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Highly efficient Z-scheme WO_{3-x} quantum dots/ TiO_2 for photocatalytic hydrogen generation

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ABSTRACT

Z-scheme semiconductors are a promising class of photocatalysts for hydrogen generation. In this work, Z-scheme semiconductors composed of WO_{3-x} quantum dots supported on TiO_2 (WO_{3-x} QDs/ TiO_2) were fabricated by solvothermal and hydrogen-reduction methods. Characterization by transmission electron microscopy and X-ray diffraction indicated that the amount and size of the WO_{3-x} QDs could be tuned by modulating the addition of the W precursor. Evidence from X-ray photoelectron spectroscopy and photoluminescence spectroscopy suggested that the hydrogen reduction of the composite induced the formation of oxygen vacancy ($\text{W}^{5+}/\text{V}_\text{O}$) defects in WO_3 . These defects led to ohmic contact between WO_{3-x} and TiO_2 , which altered the charge-transfer pathway from type II heterojunction to Z-scheme, and maintained the highly reductive and oxidative ability of TiO_2 and WO_{3-x} , respectively. Therefore, the Z-scheme sample showed 1.3-fold higher photoactivity than pure TiO_2 in hydrogen generation. These results suggest that the formation of $\text{W}^{5+}/\text{V}_\text{O}$ defects at the interface is highly beneficial for the fabrication of Z-scheme photocatalysts.

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1. Introduction

TiO_2 is a technologically important semiconductor that has been widely used in a variety of applications, including solar cells, photocatalysis, and environmental remediation [1–5]. Its widespread use owes to its highly favorable properties, such as suitable band alignment to water redox potentials, biological and chemical inertness, availability, environmental friendliness, low cost, and long-term stability against photo- and chemical corrosion [1–4,6]. However, some drawbacks of TiO_2 remain, among which the most severe is the low photocatalytic activity due to rapid charge recombination [2]. To solve this problem, the construction of Z-scheme systems incorporating other

photocatalysts with suitable band structure has proven an effective approach [7]. Several materials have been used to construct Z-scheme systems based on TiO_2 , including SrTiO_3 [8], $\text{g-C}_3\text{N}_4$ [9,10], CdS [11,12], Ag_2S [13], and CaIn_2S_4 [14], in which the increased spatial isolation of the photogenerated electrons and holes inhibits their recombination in the bulk. There are two kinds of all-solid Z-scheme system: PSI-C-PSII and PSI-PSII [7,15]. The difference is that the former requires a conductor layer (such as Au, Ag, or rGO) to realize ohmic contact [7]. Although PSI-PSII systems are easier to fabricate, the rational design and construction of their solid–solid contact interfaces are vital for effective Z-scheme charge transfer [7,16].

Recently, WO_3 has received considerable attention in pho-

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photocatalysis because of its earth-abundance, highly tunable composition, and excellent electrical conductivity [17]. Fabrication of a WO_3/TiO_2 Z-scheme structure (of the PSI-PSII type) can maintain the highly oxidative and highly reductive potentials of WO_3 and TiO_2 , respectively, along with efficient spatial isolation of the charges. Importantly, oxygen vacancies (V_O), or the structurally related low-oxidation-state metal ions, not only improve the absorption of light by TiO_2 , but also help to form ohmic contacts, assisting the construction of a direct Z-scheme [18]. Furthermore, fabricating the PSI and bulk PSII materials in the form of quantum dots (QDs) benefits the formation of chemical bonds between these two materials [19–22]. Therefore, in this work, we synthesized a Z-scheme composite by decorating TiO_2 nanoparticles with WO_{3-x} QDs, and obtained higher photoactivity than pure TiO_2 in hydrogen generation.

2. Experimental

2.1. Materials

Tetrabutyl titanate (TBT), WCl_6 , ethanol, methanol, ammonia, and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were all purchased from Tianjin Guangfu Fine Chemical Research Institute. Milli-Q ultrapure water with a resistivity higher than $18.2 \text{ M}\Omega\cdot\text{cm}$ was used in all experiments. All the chemicals were reagent-grade and used as received.

