclave and kept at 120 °C for 48 h. The final white product after hydrothermal treatment was isolated by filtration and washed repeatedly with deionized water until the pH value was close to 7; it was then dried at 80 °C to obtain the resultant titanium dioxides.

2.2. Characterization methods

Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range 20–80° on a Philips X'Pert Pro Super diffractometer with Cu Kα radiation (λ = 0.15406 nm) operating at 40 kV and 50 mA. The phase contents in the mixed-phase TiO₂ can be determined from the integrated intensities of the corresponding peaks. The weight fractions of anatase (W_A), brookite (W_B), and rutile (W_R) were calculated from [40]

$$W_A = \frac{k_A I_A}{k_A I_A + k_B I_B + I_R}$$

$$W_B = \frac{k_B I_B}{k_A I_A + k_B I_B + I_R}$$

$$W_R = \frac{I_R}{k_A I_A + k_B I_B + I_R},$$

where I_A , I_B , and I_R represent the integrated intensities of the anatase (101), brookite (121), and rutile (110) peaks on the basis of two coefficients, k_A and k_B , optimized as 0.866 and 2.721, respectively. The average crystallite sizes of TiO₂ in the anatase, brookite, and rutile phases were calculated according to Scherrer's formula, based on the FWHM data of each phase, with corrections for instrumental broadening.

BET surface areas were measured using a Micromeritics Tristar II 3020M system. Transmission electron microscopy (TEM) and HRTEM were performed with a JEOL JEM-2100F instrument at an acceleration voltage of 120 kV. The UV-vis spectra of the solid powder materials were obtained on a Shimadzu DUV-3700 spectrophotometer equipped with an integrating sphere attachment. The visible and UV Raman spectra were recorded at room temperature with a HORIBA LabRAM HR confocal microscope spectrograph with a spectral resolution of 0.6 cm⁻¹ and excitation lines at 514 and 325 nm, respectively. The photoluminescence (PL) spectra were measured on the HORIBA LabRAM HR spectrograph with a continuous wave 325-nm laser as the exciting source, and the signal was collected by passing through a filter with cutoff wavelength below 380 nm.

2.3. Photocatalytic reaction

Photocatalytic hydrogen production was carried out with a LAB-SOLAR-H₂ system (Beijing Trust Tech Inc., China) mainly consisting of three parts separated by valves, the photocatalytic reaction system, sampling system, and online analysis system. The reaction system contains a top-irradiation-type Pyrex reaction cell under illumination by a 300-W Xe lamp (PLS-SXE300). A shutter window is placed between the Xe lamp and the reaction cell, which is filled with circulating water to filter the infrared radiation and thus prevent any heating of the reaction suspension. The reaction cell was connected to a closed gas circulation and evacuation system. The sampling system, as the central part, is continuous with the reaction system via a six-way valve and with the analysis system via a four-way valve and also is connected to the evacuation system via a three-way valve. The analysis system part involves an online gas chromatograph (Shimadzu GC-14C) equipped with a thermal conductivity detector to determine the amount of hydrogen.

For a typical reaction, 100 mg of photocatalyst was suspended in 80 mL of aqueous solution containing 20 vol.% methanol, which

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