available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)

Enhanced photocatalytic H₂-production activity of WO₃/TiO₂ step-scheme heterojunction by graphene modification

Fei He ^a, Aiyun Meng ^a, Bei Cheng ^a, Wingkei Ho ^{b, #}, Jiaguo Yu ^{a, c, *}^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, Hubei, China^b Department of Science and Environmental Studies and State Key Laboratory in Marine Pollution, The Education University of Hong Kong, Tai Po, N. T. Hong Kong, China^c Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 28 February 2019

Accepted 16 April 2019

Published 5 January 2020

Keywords:

Step-like heterojunction

S-scheme heterojunction

S heterojunction

Photocatalyst

Hydrogen generation

ABSTRACT

Sunlight-driven photocatalytic water-splitting for hydrogen (H₂) evolution is a desirable strategy to utilize solar energy. However, this strategy is restricted by insufficient light harvesting and high photogenerated electron-hole recombination rates of TiO₂-based photocatalysts. Here, a graphene-modified WO₃/TiO₂ step-scheme heterojunction (S-scheme heterojunction) composite photocatalyst was fabricated by a facile one-step hydrothermal method. In the ternary composite, TiO₂ and WO₃ nanoparticles adhered closely to reduced graphene oxide (rGO) and formed a novel S-scheme heterojunction. Moreover, rGO in the composite not only supplied abundant adsorption and catalytically active sites as an ideal support but also promoted electron separation and transfer from the conduction band of TiO₂ by forming a Schottky junction between TiO₂ and rGO. The positive cooperative effect of the S-scheme heterojunction formed between WO₃ and TiO₂ and the Schottky heterojunction formed between TiO₂ and graphene sheets suppressed the recombination of relatively useful electrons and holes. This effect also enhanced the light harvesting and promoted the reduction reaction at the active sites. Thus, the novel ternary WO₃/TiO₂/rGO composite demonstrated a remarkably enhanced photocatalytic H₂ evolution rate of 245.8 μmol g⁻¹ h⁻¹, which was approximately 3.5-fold that of pure TiO₂. This work not only presents a low-cost graphene-based S-scheme heterojunction photocatalyst that was obtained via a feasible one-step hydrothermal approach to realize highly efficient H₂ generation without using noble metals, but also provides new insights into the design of novel heterojunction photocatalysts.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen (H₂), a source of clean and high-heat-density secondary energy, is one of the promising energy carriers that can satisfy the ever-increasing energy and environmental demands

[1–3]. Photocatalytic water splitting for H₂ production has received great attention owing to its simplicity and recyclability, and involves the conversion of solar energy to chemical energy with the help of a photocatalyst, sunlight, and water at room temperature [4–6]. Since the pioneering work of Fujishima and

* Corresponding author. Tel: +86-27-87871029; Fax: +86-27-87879468; E-mail: jiaguoyu@yahoo.com

Corresponding author. E-mail: keithho@eduhk.hk

This work was supported by the National Natural Science Foundation of China (U1705251, 21871217, 21573170, 21433007) and the National Key Research and Development Program of China (2018YFB1502001).

DOI: S1872-2067(19)63382-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 1, January 2020

Honda on TiO₂ electrodes for photoelectrochemical water splitting, various semiconductors, including TiO₂ [7], CdS [8,9], WO₃ [10], C₃N₄ [11,12], and ZnO [13,14], have been explored to develop highly active, robust, and low-cost photocatalysts and photoelectrodes for industrial application. By virtue of its high stability, environmental friendliness, and low cost [15], TiO₂ has been extensively studied and plays a vital role in H₂ production, pollutant degradation [16,17], and CO₂ reduction [18,19]. However, pure TiO₂ photocatalyst exhibits unsatisfactory photocatalytic activity owing to insufficient light harvesting (no more than 5%) and a high photogenerated electron–hole recombination rate [2,20], which severely restrict its industrial application. To date, a myriad of strategies have been proposed for enhancing the photocatalytic activity, such as loading noble metals [21], doping metallic or non-metallic elements [22], and constructing heterojunctions [23–25].

Heterojunction construction by integrating two semiconductors is a universal strategy owing to its effectiveness in spatially separating the photoexcited electron–hole pairs via appropriate band alignments between the semiconductors [1,26]. Recently, a new step-scheme heterojunction (S-scheme heterojunction) concept was proposed to explain the increased charge transfer rate observed at the interface of two photocatalysts with staggered band structures [27]. Typically, a S-heterojunction photocatalyst is formed between a reduction photocatalyst and an oxidation photocatalyst. In general, reduction photocatalysts display comparatively higher conduction bands (CBs) and Fermi levels. On the contrary, oxidation photocatalysts exhibit comparatively lower CBs and Fermi levels. Intriguingly, WO₃, with a relatively narrow bandgap, between 2.4 and 2.8 eV [28], is a representative oxidation-type photocatalyst that is amenable to the fabrication of S-heterojunction composites. Owing to its large work function (6.23 eV) and low Fermi level [27], the electrons in the CB of WO₃ can scarcely exhibit a reduction capacity, based on thermodynamics [29], and are therefore relatively useless for photocatalytic H₂-evolution reactions. By taking advantage of the S-scheme charge transfer mechanism, the unnecessary electrons in the CB of WO₃ can be recombined with the comparatively useless holes in the valence band (VB) of TiO₂. Consequently, the separation of useful photoinduced charge carriers at the heterogeneous interface is promoted, and the high redox capacities of the electrons in the CB of TiO₂ and the holes in the VB of WO₃ are retained. Additionally, WO₃ demonstrates strong light absorption and great resistance to photocorrosion [30]. As reported, WO₃ can extend its light absorption range to the visible or even near infrared (NIR) region when coupled with TiO₂ to construct a TiO₂/WO₃ S-scheme heterojunction [31,32].

Reduced graphene oxide (rGO) with a two-dimensional (2D) honeycomb lamella of C atoms is a prospective candidate for the electron container and acceptor in heterogeneous photocatalytic systems that can facilitate the shuttling of photoexcited electrons for water-splitting reaction [33]. In addition to its excellent thermal conductivity and large carrier mobility, rGO exhibits a high theoretical specific surface area and thereby offers abundant adsorption and catalytic sites for photocatalytic reactions [34]. The presence of rGO can also extend the range

of light absorption to the visible region and even to the infrared region, which may induce a positive photothermal effect and increase the photocatalytic H₂ yield. Recently, ternary composite photocatalysts have emerged as alluring candidates for photocatalytic H₂ evolution because of their cooperative effect on the successive charge transfer occurring between three different components, such as ZnO–MoS₂–rGO [35], TiO₂–MnO_x–Pt [36], and g-C₃N₄/RP/MoS₂ (RP denotes red phosphorus) [37]. Therefore, it is desirable to fabricate a rGO-based composite photocatalyst to enhance the photocatalytic activity and stability [38].