2.2. Synthesis of $\text{WO}_{3-x}/\text{TiO}_2$

For the synthesis of TiO_2 , 50 mL ethanol and 0.5 mL TBT were mixed. After stirring for 5 min, 230 μL $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added dropwise into the solution to trigger the nucleation and growth of TiO_2 . Then, the solution was stirred at room temperature for 48 h. The resulting TiO_2 powder was washed with absolute ethanol several times and dried at 60°C for 12 h.

For the synthesis of $\text{WO}_{3-x}/\text{TiO}_2$, 200 mg of the synthesized TiO_2 was dispersed in 70 mL methanol under stirring and ultrasonic treatment for 30 min, then m mg ($m = 5, 10, 15, 20$) WCl_6 was dissolved into the suspension, followed by another 30 min ultrasonic treatment. After that, the solution was transferred into a 100-mL Teflon-lined autoclave and heated at 180°C for 3 h. The obtained powders were collected, washed with absolute ethanol several times, vacuum-dried at 80°C for 12 h, and finally calcined in air at 400°C for 1 h with a heating rate of $5^\circ\text{C}/\text{min}$. The resulting samples are denoted $\text{WT}m$. The pure TiO_2 (i.e., $m = 0$) is denoted T. For hydrogen reduction, $\text{WT}m$ (or T) was placed in a quartz boat and calcined in a tube furnace under hydrogen flow (1 bar) at 300°C for 0.5 h, with a heating rate of $5^\circ\text{C}/\text{min}$. The resulting samples are denoted $\text{WTH}m$ (or TH).

2.3. Structural characterization

X-ray diffraction (XRD) patterns were recorded using a D/MAX-2500 X-ray diffractometer equipped with $\text{Cu } K_\alpha$ radiation at 40 kV and 140 mA at a scanning rate of $5^\circ/\text{min}$. High-resolution transmission electron microscopy (HRTEM)

analysis was carried out using a Tecnai G² F-20 transmission electron microscope with a field-emission gun operating at 200 kV. Raman spectra were recorded by a Raman Microscope (DXR Microscope, ThermoFisher, USA), using a 100-mW output of the 532-nm line of an Nd:YAG laser as the excitation source. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a PHI-1600 X-ray photoelectron spectroscope equipped with $\text{Al } K_\alpha$ radiation, and the binding energy was calibrated by the C 1s peak (284.8 eV) of the contamination carbon. Ultraviolet-visible diffuse-reflectance spectra (UV-vis DRS) were recorded with a Hitachi U-3010 spectrometer equipped with a 60-mm-diameter integrating sphere, using BaSO_4 as the reflectance sample. Steady-state photoluminescence (PL) spectra were measured by a Horiba JobinYvon Fluorolog3-21.

2.4. Photocatalytic tests

Photocatalytic H_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a closed glass system under irradiation by a 300-W high-pressure Xe lamp. 10 mg catalyst was dispersed in 120 mL aqueous solution containing methanol (30 vol%) as a sacrificial electron donor, and 1 wt% Pt was introduced by *in-situ* photodeposition as a co-catalyst. The temperature of the reaction solution was maintained at $0 \pm 0.2^\circ\text{C}$. The resultant H_2 was quantified by gas chromatography (Bruker 450-GC, thermal conductive detector (TCD), 5- $\text{\AA}$ molecular sieve column, and N_2 as carrier gas).

3. Results and discussion

3.1. Crystal structure

As shown in Fig. 1(a) and (b), the synthesized pure TiO_2 (TH) had an oval morphology on the nano-scale. Solvothermal treatment with the W precursor resulted in the growth of WO_{3-x} QDs on TiO_2 (Fig. 1(c)–(h)). The QDs increased in size from 2 to 4 nm as the amount of W precursor (m) was increased from 5 to 15 mg (i.e., from WTH5 to WTH15, Fig. 1(k)–(m)). However, when m was further increased to 20 mg (i.e., WTH20), the formation of QDs was reduced in amount and a newly formed WO_{3-x} layer appeared on the surface of TiO_2 (Fig. 1(i) and (j)). Moreover, the HRTEM images confirmed the high degree of crystallization of TiO_2 and the WO_{3-x} QDs, with clear lattice fringes at 0.353 nm ({101} plane) and 0.385 nm ({002} plane), respectively [23]. Additionally, there were no obvious differences in morphology between $\text{WT}m$ and $\text{WTH}m$ (images not shown).

