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Article

Black TiO₂(B)/anatase bicrystalline TiO_{2-x} nanofibers with enhanced photocatalytic performance

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ABSTRACT

Black TiO₂(B)/anatase bicrystalline TiO_{2-x} nanofibers were synthesized from a porous titanate derivative by calcination in H₂, and were characterized using field-emission scanning electron microscopy, Raman spectroscopy, N₂ adsorption-desorption analysis, X-ray photoelectron spectroscopy, thermogravimetric analysis, ultraviolet-visible diffuse reflection spectroscopy and photoluminescence measurements. Characterization results showed that no Ti³⁺ was present on the surface of black bicrystalline TiO_{2-x} and oxygen vacancies were distributed in the bulk of both TiO₂(B) and anatase phases. The O/Ti atom stoichiometric ratio of black bicrystalline TiO_{2-x} was estimated to be 1.97 from the difference of mass loss between black bicrystalline TiO_{2-x} and white bicrystalline TiO₂ without oxygen vacancies. The photocatalytic activity of black bicrystalline TiO_{2-x} was 4.2 times higher than that of white bicrystalline TiO₂ and 10.5 times higher than that of anatase TiO₂. The high photocatalytic activity of black bicrystalline TiO_{2-x} was attributed to its effective separation of electrons and holes, which may be related to the effects of both bicrystalline structure and oxygen vacancies. Black bicrystalline TiO_{2-x} also exhibited good photocatalytic activity after recycling ten times. The black bicrystalline TiO_{2-x} nanofibers show potential for use in environmental and energy applications.

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1. Introduction

Development of effective TiO₂-based photocatalysts has been a hot topic of research over the last few decades [1–3]. Most reports have focused on the effective separation of photoinduced carriers. For example, the formation of a heterojunction in the TiO₂-based photocatalyst is a typical approach to decrease the recombination of photoinduced carriers because it allows the electrons and holes of the catalyst to move in different directions. Heterojunction formation involves the syn-

thesis of polycrystalline TiO₂, such as rutile/anatase, TiO₂(B)/anatase, and brookite/anatase [4–7]. In addition, doping TiO₂ with other elements can also allow effective separation of photocarriers by formation of electron traps. The dopants include metals such as Fe³⁺, Cr³⁺, and V⁴⁺ [8–10] or non-metals, such as N, S, C, and F [11–13]. Recently, oxygen vacancies have also been used as a dopant for TiO₂ to improve photocatalytic performance [14,15]. TiO₂ doped with oxygen vacancies is black, and it can be easily formed from conventional white TiO₂. Oxygen vacancies in black TiO₂ have an analogous effect to other

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dopants, serving as a promoter of photocatalytic performance.

Improvements in the photocatalytic performance of TiO_2 have been obtained by all of the methods mentioned above. If two or more of them are coupled together, a more catalytically active TiO_2 -based material may be obtained [16–18]. For example, it may be prepared by doping oxygen vacancies into polycrystalline TiO_2 , which involves coupling of two effects. It is noteworthy that such a TiO_2 -based material consisted of only Ti and O elements without any impurities. In our previous work, we prepared bicrystalline TiO_2 composed of $\text{TiO}_2(\text{B})$ and anatase nanofibers from potassium dititanate. The resulting material exhibited better photocatalytic activity than that of commercial anatase TiO_2 because of the existence of a heterojunction between $\text{TiO}_2(\text{B})$ and anatase [4,19]. Herein, we fabricate black $\text{TiO}_2(\text{B})/\text{anatase}$ nanofibers by annealing a titanate derivative with a Brunauer-Emmett-Teller (BET) surface area $\geq 250 \text{ m}^2/\text{g}$, a precursor of polycrystalline TiO_2 , in hydrogen. The photocatalytic properties of the nanofibers are studied and their structure is also characterized in detail by various methods.

