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Homogeneous boron doping in a TiO_2 shell supported on a TiB_2 core for enhanced photocatalytic water oxidation

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ABSTRACT

Photocatalytic water oxidation for O_2 evolution is known as a bottle neck in water splitting. Various strategies have been conducted to keep the energetics of photogenerated holes or to create more holes in the bulk to reach the surface for efficient photocatalytic water oxidation. Our previous study demonstrated the effectiveness of interstitial boron doping in improving photocatalytic water oxidation by lowering the valence band maximum of TiO_2 with a concentration gradient of boron. In this study, homogeneous doping of interstitial boron was realized in a TiO_2 shell with mixed anatase/rutile phases that was produced by the gaseous hydrolysis of the surface layer of TiB_2 crystals in a moist argon atmosphere. Consequently, the homogeneous doping and lowered valence band maximum improved the energetics of holes for efficient photocatalytic water oxidation.

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1. Introduction

Photocatalysis can induce different redox reactions, including pollutant degradation, water splitting [1], and CO_2 reduction [2,3], and has attracted increasing attention for its promising energy and environmental applications. All these reactions are driven by the photogenerated electrons and holes surviving the recombination process after the photo-excitation of electrons from valence bands to conduction bands in a semiconductor photocatalyst [4,5]. It is well established that both the number and energetics of the photogenerated electrons and holes intrinsically affect photocatalysis efficiency. In many important reactions involving water oxidation, the holes induce oxidative half-reactions, which is considered a

rate-determining step. Taking photocatalytic water splitting as an example, the reduction of protons to hydrogen molecules is a one-electron process, while the oxidation of water to produce oxygen is a four-electron process [6–9]. Increasing the number and/or energetics of photogenerated holes is always favorable for oxygen evolution and overall water splitting [10].

Currently, most studies focus on improving the participation of photogenerated holes in water oxidation by introducing defects [11], doping [12], surface fluorination [13] and constructing various junctions [10]. These methods fall within the scope of narrowing the bandgap, which elevates the valence band maximum (VBM), and promoting surface transfer. Among these options, doping with the appropriate heteroatoms represents a powerful way of modifying the band structures of photocata-

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lysts to change the energetics of the charge carriers. One typical example on this aspect is that introducing interstitial boron with a concentration gradient in anatase or rutile TiO_2 microspheres can induce the downward band bending, and thus increase the energetics of photogenerated holes [14,15]. Consequently, TiO_2 with a concentration gradient of boron with its maximum at the surface shows much higher photocatalytic water oxidation ability than surface boron-free TiO_2 . However, the lower VBM of surface-layer containing boron compared to that of the boron-free internal region of TiO_2 restricts the transport of holes from the bulk to the surface. To solve this problem, it is necessary to realize homogeneous doping of interstitial boron in TiO_2 because this can modify the band structure of the whole material, as demonstrated in layered materials such as cesium titanates [16,17] and carbon nitride polymers [18,19]. Unlike layered materials with interlayer galleries that facilitate the diffusion of dopant species from the surface to the bulk for homogeneous doping, TiO_2 without natural diffusion pathways for dopants is always difficult to be doped homogeneously.

Using unique compounds containing dopants as precursors of metal oxides represents an effective method for preparing doped metal oxides, as demonstrated by the hydrolysis of metal borides to prepare boron-doped metal oxides under hydrothermal conditions [14,15]. A vapor-phase hydrothermal route for treating TaB_2 was also developed to construct $\text{TaB}_2/\text{Ta}_2\text{O}_5$ core/shell particles because of the local space-confined hydrolysis of TaB_2 and subsequent heterogeneous nucleation and growth of Ta_2O_5 on TaB_2 [20]. Moreover, the good interface contact between TaB_2 and Ta_2O_5 led to boron doping of Ta_2O_5 at the interface, which inspired us to conduct homogeneous boron doping in metal oxides supported by metal borides. In this study, a modified vapor-phase hydrothermal method in a moist argon atmosphere was developed to prepare a boron homogeneously doped TiO_2 shell supported by a TiB_2 core. The spatial distribution of the boron dopant together with the chemical state of TiO_2 was investigated. A correlation between the greatly improved photocatalytic water oxidation of boron doped $\text{TiB}_2/\text{TiO}_2$ and the modified band structures was established. The results in this study demonstrate the significance of controlling the homogeneous distribution of heteroatoms in modifying band structures of photocatalysts to increase their activity.