XRD and Raman analyses were performed to determine the crystal structure of the samples (Fig. 2). The XRD patterns indicated that TH was composed purely of the anatase polymorph. After solvothermal treatment with the W precursor, characteristic peaks at 23.1° and 23.6° , arising from the (002) and (020) planes of monoclinic WO_3 [23,24], emerged for WTH5. These peaks then gradually increased in intensity from WTH10 to WTH20. For $\text{WTH}m$, no impurities or other crystals besides anatase TiO_2 and monoclinic WO_3 were observed. Results consistent with these were also exhibited in the Raman

Fig. 1. TEM images of WTH m : TH (a, b), WTH5 (c, d), WTH10 (e, f), WTH15 (g, h) and WTH20 (i, j). (k–m) are the size distributions of the WO $_3$ nanoparticles in WTH5, WTH10, and WTH15, respectively.

spectra. Peaks appeared at 144 (636), 394, and 514 cm^{-1} , which are characteristic of the anatase TiO $_2$ phase. These peaks correspond to the E_g , B_{1g} , and A_{1g} modes, respectively, and are caused by symmetric stretching vibration, symmetric bending vibration, and asymmetric bending vibration of O–Ti–O, respectively [25]. After decoration with WO $_{3-x}$ QDs, new peaks appeared at 264, 706, and 810 cm^{-1} , which are respectively attributed to the symmetric vibration of O–W–O, asymmetric vibration of W $^{6+}$ –O, and W–O–W vibration [24]. The peaks of WO $_{3-x}$ became more pronounced with increasing amounts (m)

of the added W precursor. Additionally, the hydrogen-reduction procedure had no effect on the crystal phase or peak intensity.

3.2. Surface chemical state and band structure

WT10 and WTH10 were characterized by XPS to investigate the chemical composition and elemental states of these materials, as shown in Fig. 3. For WT10, the W 4 f peaks at *ca.* 35.5 and 37.4 eV correspond to W $^{6+}$ in WO $_3$. After the hydrogen treat-

Fig. 2. XRD patterns (a) and Raman spectra (b) of the prepared samples.

Fig. 3. W 4fXPS spectra of WT10 (a), and W 4f (b) and Ti 2p (c) spectra of WTH10.

ment, WTH10 showed new peaks at *ca.* 33.8 and 37.0 eV. These are assigned to W^{5+} [26–28] ions, which are accompanied by oxygen vacancies (V_O) [1–3]. These results indicate that the reductive treatment of WO_3/TiO_2 at 300 °C produced surface W^{5+}/V_O in WO_{3-x}/TiO_2 . However, no reduced species of Ti (e.g., Ti^{3+}) are observed in the Ti 2p spectrum of WTH10 (Fig. 3(c)), suggesting the relative stability of the TiO_2 compared with the WO_3 QDs.

The optical absorption spectra are shown in Fig. 4(a). TiO_2 (T) exhibits an absorption edge at *ca.* 380 nm, corresponding to a band gap of 3.2 eV. The materials in which TiO_2 was decorated with WO_{3-x} (i.e., $WThm$) showed similar optical absorption properties to pure TiO_2 , while the hydrogen treatment increased their absorption in the visible-light range of 400–800 nm (i.e., the samples denoted $WTHm$). For example, hydrogen-treated WT10 (WTH10) showed much higher optical absorption than WT10 (inset in Fig. 4(a)). Importantly, as the amount of WO_{3-x} decoration increased, the $WThm$ samples showed greater visible-light absorption. We attribute this to the introduction of W^{5+}/V_O , which either leads to a new shallow donor level near the conduction band (CB) of WO_{3-x} or induces local surface plasmon resonance (LSPR) [27–29], resulting in the narrowing of the band gap.

