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A new approach to inducing Ti^{3+} in anatase TiO_2 for efficient photocatalytic hydrogen production

Shunhang Wei [a], Shuang Ni [b,*], Xiaoxiang Xu [a,#]

[a] *Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China*
[b] *Science and Technology on Plasma Physics Laboratory, Laser Fusion Research Center, China Academy of Engineering Physics, Mianyang 621900, Sichuan, China*

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ABSTRACT

Ti^{3+} species and oxygen vacancies were successfully introduced into anatase TiO_2 by a simple method. The physicochemical properties of the as-prepared samples were explored by techniques including X-ray diffraction and field emission scanning electron microscopy. The amount of H_2O_2 precursor and hydrothermal reaction time were found to affect the formation of the TiO_2 nanorod-type microstructure. Possible mechanisms for the formation of this microstructure are proposed on the basis of analytical results, including electron paramagnetic resonance, where parameters such as the amount of H_2O_2 and hydrothermal reaction time were adjusted. More importantly, light absorption in the visible light region was strongly affected by the number of oxygen vacancies within the samples. The oxygen vacancy content featured an optimal level for producing the highest photocatalytic hydrogen production activity.

1. Introduction

Hydrogen is considered to be a clean and renewable energy source, which might address global concerns regarding future fossil fuel shortages. Photocatalytic water splitting into hydrogen and oxygen on the surface of a semiconductor is widely accepted to be an ideal means for hydrogen production owing to the inexhaustible nature of solar radiation and the abundance of water on earth [1–6]. Among various photocatalysts, titanium dioxide (TiO_2) has continued to attract considerable attention because of its superior chemical stability, low-toxicity, and cost effectiveness [7,8]. Nevertheless, drawbacks such as its wide band gap (3.2 eV for anatase) and fast electron-hole recombination rate substantially limit the use of TiO_2 practical applications. Considerable efforts have been devoted to modifying TiO_2 to improve its light absorption and photocatalytic activity. The doping of heteroatoms (such as N [9], C [10], Fe [11], S [12]) into TiO_2 has successfully been used to enhance the light absorption of TiO_2; however, challenges remain as these heteroatoms may act as extra electron-hole recombination centers [13].

After the pioneering work of Chen *et al.* [14], self-doping TiO_2 (i.e., Ti^{3+} species) might be a promising alternative strategy to modifying this wide band gap semiconductor. Further studies have shown that Ti^{3+} species and their charge balancing counterpart-oxygen vacancies are responsible for band-gap

* Corresponding author. E-mail: nishuang@163.com
# Corresponding author. Tel/Fax: +86-21-65956919; E-mail: xxxu@tongji.edu.cn
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narrowing and the separation of photogenerated electrons and holes [15–17]. Various preparation methods and synthetic techniques have been used to increase the oxygen vacancy concentration in TiO_2 including hydrogen plasmas [15], aluminum reduction [16], chemical oxidation [17], and electrochemical reduction [18]. The approach involving Ti^{3+} in self-doped TiO_{2-x} is distinct from these methods owing to the simpler and safer procedures (no requirement for the use of hydrogen) and better visible light photocatalytic activity. To date, methods to induce Ti^{3+} have generally been energy intensive and involved unstable Ti raw materials (such as TiO [19] and TiH_2 [17]). In this context, it is highly desirable to develop an alternative method for preparing Ti^{3+} self-doped TiO_2.

Here, we successfully prepared self-doped TiO_2 using metallic Ti and H_2O_2 as raw materials. Our method shows great advantages over previous methods in that the concentration of Ti^{3+} species and oxygen vacancies can be easily tuned by controlling the amounts of added H_2O_2 and the hydrothermal reaction time. The involvement of H_2O_2 during the synthesis not only allows control over the dopant concentration but is also critical for controlling the microstructures. Nanorod-type self-doped TiO_2 can be synthesized by the addition of appropriate amounts of H_2O_2. Possible mechanisms for the formation of such microstructures have been proposed. Photocatalytic hydrogen experiments have confirmed the high photocatalytic activity of self-doped TiO_2. The correlation between the catalytic activity and the concentration of Ti^{3+} species is discussed.