2. Experimental

2.1. Sample preparation

500 mg of TiB_2 (Sigma Aldrich, 98% metal basis) was used as the precursor in a ceramic container and was heated in an argon atmosphere with a flow rate of 50 mL/min bubbling through room temperature deionized water at 500 °C for 12 h. The ramping rate was 2 °C/min, and the sample was naturally cooled down to room temperature after the heating duration. The resultant sample was washed with deionized water at least five times to remove dissolvable byproducts and then dried in air at 90 °C overnight.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were obtained on a Rigaku diffractometer using $\text{Cu K}\alpha$ irradiation ($\lambda = 1.54056 \text{ \AA}$). The morphology and microstructures of the samples were studied by scanning (SEM, Nova NanoSEM 430) and transmission electron microscopy (TEM, FEI Tecnai-F20). Raman spectra (632.8 nm) were collected with LabRam HR 800. The chemical states of the samples were determined by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, using a monochromatic $\text{Al K}\alpha$ X-ray source). All binding energies were referred to the C 1s peak (284.8 eV) that arises from adventitious carbon. Thermogravimetry-differential scanning calorimetry (TG-DSC) analysis was conducted on a Netzsch 449C Jupiter with a flow rate of 50 mL/min of air at a ramping rate of 10 °C/min. The optical absorption spectra were recorded on a UV-visible-infrared diffuse reflectance spectrophotometer (Jasco V-770).

2.3. Photocatalytic activity measurement

Photocatalytic oxygen generation measurements were conducted in a commercial on-line automatic testing system for photocatalytic reactions (Perfectlight Sci&Tech Corp Ltd., Lab-solar-6A). The reaction container of the system had a volume of 250 mL. 100 mg of the photocatalyst was suspended in a solution of 0.85 g AgNO_3 in 100 mL water as the electron acceptor. The light source used was a 300 W Xe lamp (Perfectlight Sci&Tech Corp Ltd., PLS-SXE-300UV). The gas produced in the reaction was analyzed by gas chromatography (Shimadzu, GC2014).

3. Results and discussion

3.1. Thermal oxidation behaviors of TiB_2 and $\text{TiB}_2/\text{TiO}_2$

To determine an appropriate temperature for the hydrolysis of TiB_2 crystals in a moist argon flow, the thermal oxidation process of TiB_2 crystals in an oxygen atmosphere as a function of temperature was monitored by thermal analysis to simulate water molecule induced hydrolysis. Based on the fact that the O_2 induced oxidation of TiB_2 produced TiO_2 and B_2O_3 , the mass of materials increased with a temperature increase. The TG-DSC curves in Fig. 1(a) indicate that the oxidation process starting at temperatures above 480 °C can be divided into three distinct stages. Stage-I at the low temperature region between 480 and 520 °C is reasonably assigned to the oxidation of the surface layer of TiB_2 crystals. The formation of products, including titania and boron oxide from Stage-I, probably hinders the access of O_2 to the internal regions of the TiB_2 crystals. This results in Stage-II having a lowered oxidation rate between 520 and 620 °C. A further increase in the temperature leads to the appearance of dominant Stage-III beyond 620 °C because of the greatly enhanced oxygen diffusion ability through the external product layer. According to the characteristics of the three oxidation stages, it is reasonable to induce the oxidation of TiB_2 crystals at Stage-I to obtain the desired $\text{TiB}_2/\text{TiO}_2$ core/shell

Fig. 1. TGA (1) and DSC (2) curves of TiB₂ (a) and TiB₂/TiO₂ (b) particles performed in an oxygen atmosphere.

particles. The oxidation of TiB₂ in a moist argon atmosphere in this study was therefore conducted at 500 °C.