The efficient separation of photoinduced charges is vital for

high photocatalytic activity [30]. PL spectra of the samples are shown in Fig. 4(b). The emission bands between 350 and 400 nm, which arise from the rapid recombination of excited electrons and holes [1–3], were strongest for T and TH. However, the decoration of the TiO_2 nanosheets with WO_{3-x} QDs greatly reduced the PL intensities of all the $WThm$ samples. Initially, the emission peak intensities declined as the amount of WO_{3-x} was increased, such that WTH10 had the lowest PL emission intensity of any sample. However, as the amount of WO_{3-x} was increased further, the PL emission intensities (i.e., those of WTH15 and WTH20) increased again. The PL results thus indicate that the combination of WO_{3-x} QDs and TiO_2 inhibited the recombination of photoinduced charge pairs, and that WTH10 possessed the highest charge-separation efficiency. Furthermore, the hydrogen treatment played a very important role in the enhancement of charge separation: for example, WTH10 showed much lower PL emission intensity than WT10. These results indicate the significant enhancement of charge separation by W^{5+}/V_O sites on the surface.

The PL emission peak at about 518 nm (~ 2.4 eV) is attributed to oxygen vacancies in WO_3 . Furthermore, density functional theory (B3LYP) calculations indicated that the optical levels of the (+1/0), (+2/+1), and (+2/0) transitions were found at 2.37, 2.11, and 2.24 eV, respectively, above the top of

Fig. 4. UV DRS (a) and PL spectra (b) of the samples. The inset in (a) shows enlarged DRS spectra of WTH10 and WT10.

Fig. 5. Photocatalytic hydrogen generation over the samples (a) and the energy-level diagrams of the type II heterojunction and Z-scheme structure of WO_3/TiO_2 (b) and $\text{WO}_{3-x}/\text{TiO}_2$ (c).

the valence band (VB) [31–33]. In addition, the energy level of W^{5+} is very close to that of V_0 [31]. Therefore, the presence of oxygen vacancies results in a set of quasi-continuous energy levels of WO_{3-x} , as shown in Fig. 5(c).

3.3. Photocatalytic tests

Photocatalytic hydrogen generation was conducted to evaluate the photoactivity of the as-synthesized samples. As can be seen from Fig. 5(a), T and TH achieved similar photoreaction rates for H_2 generation, *ca.* 13.9 and 13.7 $\text{mmol h}^{-1} \text{g}^{-1}$, respectively. The slight increase of photoactivity from T to TH may have resulted from the disordering of the surface layer of TiO_2 through hydrogenation [34]. However, after the decoration of TiO_2 with WO_{3-x} QDs, the H_2 generation rate initially increased with the amount of QDs: specifically, WTH10 showed the highest reaction rate (*ca.* 17.7 $\text{mmol h}^{-1} \text{g}^{-1}$), which is *ca.* 1.3-fold higher than T or TH. However, further increasing the amount of QDs (i.e., WTH15 and WTH20) reduced the photoreaction rate. The photoactivity order is consistent with the PL spectra (Fig. 4(b)).

Although WT10 had a lower charge-recombination rate than T, it exhibited lower photoactivity in hydrogen generation. The reason for its lower photoactivity is that this composite of

unmodified WO_3 and TiO_2 had the structure of a type II heterojunction [23,24,35]. As shown in Fig. 5(b), the band structures of WO_3 and TiO_2 are well matched for the formation of a typical type II heterojunction, which delays the relaxation of photoinduced electrons back to the valence band and thus increases the charge-separation efficiency. Unfortunately, however, the conduction band of WO_3 is unable to reduce H_2O to H_2 (for which the potential is 0 V vs RHE), so the formation of the type II structure inhibits hydrogen generation. In contrast, the WTH m samples showed higher photoactivity than T, which suggests that $\text{WO}_{3-x}/\text{TiO}_2$ formed a Z-scheme structure (Fig. 5(c)). The formation of a Z-scheme can be attributed to surface W^{5+}/V_0 sites at the interfaces between TiO_2 and the WO_{3-x} QDs, which formed a set of quasi-continuous energy levels to realize ohmic contact and lower the interfacial electric resistance [7,18]. In this case, the photoinduced electrons in the CB and the W^{5+}/V_0 level of WO_{3-x} were able to recombine with the holes in the VB of TiO_2 through the ohmic contact. As a consequence, the electrons and holes in the CB of TiO_2 and the VB of WO_{3-x} were well spatially isolated, resulting in hydrogen generation and methanol oxidation, respectively. Of all the WTH m samples, the one fabricated with $m = 10$ mg of the W precursor showed the optimum charge-separation efficiency, and thus the highest activity as a Z-scheme photocatalyst. The alteration of a