2. Experimental

2.1. Materials and synthesis

The starting materials of black bicrystalline TiO_{2-x} were $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ and K_2CO_3 . First, a mixture of $\text{TiO}_2/\text{K}_2\text{O}$ (molar ratio of Ti to K is 1.9) was prepared by uniformly adding K_2CO_3 to $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ prepared by hydrolyzing TiOSO_4 in hot water with vigorous stirring, and then sintering at 860°C for 4 h to obtain potassium dititanate ($\text{K}_2\text{Ti}_2\text{O}_5$). $\text{K}_2\text{Ti}_2\text{O}_5$ was ground with water to form a paste and put into a closed container at 80°C for 24 h. The paste was then suspended in vigorously stirred aqueous HCl solution (100 mL, 0.1 mol/L) until the residual K^+ was $< 0.2 \text{ wt}\%$ in the final product (detected by inductively coupled plasma-mass spectrometry). The resulting precipitate was separated by filtration, washed with distilled water and dried in a desiccator at 60°C under vacuum. The powder obtained was hydrated titanate. The hydrated titanate was laid on a quartz boat that placed in the temperature-measurement area of the tubular furnace, and calcined in pure H_2 at 600°C for 2 h. The black $\text{TiO}_2(\text{B})/\text{anatase}$ bicrystalline TiO_{2-x} nanofibers were thus obtained.

For comparison, white $\text{TiO}_2(\text{B})/\text{anatase}$ bicrystalline TiO_2 nanofibers were prepared from the hydrated titanate derivative by calcination in air at 600°C for 2 h [19]. P25 TiO_2 (Degussa) was used as a mixed-phase TiO_2 photocatalyst. Conventional anatase was prepared from TiOSO_4 . The hydrolysis of TiOSO_4 was performed as described elsewhere [20]. The collected $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ was washed with distilled water and dried in a desiccator at 60°C under vacuum. Finally, pure anatase TiO_2 was obtained by calcination of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ at 500°C for 2 h in air.

2.2. Photocatalytic testing

The photocatalytic properties of the samples were assessed

in a Pyrex reactor attached to a 300-W high-pressure mercury lamp. Thermostated water (27°C) was circulated through a jacket between the mercury lamp and reaction chamber. At the same time, O_2 or N_2 was introduced into the Pyrex reactor continuously to keep the concentration of oxygen constant and produce a homogeneous suspension of the catalyst in the reaction solution containing methyl orange (MO). Aliquots of the reaction solution were taken out at given time intervals and filtered through a $0.22\text{-}\mu\text{m}$ syringe filter for further analysis. The MO concentration was analyzed by a standard colorimetric method with an ultraviolet-visible spectrophotometer (UV-2802S, UNICO) by measuring the absorbance of MO at 464 nm as a function of irradiation time.

2.3. Characterization

The morphology and microstructure of samples were evaluated by field-emission scanning electron microscopy (FESEM; S-4800, Hitachi). Specific areas were calculated by BET method from adsorption-desorption measurements (TristarII 3020M, Micromeritics) at -196°C . Raman spectra were obtained using a HR 800 spectrometer (Horiba) equipped with a CCD camera detector. As an excitation source, the 514-nm line of an argon/krypton ion laser system (2018, Spectra Physics) was focused through a microscope (BX41, Olympus) equipped with a $50\times$ magnification objective. The laser power did not exceed 5 mW for each sample. X-ray photoelectron spectroscopy (XPS) was performed using a spectrometer (ESCALAB 250, ThermoFisher Scientific, USA) equipped with $\text{Al K}\alpha$ radiation operated at 300 W. The shift of binding energy was corrected using the $\text{C}1\text{s}$ level at 284.7 eV as an internal standard. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (SDT 2960, TA Instruments, USA). TGA measurements were conducted over a temperature range of $35\text{--}850^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ under air. UV-Vis spectroscopy (Lambda 900, Perkin-Elmer) was used to identify the spectral properties of the samples. Photoluminescence (PL) spectra were measured at room temperature on a fluorescence spectrophotometer (Varian Cary Eclipse, Varian, USA) with an excitation wavelength of 325 nm.

3. Results and discussion

Figure 1(a) reveals that the morphology of black bicrystalline TiO_{2-x} is fiber-like with a uniform width of $0.2 \mu\text{m}$ and length of $1\text{--}5 \mu\text{m}$, which is identical to that of white bicrystalline TiO_2 (Fig. 1(b)). The surface area of black TiO_{2-x} is $28.9 \text{ m}^2/\text{g}$, which is also to that of white bicrystalline TiO_2 ($28.5 \text{ m}^2/\text{g}$). This demonstrates hydrogen treatment has no influence on the morphology of the titania materials.

The Raman spectra of black bicrystalline TiO_{2-x} and white bicrystalline TiO_2 are presented in Fig. 2. The six obvious ($3\text{E}_g+2\text{B}_{1g}+\text{A}_{1g}$) Raman-active modes of the anatase phase are detected in both samples. This indicates that the anatase phase is the main component of these TiO_2 samples [4]. In the magnified image (inset (b) in Fig. 2), two weak bands from 220 to 260 cm^{-1} are observed in both samples, which correspond to Ra-

Fig. 1. FESEM images of black bicrystalline TiO_{2-x} nanofibers (a) and white bicrystalline TiO_2 (b).