Fig. 1(b) shows TGA-DSC curves of the resultant TiB₂/TiO₂ core/shell particles in an oxygen atmosphere. Unlike the three distinct oxidation stages of pristine TiB₂, the oxidation of TiB₂/TiO₂ core/shell particles only experiences one stage that is similar to Stage-III of the pristine TiB₂. This result is consistent with the structural characteristics of the TiB₂/TiO₂ core/shell particles. In addition, based on the mass increase of TiB₂ and TiB₂/TiO₂ in an oxygen atmosphere, the percentage of TiO₂ in the TiB₂/TiO₂ core/shell particles is estimated to be around 30%.

3.2. Crystal structures of TiB₂/TiO₂ core/shell particles

XRD patterns (Fig. 2(a)) and Raman spectra (Fig. 2(b)) of the TiB₂/TiO₂ core/shell particles together with those of the pristine TiB₂ crystals were recorded to analyze crystal structure evolution. XRD peaks of TiB₂ after the thermal oxidation in a moist argon atmosphere retained similar features. An obvious

new peak at around 25.3° is attributed to the diffraction of (101) plane of anatase TiO₂. Two weak peaks at 36° and 41° confirm the existence of rutile TiO₂. The coexistence of the anatase and TiO₂ phases was also confirmed by Raman spectra. Due to the partial overlap of the major 27.4° peak of rutile TiO₂ with the 27.6° peak of TiB₂, it was difficult to directly determine the ratio of anatase to rutile based on the Reference Intensity Ratio (RIR) method. To solve this problem, the overlapped peak at around 27° is fitted with two peaks at 27.45° and 27.62° that are assigned to rutile (110) and TiB₂ (001) planes, respectively, as shown in Fig. 2(c). Based on the fitting results, the percentages of anatase and rutile in TiO₂ were determined to be around 65% and 35% respectively, by the RIR method.

3.3. Morphology and microstructure

Morphology and microstructure of pristine TiB₂ and TiB₂/TiO₂ core/shell particles were investigated by SEM and TEM. Fig. 3(a) shows the typical morphology of pristine TiB₂ crystals with the particle size of several microns and a smooth

Fig. 2. XRD patterns (a) and Raman spectra (b) of pristine TiB₂ crystals and TiB₂/TiO₂ core/shell particles. (c) Fitting curves of the XRD peak of TiB₂/TiO₂ at around 27°.

Fig. 3. SEM images of pristine TiB_2 (a) and $\text{TiB}_2/\text{TiO}_2$ core/shell (b) particles; (c) TEM image of a $\text{TiB}_2/\text{TiO}_2$ core/shell particle; (d) HRTEM image of a local region of the shell from (c). Red dash lines in (c) mark the width of the shell. A and R in (d) refer to anatase TiO_2 and rutile TiO_2 respectively.

surface. After thermal oxidation in a moist argon atmosphere, the resultant $\text{TiB}_2/\text{TiO}_2$ core/shell particles (Fig. 3(b)) have increased particle size distribution and surface roughness, with the formation of a shell consisting of TiO_2 particles. According

to the TEM image in Fig. 3(c), the thickness of the TiO_2 shell completely surrounding TiB_2 core is estimated to be around 400 nm. The dense polycrystalline TiO_2 shell consists of the mixture of anatase and rutile nanoparticles as indicated by Fig. 3(d). This is consistent with XRD results.

3.4. Composition and chemical state

The compositions of the TiO_2 shell and its chemical states were investigated by XPS, as shown in Fig. 4. The shell consists of Ti, O and B compositions. The XPS spectrum of O 1s has three distinct peaks at 530.5, 532.7 and 534.1 eV, which originates from lattice oxygen, hydroxyl groups and oxygen bonded to the interstitial boron, respectively [14,15,21,22]. Besides the major signal of Ti^{4+} in XPS spectrum of Ti 2p, a minor signal centered at 457.3 eV that is typically attributed to Ti^{3+} was formed due to the presence of interstitial boron. Fig. 4(c) shows the sputtering time dependent XPS signal of B 1s. The atomic ratio of boron to titanium determined from the pristine surface is 3:10. The value of 192.0 eV is a typical binding energy for the core electrons of interstitial boron in TiO_2 . The less changed intensity of the XPS B 1s peak with the increase of sputtering time suggests a homogeneous distribution of the interstitial boron in the TiO_2 shell. It is known that the interstitial boron tends to diffuse from the bulk towards the surface and finally concentrates in the surface layer upon thermal treatment [11]. The homogeneous distribution of interstitial boron in the TiO_2 shell sup-

