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

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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 nano-rod-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.

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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

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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 $^\circ\text{C}$ 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 $^\circ\text{C}$ 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 1s (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 $^\circ\text{C}$ 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 2p 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 1s 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 $^\circ\text{C}$, 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,

Fig. 1. XRD patterns (a) and Raman spectra (b) of samples.

Fig. 2. Ti 2p XPS spectra of 500-100-12 (a) and 100-12 (c), O 1s XPS spectra of 500-100-12 (b) and 100-12 (d).

likely because of the detection limitations of XPS, which can generally only penetrate to a depth of 1–3 nm from the surface. High-resolution TEM (HRTEM) images of the 500-100-12 samples (Fig. S1) showed that the distance in the crystal lattices of

the outer layer was 0.352 nm, which is consistent with the (101) lattice planes of anatase. The binding energies of Ti in 500-100-24 and 500-100-30 samples were also ascribed to Ti^{4+} (Fig. S2). For all samples, no Ti^{3+} peaks were detected by XPS.

Fig. 3. EPR results (a) of samples, FESEM images of 100-12 (b), 500-100-12 (c), 500-50-12 (d), 500-20-12 (e), and 500-0-12 (f) samples.

Electron paramagnetic resonance (EPR) is a useful technique to detect paramagnetic species owing to its high sensitivity toward unpaired electrons. Notably, the calcined samples exhibited strong responses at g -values of ~ 2.001 and ~ 1.997 in their EPR spectra (Fig. 3(a)), which could be attributed to surface oxygen vacancies [23,24]. The amount oxygen vacancies appeared to increase as the amount of added H_2O_2 was increased and also correlated with the hydrothermal reaction time. However, the uncalcined sample (100-12) did not show oxygen vacancy signals. Notably, few nanorods were formed by the hot alkali method in the 100-12 samples and the nanorods length was short. Conversely, a number of long nanorods were formed in the 500-100-12 samples after calcination, as shown in Fig. 3(b) and (c) (larger version in Fig. S3). In addition, the nanorod structure was hardly found in the 500-20-12 (Fig. 3(e)), 500-0-12 (Fig. 3(f)), 500-100-24 (Fig. S4a), and 500-100-30 (Fig. S4b) samples except for the 500-50-12 (Fig. 3(d)) samples.

The presence of oxygen vacancies may be ascribed to either the reduction of TiO_2 by the remaining metallic Ti or the loss of oxygen by the removal of surface OH groups. According to XRD results of the uncalcined sample (Fig. S5), the amount of Ti decreased as the hydrothermal reaction progressed and Ti was fully converted with a hydrothermal reaction period of 24 h, implying that the contribution from metallic Ti to the formation of oxygen vacancies should decreased over a long hydrothermal time. However, the opposite trend was found. More oxygen vacancies were found for the sampled subjected to long hydrothermal time. In this regard, the oxygen vacancies might be attributed to the removal of surface OH groups. This loss of

oxygen from Ti–O might be associated with a change of the morphology. We propose the following mechanism. On the basis of the morphology of 500-0-12, 500-20-12, 500-50-12, and 500-100-12 samples, it is likely that H_2O_2 promoted the formation of hydroxyl groups bonded with Ti, such that Ti–O–Ti bonds were generated along one direction through selective dehydration of Ti–OH groups in a certain region under the calcination conditions. In other regions, the hydroxyl groups that were not dehydrated could be removed to form oxygen vacancies. On the basis of our EPR results for the 500-100-12, 500-100-24, and 500-100-30 samples, we deduced that an appropriate vacancy defect content enabled dehydration of Ti–OH along one direction owing to a change of

Fig. 4. UV-Vis absorbance spectra of the samples.

Fig. 5. (a) H₂ generation of samples under AM1.5 irradiation, (b) XPS valence band spectra of 500-100-30 and 500-100-24 samples.

surface tension and Coulomb forces acting on the surface, which induced the formation of nanorods from disordered structures [25]. In the calcination process, the oxygen vacancy formation process through the removal of hydroxyl groups occurs prior to the generation of Ti–O–Ti bonds via a dehydration process of Ti–OH groups. The reason is probably due to the presence of oxygen vacancies which may direct the formation of Ti–O–Ti bonds.

Fig. 4 shows the ultraviolet-visible (UV-Vis) absorbance spectra of freshly prepared samples. According to the results of 500-100-24 and 500-100-30 samples, the absorbance increased with higher Ti³⁺ content, which might also correlate with better photocatalytic activity. Hydrogen production from water splitting was performed to investigate the photocatalytic activity of the as-prepared samples, as shown in Fig. 5(a). Compared with the 500-100-12 samples, the 100-12 sample did not show any discernable photocatalytic activity, likely because of its poor crystallinity. On the basis of the results for 500-0-12, 500-20-12, 500-50-12, and 500-100-12 samples, the amount of H₂O₂ added during their synthesis was an important factor determining the photocatalytic activity through its control over the amounts of oxygen vacancies in the samples. However, there seemed to be certain oxygen vacancy content for optimal photocatalytic activity because further increases of oxygen vacancies at longer hydrothermal times (sample 500-100-30) decreased the activity. According to theoretical calculations [16,26–30], oxygen vacancies tend to elevate the valence band maximum (VBM) 0.4 V higher than that of normal titania by forming a tail in the density of states, which is generally favorable for catalytic activity. Fig. 5(b) shows valence band (VB) XPS of 500-100-24 and 500-100-30 samples. The VB XPS of 500-100-24 shows that the main absorption onset was located at 2.16 eV below the Fermi energy, whereas the maximum energy associated with the band tail blue-shifted further toward the vacuum level at approximately 1.7 eV. The values of 500-100-30 were 2.62 and 2.02 eV, respectively. For the 500-100-24 sample, the tail was approximately 0.46 eV above the VBM which was consistent with the theoretical value that should result in better photocatalysis. Furthermore, oxygen