Fig. 2. Raman spectra of black bicrystalline TiO_{2-x} (1) and white bicrystalline TiO_2 (2).

man-active modes of $\text{TiO}_2(\text{B})$ [21], confirming the presence of $\text{TiO}_2(\text{B})$ in both samples. Furthermore, inset (a) in Fig. 2 indicates that there is a blue shift of the E_g band observed for black bicrystalline TiO_{2-x} (146 cm^{-1}) compared with that of white bicrystalline TiO_2 (141 cm^{-1}). The E_g band of titania is related to the structural properties of the bulk anatase phase. Localized defects in the bulk anatase phase are the main factor responsible for the blue shift of the E_g band of black bicrystalline TiO_{2-x} [22]. Simultaneously, it can also be observed that there is a slight blue shift of bands assigned to the $\text{TiO}_2(\text{B})$ phase in black bicrystalline TiO_{2-x} compared with that of white bicrystalline TiO_2 , which illustrates that the $\text{TiO}_2(\text{B})$ phase of black bicrystalline TiO_{2-x} has the defects as well. Thus, defects should be present in both the $\text{TiO}_2(\text{B})$ and anatase phases of black bicrystalline TiO_{2-x} .

The Ti $2p$ XPS measurements for black bicrystalline TiO_{2-x} and white bicrystalline TiO_2 are shown in Fig. 3. The Ti region of black bicrystalline TiO_{2-x} is regular, and the binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at 459.4 and 464.9 eV, respectively, compared well with data for Ti^{4+} in TiO_2 [23]. The same XPS peak shape of Ti $2p$ for both samples demonstrates the similar electronic state of Ti atoms in them. This means that the defects are not distributed on the surface of black bicrystalline TiO_{2-x} . Similar results were obtained Chen et al. [24] and Pen et al. [25]. According to simulations by Chen et al. [26], the energy barrier for oxygen vacancies of anatase TiO_2 to diffuse from surface sites to subsurface ones is sufficiently low to ensure rapid equilibration of the vacancy distribution at typical an-

Fig. 3. XPS spectra of the Ti $2p$ peaks (a) and O $1s$ peaks (b) for black bicrystalline TiO_{2-x} (1) and white bicrystalline TiO_2 (2).

nealing temperatures. That is, the oxygen vacancies of anatase TiO_2 can spontaneously diffuse from surface to subsurface sites during the preparation process. Thus, combined with the Raman analysis, it can be confirmed that the oxygen vacancies (i.e., defects) are located in the bulk of black bicrystalline TiO_{2-x} .

The content of oxygen vacancies in TiO_{2-x} is difficult to determine directly, unlike the analysis of other conventional elements. Herein, we tried to measure the change in the mass of samples by TGA to estimate the content of oxygen vacancies in black bicrystalline TiO_{2-x} . As shown in Fig. 4, the mass loss of white bicrystalline TiO_2 is mainly ascribed to the desorption of physically adsorbed H_2O and hydroxyl groups [27]. The mass of TiO_2 remained constant until the temperature exceeded 600 °C.

Fig. 4. TGA curves of black bicrystalline TiO_{2-x} (1) and white bicrystalline TiO_2 (2).

For black bicrystalline TiO_{2-x} the TGA curve below 300 °C is the same as that of white bicrystalline TiO_2 , which indicates that both samples have the same content of physically adsorbed H_2O and hydroxyl groups. However, there is an obvious difference in mass loss between them when the temperature exceeds 300 °C. An increase of mass is observed for black bicrystalline TiO_{2-x} , which is finished at about 750 °C. Because black TiO_{2-x} consists of only Ti and O elements, the mass increase can be attributed to the oxidation of the sample. However, the mass change process of black TiO_{2-x} from 300 to 750 °C may also involve the desorption of hydroxyl groups according to the TGA of white bicrystalline TiO_2 . It is difficult to confirm the accurate mass change due to oxidation of black bicrystalline TiO_{2-x} . Comparison of the two TGA curves indicates that the maximum mass difference between them is about 0.58 wt%. Thus, it can be confirmed that the mass change ascribed to oxidation of oxygen vacancies is less than 0.58 wt%; that is, “x” of TiO_{2-x} is calculated to be less than 0.03.