Herein, we reported a facile one-step hydrothermal method to synthesize WO₃/TiO₂ S-heterojunction photocatalyst by graphene modification (WTG). TiO₂ and WO₃ formed a S-scheme heterostructure with a strong interaction at the interface, which facilitated charge transfer and separation. The S-scheme mechanism was evidenced by the greatly improved H₂ evolution performance. Additionally, rGO acted as a supporting matrix and an electron transfer channel, supplied surface active sites, enhanced the light absorption, and exhibited a unique photothermal effect in WTG composite. The cooperative effect of rGO and WO₃/TiO₂ heterojunction promoted the photocatalytic reaction. Consequently, WTG composites exhibited higher photocatalytic H₂ generation activities than pure TiO₂.

2. Experimental

2.1. Photocatalyst preparation

The WO₃/TiO₂/rGO composite was fabricated by a one-step hydrothermal approach. All the reagents employed were analytical grade and used without further purification. GO was synthesized from commercial graphite powder by using modified Hummer's method [39]. Typically, for the preparation of the WTG sample, a GO suspension (3 mL, 1 mg mL^{−1}) was diluted in a mixed solution of distilled water (35 mL) and ethanol (17.5 mL) and sonicated for 15 min. Then, D-(+)-glucose (20 mg) was dissolved in the GO suspension and stirred for 10 min. Subsequently, 1.3 mL of Ti(OC₄H₉)₄ (TBOT) as the Ti source, which was dissolved in ethanol (9 mL), was added dropwise to the mixture under magnetic stirring. After 30 min, 0.13 mmol of Na₂WO₄·2H₂O was added to the solution, and its pH was adjusted to 2 with hydrochloric acid (1 M). An hour later, the milky mixture was transferred to a Teflon-lined stainless-steel autoclave and kept at 180 °C for 12 h. The resultant dark grey precipitate was washed with distilled water and ethanol thoroughly and freeze-dried overnight to yield WO₃/TiO₂/rGO composite. In the composite, the theoretical mass ratio of rGO to TiO₂ was 1%, and the theoretical mass ratio of WO₃ to TiO₂ was 10%. The sample was designated as WTG.

Similarly, WO₃/TiO₂ was synthesized by following the same procedure as detailed above, except for the addition of GO. Likewise, TiO₂/rGO was prepared by removing the step involving Na₂WO₄·2H₂O and pH adjustment. Pristine WO₃ was produced from the Na₂WO₄·2H₂O solution of pH = 2. To prepare pure TiO₂, the TBOT ethanol solution was added to a mixture of distilled water and ethanol. All the samples were sub-

jected to the aforementioned hydrothermal process. The as-prepared WO₃/TiO₂, TiO₂/rGO, and pristine WO₃ and TiO₂ were designated as WT, TG, W, and T, respectively. Inductively coupled plasma (ICP)-optical emission spectrometry was conducted to investigate the actual contents of Ti and W elements. The results are listed in Table 1.

2.2. Characterization

Powder X-ray diffraction (XRD) was performed by using a D/MAX-RB diffractometer (Rigaku, Japan) with Cu K α radiation. To characterize the morphological structures and microscopic details of the samples, field-emission scanning electron microscopy (FESEM) images were obtained by using a JSM-7500F scanning electron microscope (SEM; JEOL, Japan). Transmission electron microscopy (TEM) was carried out by using a JEM-2100F instrument (JEOL, Japan) with an accelerating voltage of 200 kV. The pore size distribution and specific surface area were obtained from nitrogen (N₂) adsorption-desorption isotherms on a Micromeritics ASAP 2020 instrument. The specific surface area results were determined by using the adsorption data in the relative pressure (P/P_0) range 0.05–0.3. Raman spectra were recorded with the help of a micro-Raman spectrometer (Renishaw inVia, U.K.). X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 Xi electron spectrometer (Thermo Scientific Corporation, USA) to estimate the surface elemental composition and chemical states. To investigate the optical properties of the samples, the UV-vis diffuse reflectance spectra (DRS) were obtained by using a Shimadzu UV 2600 UV-vis spectrometer with BaSO₄ as the reference. The elemental contents were analyzed on an ICP-optical emission spectrometer (Prodigy 7, Leeman Labs Inc.).

2.3. Photocatalytic H₂ generation test

The photocatalytic activities of the samples were evaluated based on the photocatalytic yields of H₂ from water splitting in a 100 mL Pyrex flask. First, 50 mg of a sample was suspended by ultrasonication in 80 mL of 20 vol% aqueous methanol solution. Then, the sealed system was bubbled with N₂ for 0.5 h to ensure anaerobic conditions during photocatalytic water splitting. A 350 W Xe arc lamp was used as the light source. After an hour of irradiation, 0.4 mL of gas was extracted from the flask by using a syringe to analyze the H₂ concentration by gas chromatography (GC-14C, Shimadzu, Japan) with the assistance of a thermal conductivity detector. Photocatalytic H₂ production cycled tests were conducted by continuously sampling gas from the flask at an interval of an hour and rebubbling the solution with N₂ for 0.5 h every 3 h. The apparent quantum effi-

ciency (AQE) was measured under the irradiation of four low-power light-emitting diode (LED) lamps ($\lambda = 365$ nm). The AQE can be computed by the following equation.

$$\text{AQE} = \frac{2 \times \text{Amount of H}_2 \text{ yielded}}{\text{Total number of incident photons}} \times 100\% \quad (1)$$

2.4. Photoelectrode fabrication and photoelectrochemical measurements

Photoelectrochemical measurements were conducted on a typical three-electrode system by using a CHI-660C electrochemical workstation (Chenhua Instrument, Shanghai, China). A Pt wire and Ag/AgCl electrode were employed as the counter and reference electrodes, respectively. The working electrode was the photocatalyst film, which was deposited on the conductive surface of a F-doped tin oxide (FTO) glass with an active area of ca. 1 cm². The preparation process was as follows: 20 mg of the photocatalyst was added to 1 mL of ethanol and ground to a sticky slurry for approximately 0.5 h. Afterwards, the homogeneous paste was evenly applied on the conductive surface of the FTO glass by doctor blading technique and then dried in air. A LED ($\lambda = 365$ nm) with an intensity of ca. 44.0 mW cm⁻² acted as the light source. A volume of 20 mL of 0.5 M aqueous Na₂SO₄ solution was used as the electrolyte. The initial bias potential in the transient photocurrent responses and electrochemical impedance spectroscopy (EIS) tests was the open-circuit voltage.

3. Results and discussion

3.1. Physicochemical properties of the samples

A facile one-step hydrothermal method was utilized to fabricate the samples, and the as-obtained samples, including pristine WO₃ and TiO₂, WO₃/TiO₂, TiO₂/rGO, and WO₃/TiO₂/rGO, were designated as W, T, WT, TG, and WTG, respectively. The representative SEM images of WTG are shown in Fig. 1. The pristine TiO₂ and WO₃ tended to self-aggregate with the irregular bulk. However, for the WTG composites, the TiO₂ and WO₃ particles were homogeneously mixed, thus forming a WO₃/TiO₂ heterostructure via strong interactions between TiO₂ and WO₃. The particles were closely and evenly grown in-situ on the anchoring sites of GO, which implied that the graphene sheets

Table 1

Elemental contents of the prepared samples.