Graphical Abstract

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Highly efficient Z-scheme WO_{3-x} quantum dots/ TiO_2 for photocatalytic hydrogen generation

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Z-scheme WO_{3-x} quantum dots (QDs) supported on TiO_2 , fabricated by solvothermal and reduction methods, exhibit highly efficient charge separation and enhanced photocatalytic H_2 generation.

type II heterojunction to a Z-scheme induced by the presence of oxygen vacancies has also been observed for CdS/CdWO_4 [17]. The present study thus provides further evidence that the introduction of oxygen defects to the interface facilitates the formation of a Z-scheme structure.

4. Conclusions

We fabricated Z-scheme semiconductors composed of WO_{3-x} quantum dots supported on TiO_2 by *in-situ* solvothermal and hydrogen-reduction methods. The added amount of the W precursor was adjusted to vary the amount and size of the WO_{3-x} QDs. Hydrogen-reduction treatment led to the appearance of $\text{W}^{5+}/\text{V}_\text{O}$ defects in WO_{3-x} . The existence of these defects at interfaces led to the formation of Z-scheme structures, resulting in the effective separation and spatial isolation of charges, thus maintaining the high reductive and oxidative potentials of TiO_2 and WO_{3-x} , respectively, and strengthening the ohmic contact between them. Therefore, the most active of the Z-scheme composites showed 1.3-fold higher photoactivity than pure TiO_2 in hydrogen generation.

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基于WO_{3-x}量子点和TiO₂构建高效Z型光催化产氢催化剂

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摘要: TiO₂具有高效、廉价、无毒及光化学稳定性好等优点, 因而被广泛应用于光能转化和利用领域, 如太阳能电池、光催化分解水制氢和环境污染降解等。但是, TiO₂仍然存在一些缺陷制约了其应用, 其中, 最关键的问题是光生电荷分离效率低。因此, 人们对其进行了掺杂、异质结构构建和Z型结构构建等来解决这一问题, 其中Z型结构近年来备受关注。

全固体Z型结构的构建目前主要有两种方式: PSI-C-PSII和PSI-PSII。前者PSI与PSII间要插入中间导电层(如Au、rGO等)来实现界面欧姆接触; 后者则无中间层, 而是基于界面设计来实现欧姆接触。本文以构建PSI-PSII Z型结构为目标, 以TiO₂和WO₃为基础半导体材料, 采用原位溶剂热生长的方法构建WO₃量子点/TiO₂结构, 借助氢气还原反应在界面处引入氧缺陷。采用透射电子显微镜、X射线衍射和拉曼光谱研究了复合晶体结构, 采用X射线光电子能谱、紫外可见光谱和荧光光谱等手段研究了Z型结构的界面结构和能带结构。结合光催化分解水产氢活性来建立Z型结构与光催化性能的关联关系。

表征结果表明, 在TiO₂上进行原位溶剂热成核反应可点缀WO₃量子点, 并且量子点粒径随W前驱体用量的增加而变大。两种半导体材料为TiO₂锐钛矿和WO₃晶体结构, 且WO₃的XRD特征峰和Raman特征吸收峰会随W前驱体用量增加而变大。通过对WO₃/TiO₂进行氢气还原处理, 使其表面形成大量W⁵⁺和氧缺陷, 一方面提高了催化剂对可见光的吸收, 另一方面在界面形成欧姆接触, 实现了Z型结构的构建。Z型结构实现了光催化分解水产氢反应, 其中WTH10光催化活性最好。本文为新型Z型光催化剂的设计和构建提供了新思路 and 策略。

关键词: WO_{3-x}; 二氧化钛; 产氢; 量子点; W⁵⁺/氧缺陷

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