Figure 5 depicts the UV-Vis diffuse reflection spectra of black bicrystalline TiO_{2-x} and white bicrystalline TiO_2 . A large absorption peak is observed for white bicrystalline TiO_2 below 400 nm, but there is no absorption in the visible region. This is identical to the typical characteristics of general TiO_2 [28]. Black bicrystalline TiO_{2-x} exhibits an absorption peak in the UV region but the intensity is a little lower than that of white bicrystalline TiO_2 . More importantly, a broad absorption spanning the whole visible region is observed, which makes the sample black.

Figure 6(a) shows the degradation curves of MO in the presence of different TiO_2 samples. The influence of absorption (control sample) and self-degradation of MO (blank sample) on the photocatalytic performance of the catalysts can be ignored. It reveals that the degradation rate of conventional anatase TiO_2 is about 50% after 15 min. Meanwhile, 75% of MO is degraded after 15 min by white $\text{TiO}_2(\text{B})/\text{anatase}$ bicrystalline TiO_2 , which is similar to the efficiency of commercial titania P25. This enhanced performance can be attributed to the heterojunction of $\text{TiO}_2(\text{B})$ and anatase limiting the recombination of photoinduced carriers [29]. As expected, black bicrystalline

Fig. 5. UV-Vis diffuse reflection spectra of black bicrystalline TiO_{2-x} (1) and white bicrystalline TiO_2 (2).

TiO_{2-x} exhibits better photocatalytic performance than white $\text{TiO}_2(\text{B})/\text{anatase}$ bicrystalline TiO_2 , with the degradation ratio reaching up to 98% after 15 min. This indicates that the introduction of oxygen vacancies improves the photocatalytic activity of black bicrystalline TiO_{2-x} . As shown in the inset of Fig. 6(a), the reaction rate constant (k) of black bicrystalline TiO_{2-x} (0.38 min^{-1}) is 4.2 times higher than that of white bicrystalline TiO_2 (0.09 min^{-1}) and 10.5 times higher than that of anatase (0.04 min^{-1}). Thus, black bicrystalline TiO_{2-x} exhibits excellent photocatalytic performance because of the formation of bicrystalline structure and incorporation of oxygen vacancies.

Furthermore, recycling experiments were carried out to study the photocatalytic stability of black bicrystalline TiO_{2-x} ; the results are presented in Fig. 6(b). Taking into account the mass loss of the catalyst, the photocatalytic activity of black bicrystalline TiO_{2-x} shows only a very slight decrease after ten cycles. Therefore, compared with impurity dopants, the oxygen vacancies in TiO_2 show a marked advantage in terms of photocatalytic stability.

PL analysis can provide the information about the separation of photogenerated electron-hole pairs. Fig. 7 shows that

Fig. 6. (a) Comparison of photocatalytic degradation of MO by various samples. (1) Black bicrystalline TiO_{2-x} ; (2) White bicrystalline TiO_2 ; (3) Conventional anatase TiO_2 ; (4) P25; (5) Control sample (absorption of anatase TiO_2 in the dark); (6) Blank sample (without catalytic materials). (b) The recyclability of black bicrystalline TiO_{2-x} in photocatalysis of MO.

Fig. 7. PL spectra of white bicrystalline TiO_2 (1) and black bicrystalline TiO_{2-x} (2).

the PL spectra of black bicrystalline TiO_{2-x} and white bicrystalline TiO_2 are characterized by two peaks at around 360 and 380 nm corresponding to the direct and indirect bandgap transitions of TiO_2 , respectively [30]. The PL intensity of black bicrystalline TiO_{2-x} is obviously lower than that of white bicrystalline TiO_2 . This indicates that in addition to the heterojunction effect of white bicrystalline TiO_2 , the photoinduced carriers can be further separated by the oxygen vacancies in black bicrystalline TiO_{2-x} . The effect of oxygen vacancies on the band structure of anatase and rutile TiO_2 has been reported [31,32]. Oxygen vacancies can narrow the bandgap of TiO_2 and form a similar impurity level in the bandgap of two-phase TiO_2 . However, how to influence the band structure of $\text{TiO}_2(\text{B})$ using oxygen vacancies has not been reported. Thus, we were unable to confirm the band structure of black bicrystalline TiO_{2-x} and their charge-hole transfer. The PL results reveal that incorporation of oxygen vacancies into black bicrystalline TiO_{2-x} is beneficial for hole-charge separation, providing direct evidence for the origin of its improved photocatalytic performance.