Sample	Ti (wt%)	W (wt%)
WTG	61.63	6.52
WT	63.17	6.58
TG	75.45	–

Fig. 1. (a, b) SEM images of the WTG samples; (c) EDS elemental maps of Ti, O, C, and W in the WTG sample.

prevented the TiO_2 and WO_3 nanoparticles from assembling as an underlying substrate in WTG. This intimate interaction is beneficial for electron transfer from the TiO_2 or WO_3 particles to the graphene sheet during photoexcitation. After the hydrothermal treatment, the rGO retained the morphology of micron-sized 2D sheets with spontaneous wrinkles. The TiO_2 and WO_3 nanoparticles adhering to the oxidized graphene prevented the naked sheets from restacking, thus preserving the active surfaces. In addition, in the EDS elemental mapping images of WTG (Fig. 1(c)), the distributions of C, O, Ti, and W elements all matched well with the outline of the FESEM image, which suggested that the TiO_2 and WO_3 particles were evenly decentralized on the surface of rGO.

For a better illustration of the microstructure, the $\text{WO}_3/\text{TiO}_2/\text{rGO}$ composite was characterized by TEM. Fig. 2(a) clearly shows that highly dispersed nanoparticles of TiO_2 and WO_3 were deposited on the surface of the transparent and wrinkled rGO nanosheets. The particle sizes were *ca.* 10 nm on average. Moreover, the WO_3 particles were tightly connected with the TiO_2 particles even after ultrasonication, which suggested the formation of a heterostructure interface instead of a simple physical mixture. In the HRTEM image (Fig. 2(b)), the lattice fringe spacings of 0.35 and 0.19 nm corresponded to the (101) and (200) planes of the TiO_2 nanoparticles [40], whereas the lattice spacing of 0.27 nm corresponded to the (022) planes of monoclinic WO_3 , which suggested that the WO_3 existed in the monoclinic form [10].

XRD (Fig. 3) was employed to investigate the phase structures of the samples. For the T sample, the characteristic diffraction peaks at 25.1° , 38.6° , 46.4° , and 55.1° well matched with those of anatase (JCPDS # 21-1272) [41]. The diffraction peaks of W indicated that WO_3 crystallized in the monoclinic phase (JCPDS # 71-2141) [30]. For TG, WT, and WTG, the observed characteristic peaks could be attributed to anatase. No evidence of a tungsten oxide phase was found in the XRD patterns of WTG and WT. Besides, no peak shift was observed in the composites, compared with the case of pristine TiO_2 , which suggested that the crystal structure of anatase was maintained. Similar broad diffraction peaks of the anatase phase were observed, which indicated small crystallite sizes. Monoclinic WO_3 was not observed in the WTG and WT samples, because the amount of WO_3 was too low to be revealed by XRD. The amounts of W element in WTG and WT were 6.52 and 6.58 wt%, respectively, which were obtained by ICP analysis. According to a previous report, WO_3 is present in the form of highly dispersed nanocrystallites or clusters when its content is very low. At least 8 wt% of WO_3 is necessary to cover the TiO_2

Fig. 2. TEM (a) and HRTEM (b) images of the WTG composite.

Fig. 3. XRD patterns of the T, W, TG, WT, and WTG samples.

surface with a monolayer, the thickness of which can be determined by XRD [42–44]. Moreover, after the hydrothermal treatment, no characteristic diffraction peak of GO or graphene was found in the patterns of TG and WTG, which was ascribed to the low concentration and inherently low diffraction intensity of rGO relative to those of metallic oxides [45].

Raman spectra were recorded to verify the presence of C in the composites and reveal the significant structural change from GO to rGO after the hydrothermal reaction. In Fig. 4(a), the Raman spectrum of GO showed two typical peaks at approximately 1351 cm^{-1} (D band) and 1586 cm^{-1} (G band), which were attributed to the breathing mode of the k-point phonons of A_{1g} symmetry and first-order scattering of the E_{2g} vibration mode of sp^2 -bonded C atoms [46], respectively. The D band moved to 1344 cm^{-1} for WTG, while the G band moved to 1600 cm^{-1} for both TG and WTG (Fig. 4(b)), which indicated the reduction of GO and interaction between rGO and particles [47]. In comparison with that of pure GO, the D/G intensity ratios (I_D/I_G) of WTG and TG apparently increased. The increase in I_D/I_G indicated that the size of the sp^2 domains within the plane decreased in terms of the average value, which further testified the transformation from GO to rGO [48,49]. For the T sample shown in Fig. 4(a), the several typical bands observed at 399, 518, and 640 cm^{-1} were ascribed to the $B_{1g(1)}$, $A_{1g} + B_{1g(2)}$, and $E_{g(2)}$ modes of anatase, respectively. For W, the major Raman bands at 807 and 717 cm^{-1} were ascribed to W–O stretching modes, and the other two bands at 273 and 327 cm^{-1} corresponded to the W–O bending modes of bridging O, which are characteristic of monoclinic WO_3 [50]. Bands of anatase were observed in the spectra of the corresponding composites, whereas no traces of monoclinic WO_3 were found in the WT and WTG samples. The results reflected the fact that the signal of WO_3 is too weak relative to that of TiO_2 . Strikingly, in the TiO_2 composites, no shift in the main Raman scattering bands was found, compared with the case of pure TiO_2 , which was sensitive to the insertion of ions into the TiO_2 unit cell, suggesting that ion diffusion had not occurred in the composites [51].

XPS was employed to investigate the surface chemical states

Fig. 4. (a) Raman spectra of the T, WT, WTG, TG, GO, and W samples; (b) enlarged spectra of the GO, TG, and WTG samples in the range 1100–1750 cm^{-1} .

of the WTG composite photocatalysts. Fig. 5(a) shows that the XPS C 1s pattern of the $\text{WO}_3/\text{TiO}_2/\text{rGO}$ composite can be deconvoluted into four peaks at 284.8, 285.3, 286.6, and 289.1 eV, which can be assigned to the surface adventitious C (C–C), epoxide and hydroxyl C (C–O), and carbonyl (C=O) and carboxyl (O–C=O) groups, respectively [52]. The results testified to the existence of rGO. The O 1s XPS pattern (Fig. 5(b)) displayed three peaks at 530.3, 531.9, and 533.2 eV, corresponding to lattice O (Ti–O, W–O), hydroxyl O (–OH), and the O of the C–O

or C=O bonds [53], respectively. Fig. 5(c) shows the high-resolution Ti 2p spectra of T, WTG, and WTG obtained under light irradiation that reveals two symmetrical peaks corresponding to $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ of TiO_2 , respectively [54]. Notably, the binding energy of Ti 2p for WTG showed a positive shift, compared with that for pristine TiO_2 , suggesting that electrons transferred from TiO_2 to rGO or WO_3 at the interfaces.