Fig. 4. XPS spectra of O 1s (a) and Ti 2p (b) recorded from pristine surface of the $\text{TiB}_2/\text{TiO}_2$ core/shell particles. (c) XPS spectra of B 1s recorded (after every 100 s of sputtering) from the $\text{TiB}_2/\text{TiO}_2$ core/shell particles as a function of the Ar^+ sputtering time.

ported on the TiB_2 core is largely contributed by the sufficient supply of boron from the core.

3.5. Band alignments

As demonstrated in previous studies [11], introducing interstitial boron can cause the downward shift of the VBM of TiO_2 to enhance photocatalytic oxygen evolution because of the increased oxidative power of photogenerated holes. A comparison of the XPS valence band spectra of boron homogeneously doped TiO_2 shell on the $\text{TiB}_2/\text{TiO}_2$ core/shell particles, commercial rutile TiO_2 and anatase TiO_2 in Fig. 5(a) reveals that the VBM of the $\text{TiB}_2/\text{TiO}_2$ core/shell particles is lowered by around 0.3 eV than that of anatase or rutile TiO_2 . This downward shift caused by the homogeneous boron doping is comparable to the shift caused by a gradient doping of interstitial boron in TiO_2 [14,15].

The UV-visible absorption spectrum of the $\text{TiB}_2/\text{TiO}_2$ sample in Fig. 5(b) shows a typical intrinsic absorption band before 400 nm and additional absorption bands beyond 400 nm. Similar absorption features were also observed in other metallic/semiconducting core/shell particles [20,23]. Based on the results of the XPS valence band spectra and UV-visible absorption spectrum, the band alignments of the $\text{TiB}_2/\text{TiO}_2$ sample refers to un-doped TiO_2 and is proposed in Fig. 5(c). The homogeneous doping of interstitial boron in the shell of $\text{TiB}_2/\text{TiO}_2$ core/shell particles leads to the downward shift of both valence band and conduction band edges, with no bandgap changes. This is due to interstitial boron doping, which brings some localized states close to the conduction band minimum [24]. Compared to the band bending caused by the gradient doping of boron, the advantages of this band alignment for photocatalytic water oxidation include not only the lowering of the VBM for the generation of the holes with higher energetics, but also the facilitate transport of the holes from the bulk to the surface.

3.6. Photocatalytic water oxidation

Fig. 6(a) compares the photocatalytic water oxidation activ-

ity of the $\text{TiB}_2/\text{TiO}_2$ sample with three reference samples (commercial anatase TiO_2 , rutile TiO_2 with a particle size of several hundreds of nanometers, and P25 TiO_2 with a particle size of around 20 nm, with a mixed phase of anatase to rutile in a ratio of 4:1) in the presence of AgNO_3 as sacrificial agent. The $\text{TiB}_2/\text{TiO}_2$ sample shows a much superior activity in producing oxygen from photocatalytic water oxidation when compared to the three reference samples, though the former has a much larger particle size and smaller specific surface area. The oxygen evolution rate of the $\text{TiB}_2/\text{TiO}_2$ sample is 154 $\mu\text{mol/h}$, which is around 5 times higher than that of the benchmark P25 TiO_2 photocatalyst. Considering the mixed phases of anatase and rutile that are favorable for the charge separation in these two samples, the superiority of the $\text{TiB}_2/\text{TiO}_2$ sample is largely attributed to the lowered VBM of the homogeneous boron doped TiO_2 shell. The stability test in Fig. 6(b) shows the good stability of the $\text{TiB}_2/\text{TiO}_2$ sample as a photocatalyst. In addition, it should be pointed out that the $\text{TiB}_2/\text{TiO}_2$ sample has no activity under visible light irradiation. This observation can be understood as the localized states below the conduction band usually not being unable to produce charge carriers with sufficiently high energetics as observed in oxygen-deficient TiO_2 [25].