2. Experimental

2.1. Photocatalyst preparation

Ti^{3+} self-doped TiO_2 was prepared by annealing in a N_2 atmosphere after a hydrothermal reaction. In a typical preparation procedure, 0.3 g of Ti power (99.99%, Aladdin) was mixed with 20 mL of water, 8 g of sodium hydroxide and a certain amount of H_2O_2 solution (30%) (0, 20, 50, and 100 μL). The suspension was transferred into an autoclave for the hydrothermal reaction. Various hydrothermal reaction times at 180 °C were used (12, 18, 24, and 30 h). The resultant precipitates were then collected, washed with hydrochloric acid and water until the pH of the washings was neutral. The obtained precipitates were grinded for approximately 30 min with an agate pestle and mortar and then calcined at 500 °C for 3 h. The samples were named according to the calcination atmosphere, the amount of H_2O_2 and hydrothermal reaction time. The samples calcined in N_2 were designated as 500-0-12, 500-20-12, 500-50-12, 500-100-12, 500-100-18, 500-100-24, and 500-100-30. An uncalcined sample was designated similarly as 100-24 (with 100 μL H_2O_2 and a hydrothermal reaction time of 24 h).

2.2. Photocatalytic reactions

The photocatalytic hydrogen evolution was evaluated in a top-irradiation-type reactor connected to a gas closed circulation and evacuation system (Perfect Light, Labsolar-IIIAG). In a typical experiment, 0.1 g of the sample powders were dispersed in 100 mL of aqueous solution containing 10% methanol by volume. Pt was loaded onto the samples at 1 wt% by a photo-deposition method: H_2PtCl_6 aqueous solution was reduced into Pt nanoparticles over 1 h under full spectra irradiation [20]. A 300 W xenon lamp (Perfect Light, PLX-SXE300) was used as a light source. An AM1.5 filter was applied to simulate natural sunlight. The gas component within the reactor was then analyzed using an online gas chromatograph (Techcomp, GC7900) with a TCD detector.

2.3. Characterization

Crystal structure was examined by X-ray powder diffraction (XRD) techniques (DX-2700B X-ray Diffractometer, Haoyuan). Raman spectra were collected on an inVia Raman Microscope (Renishaw). The morphologies of the samples were inspected with a field-emission scanning electron microscope (Hitachi S4800). The optical absorption spectra of samples were obtained at room temperature with a UV-Vis spectrophotometer (JASCO-750) and the JASCO software suite. $BaSO_4$ was used as a reference non-absorbing material. The X-ray photoelectron spectra (XPS) measurements were measured on a Thermo ESCALAB 250XI equipped with monochromatized Al K_α radiation using C 1*s* (284.8 eV) as the reference. Electron paramagnetic resonance (EPR) spectra were collected with the use of a JES FA200 spectrometer at room temperature.

3. Results and discussion

XRD patterns of as-prepared samples are shown in Fig. 1(a). Analysis of these patterns suggested that 100 μL of H_2O_2 and a hydrothermal reaction time longer than 24 h were needed to fully convert all the metallic Ti. The subsequent calcination in a N_2 atmosphere at 500 °C was necessary to crystallize the hydrothermal precursors into an anatase phase (JCPDS Card no. 21-1272). Raman spectra were recorded to further examine the structure of the as-prepared sample. As shown in Fig. 1(b), five characteristic Raman peaks at 143.2 (E_g), 196 (E_g), 396 (B_{1g}), 515 (A_{1g} or B_{1g}) and 637(E_g) cm^{-1} emerged for all samples after calcination, assignable to the Raman modes of the anatase phase [21,22]. Thus, we confirmed the successful preparation of anatase TiO_2 from metallic Ti.

X-ray photoelectron spectroscopy (XPS) was further used to investigate the surface chemistry of the as-prepared samples. As shown in Fig. 2(a), binding energies for the Ti 2*p* state in the 500-100-12 samples were consistent with typical peaks of TiO_2 with Ti $2p_{3/2}$ (458.43 eV) and $2p_{1/2}$ (464.12 eV) peaks [9,16]. The O 1*s* state in Fig. 2(b) featured two overlapping peaks: one locating at 529.69 eV was typical for lattice oxygen in TiO_2; the other one located at 531.29 eV was assigned to surface OH groups [15]. Compared with the 100-12 samples (Fig. 2(c) and (d)), there was a small decrease in the binding energy of Ti and O after calcining the sample in N_2 at 500 °C, indicating the importance of the thermal treatment in weakening the bond strength between Ti and O. Interestingly, signals from elemental Ti were not detected in either of these two samples,