In the W 4f spectrum of W, shown in Fig. 5(d), the main peaks at approximately 37.7 and 35.6 eV are observed, which

Fig. 5. High-resolution XPS patterns of C 1s (a) and O 1s (b) of WTG composites; (c) in situ and ex situ XPS patterns of Ti 2p of T and WTG samples; (d) high-resolution XPS patterns of W 4f of W and WTG samples. The in situ XPS patterns were recorded under light irradiation.

Fig. 6. N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (insets) of the T and WT (a), and TG and WTG (b) samples.

result from $W 4f_{5/2}$ and $W 4f_{7/2}$ of W^{6+} , respectively [55]. Two shoulder peaks assigned to W^{5+} and centered at approximately 37.5 and 35.4 eV are also noticed [56]. The appearance of W^{5+} implied the existence of O vacancies, which was in accordance with the UV-vis DRS. From the peak areas, we could roughly estimate that the ratio of W^{5+} to W^{6+} was 0.279:1. For the WTG sample, a well-resolved doublet at 36.6 ($W 4f_{7/2}$) and 38.7 eV ($W 4f_{5/2}$) indicated the existence of the W^{6+} species of stoichiometric WO_3 [57], which overlapped with $Ti 3p$ at 37.6 eV [58]. Therefore, both TiO_2 and WO_3 were successfully anchored on the rGO nanosheets. As reported [56], the $W 4f$ peaks of the composite shifted to higher binding energies, which confirmed the massive decrease in the number of unsaturated W ions.

N_2 adsorption-desorption measurements were conducted to characterize the specific surface areas and pore size distributions of the samples. In Fig. 6, the representative N_2 adsorption-desorption isotherms of T and WT (Fig. 6(a)), and TG and WTG (Fig. 6(b)), correspond to type IV, which indicate the existence of large mesopores and macropores. According to the International Union of Pure and Applied Chemistry classification, the isotherms of the T and WT samples exhibited an obvious H2-type hysteresis with ink-bottle mesopores that are derived from the aggregation of the TiO_2 and WO_3 nanoparticles. For the TG and WTG samples shown in Fig. 6(b), the isotherms exhibited a combination of H2 and H3 hysteresis loops, which were associated with the pores caused by the aggregated nanoparticles and the slit-shaped mesopores due to the stacking of the rGO sheets [59], respectively. Accordingly, the Barret-Joyner-Halenda pore size distributions (shown in the insets of Fig. 6(a) and (b)) displayed a relatively wide range, 2–100 nm, with a distinct peak at ca. 10 nm, which coincided with the results of TEM analysis. In addition, the Brunauer-Emmett-Teller (BET) specific surface areas of WTG and TG (Table 2) were 165 and 160 $m^2 g^{-1}$, respectively, which were larger than those of the other two samples, indicating that the presence of graphene tended to boost the specific surface areas and provided abundant active sites for adsorption and surface reactions.

UV-vis DRS were utilized to determine the optical absorption properties of the samples (Fig. 7). Obviously, pure TiO_2 exhibited an intrinsic absorbance edge at 388 nm, which was

ascribed to its bandgap of 3.20 eV. For the W sample, WO_3 revealed a large light absorption edge at 466 nm, corresponding to its inherently narrow bandgap of 2.66 eV. Interestingly, the absorption curve of WO_3 revealed a slight increase from 500 to 900 nm, which was a combined result of the excitation via the $d \rightarrow d$ internal transitions of the W ions [60], polaron hopping [61], and the absorption induced by localized surface plasmon resonance [62]. In contrast with the commercial yellow-colored WO_3 , the blue-green color of the tungsten oxide obtained in this work (inset of Fig. 7) proved that it existed partially in its sub-stoichiometric phases, which was associated with the defect levels introduced by O vacancies below the CB. The presence of O vacancies was beneficial for the photocatalytic reactions [63]. The WO_3/TiO_2 composite displayed increased absorption in the wavelength range corresponding to the UV, visible, and NIR regions, which was attributed to the intrinsic optical absorption of TiO_2 and WO_3 with O vacancies. With the

Table 2

Texture properties of the prepared samples.

Sample	A_{BET} ($m^2 g^{-1}$)	PV ($cm^3 g^{-1}$)	APS (nm)
T	154	0.31	8.1
TG	160	0.35	8.9
WT	145	0.26	7.2
WTG	165	0.30	7.3

A_{BET} : specific surface area; PV : pore volume; APS : average pore size.

Fig. 7. UV-vis DRS of the T, W, WT, TG, and WTG samples. The insets show the colors of the corresponding samples.

introduction of graphene, the TG and WTG samples extended their broad background absorption range to the visible-light region, because graphene not only decreased the optical reflection but also was associated with the electronic transitions $n \rightarrow \pi^*$ between the n -orbits of the O species and graphene and the $\pi \rightarrow \pi^*$ of graphene [64]. Moreover, graphene can convert light to heat under optical irradiation, which accelerates the reaction. The photothermal conversion abilities of the samples were measured by using a thermos-imager. Fig. 8 exhibits the variations in the surface temperatures of the T, W, GO, and WTG samples. In fact, the surface temperatures of T and W changed slightly under LED illumination (365 nm, 44.0 mW cm^{-2}) for 20 s. Under the same conditions, the average temperatures of the GO and WTG surfaces increased by 9.1 and 4.5 $^{\circ}\text{C}$, respectively. These results revealed the photothermal conversion characteristic of GO.

Electron spin resonance (ESR) spectroscopy was employed to further monitor the presence and concentrations of O vacancies, as it is a pivotal tool that is used to examine unpaired spins in magnetism. Fig. 9 shows that the spectrum of WO_3 contains an asymmetric resonance signal (signal A), identified as that of W^{5+} [65], and another signal (signal B) at the g -value of 1.9036, which was typical of O (paramagnetic O^-) defects [66]. The pristine TiO_2 exhibited a weak, slightly anisotropic paramagnetic response that was centered at approximately $g = 2.0027$; it resulted from the localized $\text{Ti}^{3+} 3d^1$ states, which was consistent with the results of a previous study [67]. Notably, the spectrum of WT showed superparamagnetic behavior at $g = 2.0034$. The slight increase in g indicated interaction at the heterogeneous surface between TiO_2 and WO_3 , which influ-

Fig. 9. ESR spectra of the T, W, and WT samples.

enced the magnetic surroundings of the unpaired spins. Furthermore, the signal intensity was significantly enhanced, which reflected the increase in the concentration of O vacancies; this can be observed in the orange line of WT in the figure. The presence of O vacancies, which serve as shallow donors, is favorable for enhancing the electron density in n -type semiconductors and thus increasing the electrical conductivity. Moreover, they can improve the adsorption of surface species, making these composites attractive as photocatalytic materials [68].