4. Conclusions

At high temperatures, hydrolysis of TiB_2 in a wetting argon atmosphere was used to grow TiB_2 /homogeneous boron doped TiO_2 core/shell particles. The resultant TiO_2 shell has the mixed phases of anatase and rutile. Because of the homogeneous boron doping in the shell, the downward shift of the valence band edge of TiO_2 is realized to increase the oxidative power of photogenerated holes. Compared to three relevant reference samples (anatase, rutile, anatase/rutile TiO_2), the resultant core/shell particles show greatly improved photocatalytic water oxidation activity to produce oxygen under UV-visible light irradiation. The results obtained in this study demonstrate the significance of modulating the redox power of photogenerated carriers in improving photocatalytic activity.

Fig. 5. (a) XPS valence band spectra of $\text{TiB}_2/\text{TiO}_2$, commercial rutile and anatase TiO_2 ; (b) UV-visible absorption spectrum of $\text{TiB}_2/\text{TiO}_2$ sample; (c) Band alignments of boron homogeneously doped TiO_2 shell that was supported on the TiB_2 core together with un-doped TiO_2 .

Fig. 6. (a) Comparison of photocatalytic oxygen evolution from 100 mL of aqueous solution containing 0.85g AgNO_3 as an electron scavenger with 100 mg of photocatalyst. (b) Photocatalytic oxygen evolution with $\text{TiB}_2/\text{TiO}_2$ as a photocatalyst as a function of irradiation time.

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Graphical Abstract

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Homogeneous doping of interstitial boron in the TiO_2 shell supported on a TiB_2 core leads to a greatly enhanced photocatalytic water oxidation by shifting valence band maximum downwards.

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TiB₂/均相硼掺杂TiO₂核/壳结构提升光催化氧化水产氧活性

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摘要: 光催化可实现污染物降解、分解水制氢和CO₂还原等多种氧化还原反应, 因而受到了广泛关注. 光催化材料中光生电荷的数目与氧化还原能力直接影响光催化反应效率, 在许多光催化反应中, 光生空穴氧化反应被认为速控步骤. 以光催化分解水为例, 质子的还原是单电子过程, 水氧化产生氧气则涉及四个电子. 空穴的高能量不仅可赋予其高的氧化能力, 还能提高其迁出表面的能力, 因此具有重要研究价值.

我们组的前期工作表明, 以TiB₂作为前驱体, 采用水热合成和焙烧两步法可制备出间隙硼掺杂的金红石相或锐钛矿相TiO₂, 间隙硼掺杂可显著降低价带顶, 提升光催化氧化水产氧性能. 然而, 在已有的结果中, 间隙硼掺杂浓度在TiO₂中均呈现从内向外逐渐增加的梯度分布, 这意味着硼掺杂浓度有限, 且表层更低的价带顶不利于体相光生空穴向表面迁移, 因此亟需实现TiO₂中均相的间隙硼掺杂.

本文以湿化的氩气为水解环境, 将水解过程限域在TiB₂的表面以减少硼原子流失; 同时提高水解温度, 使残留的硼原子形成间隙掺杂, 避免其在二次焙烧时扩散, 从而在TiB₂核的表面所形成的TiO₂壳层中实现均相间隙硼掺杂, 显著提高了光催化氧化水产氧活性. 多种表征结果表明, 直径约为6–10 μm的TiB₂核表面形成了厚约400 nm的TiO₂壳层, 在TiO₂/TiB₂中TiO₂壳层重量比约为30%, TiO₂壳层中锐钛矿相TiO₂占比为65 wt%, 金红石相TiO₂占比为35 wt%. TiO₂壳层中间隙硼为均相分布, 硼掺杂显著降低了价带顶位置, 提高了光生空穴的氧化能力, 从而使得TiB₂/TiO₂展现出比未掺杂的金红石、锐钛矿相及两者混合相的TiO₂均具有更高的光催化氧化水产氧的能力.

关键词: 光催化; 产氧; 二氧化钛; 均相掺杂

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