vacancies also introduce localized states below the conduction band (CB) minimum [30,31], and the width of the vacancy band increased together with the concentration of vacancies. Large amounts of oxygen vacancies in the 500-100-30 samples likely shifted the vacancy band to special location below the CB, resulting in low mobility of the electrons at these levels and their becoming electron/hole recombination centers. These findings resemble results for reduced rutile titania [27,29]. Therefore, an optimal oxygen vacancy level exists for these samples.

4. Conclusions

In summary, Ti³⁺ self-doped anatase titania was prepared by removing hydroxyl groups through high temperature calcination. When the amount of H₂O₂ was 100 μL and the hydrothermal reaction time reached 12 h, appropriate oxygen vacancy defects formed after calcining in a N₂ atmosphere. These defects enabled dehydration of Ti–OH along one direction through a change of the surface tension and Coulomb forces to form nanorod structures from the disordered structure. Based on our EPR and morphology studies, we deduced that hydroxyl groups were removed prior to the dehydration process. Comparing the 500-100-24 with 500-100-30 samples, we found that more oxygen vacancies can improve visible-light absorption but do not necessarily contribute to photocatalytic activity. The VB of the samples determined by XPS and previous calculations suggested that these findings can be ascribed to the following: (1) The tail of the VBM was approximately 0.46 eV above the VBM of 500-100-24, which was consistent with the theoretical value believed to contribute to enhanced photocatalysis; (2) more oxygen vacancies in the 500-100-30 samples likely caused the vacancy band width reaching to special location below CB, where it acted as an electron/hole recombination center.

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Graphical Abstract

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In the synthesis of TiO_2 , the amount of a H_2O_2 precursor and hydrothermal reaction time were adjusted to show that the highest photocatalytic hydrogen production activity featured an optimal oxygen vacancy content.

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一种将三价钛引入锐钛型二氧化钛的新方法：用于有效的光催化产氢

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摘要: 伴随着科技的日益进步, 人们的生活水平有了极大的提升, 但是随之而来的环境污染问题也成为当前世界亟待解决的重大问题之一。太阳能是地球上最大的清洁能源来源, 有效地利用太阳能将为解决环境污染问题提供巨大的帮助。而光催化技术的一个关键材料就是催化剂, 催化剂对太阳能利用的好坏也就决定了光催化技术的应用前景。因此, 人们对催化剂的研究也在逐步深入。1972年, Fujishima和Honda在*Nature*杂志上首次报道了二氧化钛电极在紫外光照射下分解水产生氢气的现象, 自此掀起了半导体光催化的研究热潮。

二氧化钛因具有无毒、廉价和耐腐蚀等优点而在光催化领域广受关注。传统白色二氧化钛具有两大劣势(宽的禁带宽度与高的电子/空穴复合率)大大限制了它的应用。人们对于改变二氧化钛性质进行了大量的尝试, 例如金属/非金属掺杂、形貌的改变等。黑色二氧化钛(存在大量的氧空位和三价钛)的出现极大地克服了传统白色二氧化钛的缺点, 其具有窄的禁带宽度和低的电子/空穴复合速度。目前, 黑色二氧化钛的制备方法大致分为以下几种: (1)高压下氢化; (2)高温常压下氢化; (3)铝热还原法; (4)溶液蒸发法; (5)化学氧化法; (6)电化学还原等。由于更简单安全(不涉及氢气使用)和更好的可见光光催化活性, 三价钛自掺杂的二氧化钛从这些方法中脱颖而出。迄今为止, 诱导三价钛的方法通常是能量密集型的, 涉及不稳定的Ti原料(如TiO和TiH₂)。研究用于制备三价钛自掺杂二氧化钛的新方法是十分必要的。

我们以稳定的钛粉为原料, 通过简单的方法将三价钛和氧空位成功地引入锐钛型二氧化钛。通过X射线衍射、场致发射扫描电子显微镜等技术研究了制备样品的物理化学性质, 发现H₂O₂和水热反应时间对纳米棒型微观形貌的形成至关重要。通过调整诸如H₂O₂量和水热反应时间的参数, 根据实验结果提出了形成这种微观结构的可能机制。更重要的是, 可见光区域的光吸收受到样品中氧空位量的控制, 存在氧空位的最佳值使光催化产氢活性最高。

关键词: 三价钛; 氧空位; 二氧化钛; 光催化剂; 产氢

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