3.2. Photocatalytic activity and stability

The performances of the photocatalysts in H_2 generation via water splitting were evaluated under irradiation with a Xe arc lamp. In the preliminary control experiments, we did not detect appreciable H_2 evolution in the absence of irradiation or photocatalysts, which suggested that H_2 was generated by photocatalysts through a series of reactions under irradiation. Fig. 10(a) shows that the W, G, and WG samples exhibit no H_2 generation activity, while pure TiO_2 displays a relatively low photocatalytic activity, attributable to the large recombination rate of the electrons in the CB and the holes in the VB. After combination with 1 wt% graphene, the H_2 evolution activity of the TG sample increased, and was approximately 2.6-fold that of pure TiO_2 , which was ascribed to the formation of a Schottky junction between TiO_2 and rGO. The electrons in the TiO_2 CB tended to migrate to rGO, with a lower Fermi level and greater carrier mobility, which inhibited the recombination of the charge carriers. Furthermore, the presence of rGO as an ideal support for photocatalytic reactions offered numerous adsorption and catalytic sites, which extended the light absorption range to the visible region and even to the IR region and induced a positive photothermal effect.

For the WT sample, the H_2 yield rate was $105.2 \mu\text{mol g}^{-1} \text{h}^{-1}$, which was approximately 1.5 times that of pure TiO_2 . Hence, the improved photocatalytic activity can not only be attributed to the improved light harvesting, because WT displayed limited UV-visible light absorption. This finding might be attributed to the formation of the WO_3/TiO_2 S-scheme heterostructure,

Fig. 8. Device schematics and changes in the surface temperatures of (a–c) T, (d–f) W, (g–i) GO, and (j–l) WTG samples under LED illumination (365 nm, 44.0 mW cm^{-2}) for 20 s.

Fig. 10. (a) Photocatalytic activities of the prepared samples; (b) the stability of the WO₃/TiO₂/rGO composite.

which expedited both the separation of useful electrons and holes and the recombination of relatively useless electrons and holes. Over the WTG composite, the H₂ evolution rate was greatly enhanced to 245.8 μmol g⁻¹ h⁻¹, which was approximately 2.3 times that over WT. Further, the AQE of the WTG composite was measured as 1.4% at the wavelength of 365 nm. The superior activity of WTG implied that rGO and the S-scheme heterojunction between WO₃ and TiO₂ had a positive synergistic effect that maximized the separation and transfer efficiency of the useful photogenerated electrons and holes. Fig. 10(c) shows the photocatalytic stability of the WTG sample, which was investigated over four consecutive cycles under the same conditions. Obviously, no remarkable deactivation was

detected after four runs, indicating that the WO₃/TiO₂/rGO composite displayed good stability.

3.3. Electrochemical properties

Photoelectrochemical measurements were employed to investigate the migration of the photoinduced charge carriers. Fig. 11(a) and (b) shows that all five samples exhibit relatively settled photocurrent curves with several on-off runs under intermittent ultraviolet (365 nm) irradiation. The WTG sample showed remarkably increased photocurrent density, compared with those of the other four monocomponent and dual-component photocatalysts, which was consistent with the

Fig. 11. Photoelectrochemical characteristics of the prepared samples. (a) Transient photocurrent responses (at 365 nm) of the as-prepared samples; (b) enlarged graphs of the W and WT samples; (c) EIS Nyquist plots of the T, W, TG, WT, and WTG samples; and (d) enlarged graphs of the W, WT, and TG samples.

photocatalytic performances. This increase in the photocurrent indicated an enhancement in the photogenerated charge carrier separation efficiency due to the TiO₂/WO₃ S-scheme heterostructure in the presence of the highly conductive rGO for electron transfer.

In addition, the photocurrent responses of the five samples revealed different characteristics. When light was turned off, the photocurrents of the T, W, and TG samples sharply dropped to zero. Afterwards, the photocurrent intensity of the W sample gradually increased even after the removal of irradiation, whereas those of the T and TG samples remained zero. By considering the change in the color of WO₃ to blue from yellow upon irradiation, we can deduce that electrons were released during reoxidation of W⁶⁺/W⁵⁺, which was reported in previous work [69,70]. By contrast, the photocurrents of the WT and WTG samples slowly decreased to zero upon turning off the light, due to the reversible oxidation of W⁵⁺ to W⁶⁺.

The charge transfer kinetics was further investigated by using EIS. Fig. 11(c) and (d) shows that the WTG sample displayed the smallest semicircle relative to those of the other samples, which suggested that the WO₃/TiO₂/rGO composite exhibited the lowest interfacial electron-transfer resistance, which was beneficial for improving the separation and migration rates of the photoinduced charge carriers.

3.4. Photocatalytic mechanism

The Mott-Schottky plots were analyzed to ascertain the band structures of the T and W samples. In Fig. 12, the Mott-Schottky plots of TiO₂ and WO₃ exhibited positive slopes at 1000 Hz, which was typically characteristic of an n-type semiconductor. From the x-intercepts, the extrapolated flat-band potentials of TiO₂ and WO₃ were obtained as −0.84 and −0.50 V versus the saturated Ag/AgCl reference electrode (pH = 7), respectively.

With reference to the Mott-Schottky plots, the flat-band potentials of TiO₂ and WO₃ can be calculated according to the following conversion formula:

$$E(\text{RHE}) = E(\text{Ag/AgCl}) + E^0 + 0.059 \text{ pH} \quad (2)$$

where $E^0(\text{Ag/AgCl}) = 0.197 \text{ V}$, and the flat-band potentials of

TiO₂ and WO₃ were −0.23 and 0.11 V (vs. RHE, pH = 0), respectively. It was speculated that the bandgaps of TiO₂ and WO₃ were approximately 3.2 and 2.6 eV, based on the UV-vis DRS. Both the CB and VB energy levels of TiO₂ were higher than those of WO₃. The redox potential of graphene/graphene•[−] was −0.08 V [71].

Thermodynamically, the CB electrons of WO₃ and the internal electrons of rGO cannot participate in the photocatalytic H₂-production reactions. Interestingly, the WO₃/TiO₂/rGO composite exhibited 3.5-fold H₂ evolution activity compared to that of pure TiO₂. If the charge carriers of the WTG sample are transferred in accordance with the traditional type-II model, the electrons in the CB of TiO₂ would migrate to the CB of WO₃ with decreased reduction ability, while the holes in the VB of WO₃ would migrate to the VB of TiO₂ with decreased oxidation ability, under illumination. However, transfer of the electrons accumulated in the CB of WO₃ to rGO would be thermodynamically unfavorable and retard the continual charge transfer from the CB of TiO₂. In this case, the WTG composite would show almost no photocatalytic H₂-production activity, which is distinctly opposite to the result obtained experimentally.

The TEM and XPS analyses showed that the S-scheme heterojunction was formed at the interface between TiO₂ and WO₃ in the WTG and WT samples. The work function of WO₃ is greater than that of TiO₂, and the difference drives the charge transfer from TiO₂ to WO₃ upon contact until the Fermi levels equilibrate [72]. Consequently, a built-in electric field can be formed at the heterogeneous interface that is directed from TiO₂ to WO₃ that favors the transfer and separation of the photogenerated charge carriers. In light of the S-scheme mechanism (Fig. 13), under optical irradiation, the relatively useless photoinduced electrons in the CB of WO₃ will migrate to the VB of TiO₂ via the intimate interface and recombine with the relatively useless holes under the driving force of the built-in electronic field. This process expedites the separation of the relatively useful electrons in the CB of TiO₂ and the holes in the VB of WO₃ and maintains their high reduction and oxidation abilities, respectively. Furthermore, the electrons collected in the CB of TiO₂ are prone to migration to the surface of rGO via the

Fig. 12. Mott-Schottky plots of W (a) and T (b) samples.