4. Conclusions

We prepared black $\text{TiO}_2(\text{B})/\text{anatase}$ bicrystalline TiO_{2-x} nanofibers from a porous titanate derivative by calcination in hydrogen. Hydrogen treatment had no influence on the morphology of black bicrystalline TiO_{2-x} . XPS results showed that there was no Ti^{3+} on the surface of black bicrystalline TiO_{2-x} . According to Raman analysis, the oxygen vacancies of black bicrystalline TiO_{2-x} were distributed in both the anatase and $\text{TiO}_2(\text{B})$ phases. The results suggested that the content of oxygen vacancies in black bicrystalline TiO_{2-x} was about 0.58 wt%, according to which the O/Ti atom stoichiometric ratio was 1.97. The photocatalytic activity of black bicrystalline TiO_2 was 4.2 times higher than that of white bicrystalline TiO_{2-x} and 10.5 times higher than that of anatase TiO_2 . There was no deactivation of black bicrystalline TiO_{2-x} after recycling ten times. Because of its unique characteristics, our group is undertaking further studies of the use of this catalyst in the fields of environment and energy.

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Graphical Abstract

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Black $\text{TiO}_2(\text{B})/\text{anatase}$ bicrystalline TiO_{2-x} nanofibers with enhanced photocatalytic performance

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A TiO_2 photocatalyst with both oxygen-vacancy doping and heterojunction structure exhibited effective separation of photoinduced carriers, resulting in improved photocatalytic performance compared with that of control samples.

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具有高光催化活性的黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}纳米纤维

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摘要: 高效TiO₂基光催化材料的开发一直是催化领域的研究热点, 主要的策略是如何有效地分离光生载流子。制备多晶相的TiO₂材料可引入异质/相结结构使电子与空穴朝不同方向移动, 从而避免电子与空穴复合; 另外, 在TiO₂中掺杂其他金属或非金属也可以有效地降低电子与空穴的复合率, 掺杂的元素作为电子捕获阱俘获光生电子, 以实现电子空穴的有效分离。近些年, 作为一种全新的掺杂剂, 氧空穴可以有效改善TiO₂的光催化活性, 所制TiO₂具有可见光的全光谱吸收能力, 因此该类TiO₂呈现出黑色。

通过上述方法均可以制备出高活性TiO₂基光催化材料, 如果能够将这些方法耦合一起, 则可能制备出活性更高的光催化剂。因此, 本文将异相结结构和空穴掺杂耦合起来, 用多孔钛酸盐衍生物在H₂中高温焙烧制得一种全新的黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}纳米纤维。不同于其他TiO₂基光催化材料, 该样品仅由Ti和O元素组成, 通过Ti和O元素的组合, 形成了双晶结构和空穴掺杂两种特殊的结构, 借助场发射(FESEM)、拉曼光谱(Raman)、氮气物理吸附脱附、X射线光电子能谱(XPS)、热重(TG)、紫外可见漫反射光谱(UV-Vis)和荧光光谱(PL)等表征分析了样品的结构及其光催化性能间构效关系。

FESEM结果显示, 黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}为长1–5 μm、宽0.2 μm的纤维结构, Raman结果表明, 锐钛矿相在特征波段(140 cm⁻¹左右)和TiO₂(B)的特征波段(220–260 cm⁻¹)均发生蓝移, 说明该两相中均存在氧空穴; 该样表面未检测到Ti³⁺, 因此氧空穴可能分散在TiO₂(B)和锐钛矿相的体相中。根据黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}和白色TiO₂(B)/锐钛矿双晶TiO₂的失重差, 估算出前者的O/Ti原子比为1.97。光催化降解甲基橙实验结果显示, 黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}的光催化活性是白色双晶TiO₂的4.2倍, 锐钛矿TiO₂的10.5倍, 且连续反应10次后未出现失活现象, 显示出了良好的光催化稳定性。前期, 我们已经证明了白色TiO₂(B)/锐钛矿双晶TiO₂由于具有TiO₂(B)和锐钛矿的异相结结构, 致使其电子空穴有效地分离, 从而表现出优异的光催化活性; 本文的PL结果显示, 由于氧空穴的引入, 异相结与氧空穴两者共同作用, 进一步促进了黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}电子与空穴的有效分离, 因此黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}表现出高的光催化活性。由于其特殊的结构, 黑色TiO₂(B)/锐钛矿双晶TiO_{2-x}纳米纤维将在环境与能源领域表现出良好的应用前景。

关键词: 黑色氧化钛; 双晶; 光催化; 氧空穴

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