Fig. 13. Schematic illustration of the S-scheme heterojunction-based charge transfer mechanism in $\text{WO}_3/\text{TiO}_2/\text{rGO}$ composite.

Schottky junction owing to their 2D π -conjugation structure and relatively lower potential than the CB of TiO_2 , which facilitates free flow along the conductive network. The process further facilitates the migration of electrons, thus avoiding the accumulated electrons in the CB of TiO_2 from retarding the continual photocatalytic excitation of electron from the VB of TiO_2 in the S-scheme heterojunction system. As for the in situ XPS pattern of $\text{Ti } 2p$ of the WTG sample, the binding energy of $\text{Ti } 2p$ under light irradiation exhibited a slight shift relative to that measured in darkness, which was a result of the combination of the S-scheme heterojunction and the Schottky junction, where electrons migrated from WO_3 across TiO_2 to rGO. From a macroscopic viewpoint, the transfer of photogenerated electrons occurs like a “step,” with TiO_2 acting as a “bridge”.

In summary, in the ternary $\text{WO}_3/\text{TiO}_2/\text{rGO}$ composite system, the cross-coupling effect of rGO and the S-scheme heterojunction formed between TiO_2 and WO_3 suppresses the recombination of comparatively useful carriers and provides a variety of potential pathways for charge carrier transfer. In addition, the use of rGO as a supporting matrix can provide more surface-active sites and enhance the light absorption. The collective and positive synergy of rGO and the S-scheme heterojunction formed between TiO_2 and WO_3 results in a large driving force for the photocatalytic reaction, which increases the water-splitting H_2 -evolution activity.

4. Conclusions

We successfully fabricated a graphene-modified WO_3/TiO_2 S-scheme heterojunction photocatalyst. The WTG composite was prepared by a facile one-step hydrothermal approach, and exhibited superior photocatalytic activity for H_2 production through water splitting, which was 3.5-fold that of bare TiO_2 under the same conditions. It was observed that the positive cooperative effect between the S-scheme heterojunction formed between WO_3 and TiO_2 and the Schottky heterojunction formed between TiO_2 and graphene sheets could effectively suppress the recombination of useful carriers, enhance the light harvest, and increase the number of active sites for the reduction reaction. This work provides new insights for the design and fabrication of novel S-scheme heterojunction photocatalysts and highlights the potential of utilizing the unique properties of rGO to design inexpensive, active photocatalysts with durability and stability for H_2 production.

References

- [1] W. Yu, D. Xu, T. Peng, *J. Mater. Chem. A*, **2015**, 3, 19936–19947.
- [2] J. Fu, J. Yu, C. Jiang, B. Cheng, *Adv. Energy Mater.*, **2018**, 8, 1701503.
- [3] Q. Xu, L. Zhang, J. Yu, S. Wageh, A. A. Al-Ghamdi, M. Jaroniec, *Mater. Today*, **2018**, 21, 1042–1063.
- [4] M. Tapajna, R. Stoklas, D. Gregusova, F. Guemann, K. Husekova, S. Hascik, K. Frohlich, L. Toth, B. Pecz, F. Brunner, J. Kuzmik, *Appl. Surf. Sci.*, **2017**, 426, 656–661.
- [5] F. Ye, H. F. Li, H. T. Yu, S. Chen, X. Quan, *Appl. Surf. Sci.*, **2017**, 426, 177–184.
- [6] R. Shen, J. Xie, Q. Xiang, X. Chen, J. Jiang, X. Li, *Chin. J. Catal.*, **2019**, 40, 240–288.
- [7] D. C. Sun, W. Y. Yang, L. Zhou, W. Z. Sun, Q. Li, J. K. Shang, *Appl. Catal. B*, **2016**, 182, 85–93.
- [8] A. Y. Meng, B. C. Zhu, B. Zhong, L. Y. Zhang, B. Cheng, *Appl. Surf. Sci.*, **2017**, 422, 518–527.
- [9] T. Di, Q. Xu, W. Ho, H. Tang, Q. Xiang, J. Yu, *ChemCatChem*, **2019**, 11, 1394–1411.
- [10] W. Yu, J. Chen, T. Shang, L. Chen, L. Gu, T. Peng, *Appl. Catal. B*, **2017**, 219, 693–704.

Graphical Abstract

Chin. J. Catal., 2020, 41: 9–20 doi: S1872-2067(19)63382-6

Enhanced photocatalytic H_2 -production activity of WO_3/TiO_2 step-scheme heterojunction by graphene modification

Fei He, Aiyun Meng, Bei Cheng, Wingkei Ho *, Jiaguo Yu *

Wuhan University of Technology, China;

The Education University of Hong Kong, China;

King Abdulaziz University, Saudi Arabia

WO_3/TiO_2 S-scheme heterojunction photocatalysts modified by graphene (WTG) exhibited remarkably enhanced photocatalytic H_2 -production activities.

- [11] Y. Fu, Z. Li, Q. Liu, X. Yang, H. Tang, *Chinese J. Catal.*, **2017**, 38, 2160–2170.
- [12] S. Meng, X. Ning, T. Zhang, S. F. Chen, X. Fu, *Phys. Chem. Chem. Phys.*, **2015**, 17, 11577–11585.
- [13] F. C. Romeiro, M. A. Rodrigues, L. A. J. Silva, A. C. Catto, L. F. da Silva, E. Longo, E. Nossol, R. C. Lima, *Appl. Surf. Sci.*, **2017**, 423, 743–751.
- [14] S. Wang, B. Zhu, M. Liu, L. Zhang, J. Yu, M. Zhou, *Appl. Catal. B*, **2019**, 243, 19–26.
- [15] J. Low, B. Cheng, J. Yu, *Appl. Surf. Sci.*, **2017**, 392, 658–686.
- [16] Y. Li, F. T. Liu, Y. Chang, J. Wang, C. W. Wang, *Appl. Surf. Sci.*, **2017**, 426, 770–780.
- [17] Z. Wang, T. Hu, K. Dai, J. Zhang, C. Liang, *Chin. J. Catal.*, **2017**, 38, 2021–2029.
- [18] W. L. Dai, J. J. Yu, Y. Q. Deng, X. Hu, T. Y. Wang, X. B. Luo, *Appl. Surf. Sci.*, **2017**, 403, 230–239.
- [19] Y. K. Sohn, W. X. Huang, F. Taghipour, *Appl. Surf. Sci.*, **2017**, 396, 1696–1711.
- [20] X. Ma, Q. Xiang, Y. Liao, T. Wen, H. Zhang, *Appl. Surf. Sci.*, **2018**, 457, 846–855.
- [21] F. Y. Xu, Y. Le, B. Cheng, C. J. Jiang, *Appl. Surf. Sci.*, **2017**, 426, 333–341.
- [22] J. Li, Y. Peng, X. H. Qian, J. Lin, *Appl. Surf. Sci.*, **2018**, 452, 437–442.
- [23] K. Qi, B. Cheng, J. Yu, W. Ho, *Chin. J. Catal.*, **2017**, 38, 1936–1955.
- [24] W. Yu, S. Zhang, J. Chen, P. Xia, M. H. Richter, L. Chen, W. Xu, J. Jin, S. Chen, T. Peng, *J. Mater. Chem. A*, **2018**, 6, 15668–15674.
- [25] J. Xu, J. Yue, J. Niu, M. Chen, F. Teng, *Chin. J. Catal.*, **2018**, 39, 1910–1918.
- [26] J. Wang, Z. Zhang, X. Wang, Y. Shen, Y. Guo, P. K. Wong, R. Bai, *Chin. J. Catal.*, **2018**, 39, 1792–1803.
- [27] J. Fu, Q. Xu, J. Low, C. Jiang, J. Yu, *Appl. Catal. B*, **2019**, 243, 556–565.
- [28] J. Jin, J. Yu, D. Guo, C. Cui, W. Ho, *Small*, **2015**, 11, 5262–5271.
- [29] Y. P. Xie, G. Liu, L. Yin, H. M. Cheng, *J. Mater. Chem.*, **2012**, 22, 6746–6751.
- [30] L. Jiang, X. Yuan, G. Zeng, J. Liang, X. Chen, H. Yu, H. Wang, Z. Wu, J. Zhang, T. Xiong, *Appl. Catal. B*, **2018**, 227, 376–385.
- [31] D. Spanu, S. Recchia, S. Mohajernia, P. Schmuki, M. Altomare, *Appl. Catal. B*, **2018**, 237, 198–205.
- [32] H. Q. Gao, P. Zhang, J. H. Hu, J. M. Pan, J. J. Fan, G. S. Shao, *Appl. Surf. Sci.*, **2017**, 391, 211–217.
- [33] J. K. Mu, C. Y. Hou, G. Wang, X. M. Wang, Q. H. Zhang, Y. G. Li, H. Z. Wang, M. F. Zhu, *Adv. Mater.*, **2016**, 28, 9491–9497.
- [34] X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem. Rev.*, **2019**, 119, 3962–4179.
- [35] S. Kumar, N. L. Reddy, H. S. Kushwaha, A. Kumar, M. V. Shankar, K. Bhattacharyya, A. Halder, V. Krishnan, *ChemSusChem*, **2017**, 10, 3588–3603.
- [36] A. Meng, L. Zhang, B. Cheng, J. Yu, *ACS Appl. Mater. Interfaces*, **2019**, 11, 5581–5589.
- [37] H. Zhao, S. N. Sun, Y. Wu, P. P. Jiang, Y. M. Dong, Z. C. J. Xu, *Carbon*, **2017**, 119, 56–61.
- [38] Y. Lu, X. Cheng, G. Tian, H. Zhao, L. He, J. Hu, S.-M. Wu, Y. Dong, G.-G. Chang, S. Lenaerts, S. Siffert, G. Van Tendeloo, Z.-F. Li, L.-L. Xu, X.-Y. Yang, B.-L. Su, *Nano Energy*, **2018**, 47, 8–17.
- [39] H. Zou, B. He, P. Kuang, J. Yu, K. Fan, *Adv. Funct. Mater.*, **2018**, 28, 1706917.
- [40] L. Pan, J. Zhang, X. Jia, Y.-H. Ma, X. Zhang, L. Wang, J.-J. Zou, *Chin. J. Catal.*, **2017**, 38, 253–259.
- [41] B. Li, B. Xi, Z. Feng, Y. Lin, J. Liu, J. Feng, Y. Qian, S. Xiong, *Adv. Mater.*, **2018**, 30, 1705788.
- [42] B. Gao, Y. Ma, Y. Cao, W. Yang, J. Yao, *J. Phys. Chem. B*, **2006**, 110, 14391–14397.
- [43] K. K. Akurati, A. Vital, J. P. Dellemann, K. Michalow, T. Graule, D. Fetti, A. Baiker, *Appl. Catal. B*, **2008**, 79, 53–62.
- [44] A. Gutierrez-Alejandre, J. Ramirez, G. Busca, *Langmuir*, **1998**, 14, 630–639.
- [45] X. Li, J. G. Yu, S. Wageh, A. A. Al-Ghamdi, J. Xie, *Small*, **2016**, 12, 6640–6696.
- [46] D. Xu, L. Li, R. He, L. Qi, L. Zhang, B. Cheng, *Appl. Surf. Sci.*, **2018**, 434, 620–625.
- [47] Q. Xiang, J. Yu, M. Jaroniec, *J. Am. Chem. Soc.*, **2012**, 134, 6575–6578.
- [48] A. Kumar, L. Rout, L. S. K. Achary, A. Mohanty, R. S. Dhaka, P. Dash, *RSC Adv.*, **2016**, 6, 32074–32088.
- [49] A. H. Mady, M. L. Baynosa, D. Tuma, J. J. Shim, *Appl. Catal. B*, **2017**, 203, 416–427.
- [50] H. Khan, M. G. Rigamonti, G. S. Patience, D. C. Boffito, *Appl. Catal. B*, **2018**, 226, 311–323.
- [51] C. Sotelo-Vazquez, R. Quesada-Cabrera, M. Ling, D. O. Scanlon, A. Kafizas, P. K. Thakur, T. L. Lee, A. Taylor, G. W. Watson, R. G. Palgrave, J. R. Durrant, C. S. Blackman, I. P. Parkin, *Adv. Funct. Mater.*, **2017**, 27, 1605413.
- [52] J. Yu, J. Jin, B. Cheng, M. Jaroniec, *J. Mater. Chem. A*, **2014**, 2, 3407–3416.
- [53] J. H. Pan, W. I. Lee, *Chem. Mater.*, **2006**, 18, 847–853.
- [54] F. Xu, J. Zhang, B. Zhu, J. Yu, J. Xu, *Appl. Catal. B*, **2018**, 230, 194–202.
- [55] X. Zhou, X. Zheng, B. Yan, T. Xu, Q. Xu, *Appl. Surf. Sci.*, **2017**, 400, 57–63.
- [56] Q. Liu, F. Wang, H. Lin, Y. Xie, N. Tong, J. Lin, X. Zhang, Z. Zhang, X. Wang, *Catal. Sci. Technol.*, **2018**, 8, 4399–4406.
- [57] M. Seifollahi Bazarjani, M. Hojamberdiev, K. Morita, G. Zhu, G. Cherkashinin, C. Fasel, T. Herrmann, H. Breitzke, A. Gurlo, R. Riedel, *J. Am. Chem. Soc.*, **2013**, 135, 4467–4475.
- [58] M. Karbalaee Akbari, Z. Hai, Z. Wei, C. Detavernier, E. Solano, F. Verpoort, S. Zhuikov, *ACS Appl. Mater. Interfaces*, **2018**, 10, 10304–10314.
- [59] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.*, **2015**, 87, 1051–1069.
- [60] K. He, J. Xie, X. Luo, J. Wen, S. Ma, X. Li, Y. Fang, X. Zhang, *Chinese J. Catal.*, **2017**, 38, 240–252.
- [61] S. K. Deb, *Sol. Energy Mater. Sol. Cells*, **2008**, 92, 245–258.
- [62] S. Cong, F. Geng, Z. Zhao, *Adv. Mater.*, **2016**, 28, 10518–10528.
- [63] L. Liu, Y. Jiang, H. Zhao, J. Chen, J. Cheng, K. Yang, Y. Li, *ACS Catal.*, **2016**, 6, 1097–1108.
- [64] J. Low, B. Cheng, J. Yu, M. Jaroniec, *Energy Storage Mater.*, **2016**, 3, 24–35.
- [65] P. Srinivasa Rao, S. Bala Murali Krishna, S. Yusub, P. Ramesh Babu, C. Tirupataiah, D. Krishna Rao, *J. Mol. Struct.*, **2013**, 1036, 452–463.
- [66] N. Zhang, X. Li, Y. Liu, R. Long, M. Li, S. Chen, Z. Qi, C. Wang, L. Song, J. Jiang, Y. Xiong, *Small*, **2017**, 13, 1701354.
- [67] Z. Wang, C. Yang, T. Lin, H. Yin, P. Chen, D. Wan, F. Xu, F. Huang, J. Lin, X. Xie, M. Jiang, *Adv. Funct. Mater.*, **2013**, 23, 5444–5450.
- [68] Z.-F. Huang, J. Song, L. Pan, X. Zhang, L. Wang, J. J. Zou, *Adv. Mater.*, **2015**, 27, 5309–5327.
- [69] Z. He, J. Fu, B. Cheng, J. Yu, S. Cao, *Appl. Catal. B*, **2017**, 205, 104–111.
- [70] J. Fu, C. Bie, B. Cheng, C. Jiang, J. Yu, *ACS Sustain. Chem. Eng.*, **2018**, 6, 2767–2779.
- [71] J. Low, J. Yu, W. Ho, *J. Phys. Chem. Lett.*, **2015**, 6, 4244–4251.
- [72] J. Low, B. Dai, T. Tong, C. Jiang, J. Yu, *Adv. Mater.*, **2019**, 31, 1802981.

石墨烯修饰三氧化钨/二氧化钛S型异质结增强的光催化产氢活性

何 菲^a, 孟爱云^a, 程 蓓^a, Wingkei Ho^{b, #}, 余家国^{a, c, *}

^a武汉理工大学材料复合新技术国家重点实验室, 材料科学与工程国际化示范学院, 湖北武汉430070, 中国

^b香港教育大学科学与环境学系, 海洋污染国家重点实验室, 香港, 中国

^c沙特阿卜杜勒阿齐兹国王大学科学部物理系, 吉达21589, 沙特阿拉伯

摘要: 太阳光驱动的光催化分解水产氢是利用太阳能解决当前能源危机和环境问题的理想策略。二氧化钛由于其稳定、环境友好和成本低等优点受到广泛研究, 在光催化领域具有不可或缺的作用。然而, 纯二氧化钛光催化剂具有光生电子-空穴复合率高、太阳能利用率低等缺点, 使其在光催化产氢领域的应用受到限制。迄今为止, 人们探索了多种改性策略来提高二氧化钛的光催化活性, 如贵金属负载、金属或非金属元素掺杂、构建异质结等。

通过复合两个具有合适能带排布的半导体来构建异质结可以大大提高光生载流子的分离, 被认为是一种有效的解决方案。最近提出了一种新的S型异质结概念, 以解释不同半导体异质界面载流子转移分离的问题。S型异质结是在传统II型和Z型(液相Z型、全固态Z型、间接Z型、直接Z型)基础上提出的, 但又扬长避短, 优于传统II型和Z型。通常, S型异质结是由功函数较小、费米能级较高的还原型半导体光催化剂和功函数较大、费米能级较低的氧化型半导体光催化剂构建而成。三氧化钨禁带宽度较小(2.4–2.8 eV), 功函数较大, 是典型的氧化型光催化剂, 也是构建S型异质结的理想半导体光催化剂。根据S型电荷转移机制, 三氧化钨/二氧化钛复合物在光辐照下, 三氧化钨导带上相对无用的电子与二氧化钛价带上相对无用的空穴复合, 二氧化钛导带上还原能力较强的电子和三氧化钨价带上氧化能力较强的空穴得以保留, 从而在异质界面上实现了氧化还原能力较强的光生电子-空穴对的分离。同时, 石墨烯作为一种蜂窝状碳原子二维材料, 是理想的电子受体, 在异质结光催化剂中能及时转移电子。而且, 石墨烯具有较好的导热性和电子迁移率, 光吸收强, 比表面积大, 可为光催化反应提供丰富的吸附和活性位点, 已经被认为是一种重要催化剂载体和光电分解水产氢的有效共催化剂。

本文采用简便的一步水热法制备石墨烯修饰的三氧化钨/二氧化钛S型异质结光催化剂。光催化产氢性能测试表明, 三氧化钨/二氧化钛/石墨烯复合材料的光催化产氢速率显著提高($245.8 \mu\text{mol g}^{-1} \text{ h}^{-1}$), 约为纯 TiO_2 的3.5倍。高分辨透射电子显微镜、拉曼光谱和X射线光电子能谱结果证明了 TiO_2 和 WO_3 纳米颗粒的紧密接触, 并成功负载在还原氧化石墨烯(rGO)上。X射线光电子能谱中Ti 2p结合能的增加证实 TiO_2 和 WO_3 之间强的相互作用和S型异质结的形成。此外, 复合材料中的rGO大大拓展了复合物的光吸收范围(紫外-可见漫反射光谱), 增强了光热转换效应, 而且rGO与 TiO_2 之间形成肖特基结, 促进了 TiO_2 导带电子的转移和分离。总之, WO_3 和 TiO_2 的S型异质结与 TiO_2 和rGO之间的肖特基异质结的协同效应抑制了相对有用的电子和空穴的复合, 有利于氧化还原能力较强的载流子的分离和进一步转移, 加速了表面产氢动力学, 于是增强了三元复合光催化剂的光催化产氢活性。

关键词: 像梯形的异质结; S型异质结; S异质结; 光催化剂; 光解水产氢

收稿日期: 2019-02-28. 接受日期: 2019-04-16. 出版日期: 2020-01-05.

*通讯联系人. 电话: (027)87871029; 传真: (027)87879468; 电子信箱: jiaguoyu@yahoo.com

#通讯联系人. 电子信箱: keithho@eduhk.hk

基金来源: 国家自然科学基金(U1705251, 21871217, 21573170, 21433007); 国家重点研发计划项目 (2018YFB1502001).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).