available at www.sciencedirect.com

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

Article (Special Issue on the International Symposium on Environmental Catalysis (ISEC 2016))

Enhanced visible light photocatalytic H₂ production over Z-scheme g-C₃N₄ nanosheets/WO₃ nanorods nanocomposites loaded with Ni(OH)_x cocatalysts

Kelin He ^{a,b,c}, Jun Xie ^{a,b,c}, Xingyi Luo ^{a,c}, Jiuqing Wen ^{a,b,c}, Song Ma ^{a,b,c}, Xin Li ^{a,b,c,*}, Yueping Fang ^a, Xiangchao Zhang ^d

^a College of Materials and Energy, Guangzhou 510642, Guangdong, China

^b College of Forestry and Landscape Architecture, South China Agricultural University, Guangzhou 510642, Guangdong, China

^c Key Laboratory of Energy Plants Resource and Utilization, Ministry of Agriculture, Key Laboratory of Biomass Energy of Guangdong Regular Higher Education Institutions, Institute of New Energy and New Materials, South China Agricultural University, Guangzhou 510642, Guangdong, China

^d Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha 410022, Hunan, China

ARTICLE INFO

Article history:

Received 30 October 2016

Accepted 20 November 2016

Published 5 February 2017

Keywords:

Photocatalytic hydrogen evolution

Robust Ni(OH)_x cocatalyst

g-C₃N₄

Z-Scheme systems

Heterojunction

ABSTRACT

Novel WO₃/g-C₃N₄/Ni(OH)_x hybrids have been successfully synthesized by a two-step strategy of high temperature calcination and in situ photodeposition. Their photocatalytic performance was investigated using TEOA as a hole scavenger under visible light irradiation. The loading of WO₃ and Ni(OH)_x cocatalysts boosted the photocatalytic H₂ evolution efficiency of g-C₃N₄. WO₃/g-C₃N₄/Ni(OH)_x with 20 wt% defective WO₃ and 4.8 wt% Ni(OH)_x showed the highest hydrogen production rate of 576 μmol/(g·h), which was 5.7, 10.8 and 230 times higher than those of g-C₃N₄/4.8 wt% Ni(OH)_x, 20 wt% WO₃/C₃N₄ and g-C₃N₄ photocatalysts, respectively. The remarkably enhanced H₂ evolution performance was ascribed to the combination effects of the Z-scheme heterojunction (WO₃/g-C₃N₄) and loaded cocatalysts (Ni(OH)_x), which effectively inhibited the recombination of the photoexcited electron-hole pairs of g-C₃N₄ and improved both H₂ evolution and TEOA oxidation kinetics. The electron spin resonance spectra of •O₂⁻ and •OH radicals provided evidence for the Z-scheme charge separation mechanism. The loading of easily available Ni(OH)_x cocatalysts on the Z-scheme WO₃/g-C₃N₄ nanocomposites provided insights into constructing a robust multiple-heterojunction material for photocatalytic applications.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, extensive researches are focused on the development of sustainable and environmental friendly energy. Among various energy carriers, hydrogen is considered one of the most promising, green and alternative fuel sources and a

bridge to a sustainable energy future, which can effectively meet the increasing energy demands [1]. A more sustainable and green hydrogen production can be achieved by the heterogeneous photocatalysis with the aid of semiconductors and solar energy. Thus, heterogeneous hydrogen production from water splitting has gained worldwide research interest [2,3],

* Corresponding author. Tel: +86-20-85285633; Fax: +86-20-85285596; E-mail: xinliscau@yahoo.com

This work was supported by the National Natural Science Foundation of China (51672089), the Industry and Research Collaborative Innovation Major Projects of Guangzhou (201508020098), the State Key Laboratory of Advanced Technology for Material Synthesis and Processing (Wuhan University of Technology) (2015-KF-7) and the Hunan Key Laboratory of Applied Environmental Photocatalysis (Changsha University) (CCSU-XT-04). DOI: 10.1016/S1872-2067(17)62759-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 2, February 2017

since the photoelectrochemical water splitting was first reported by Fujishima and Honda in 1972 [4]. Metal oxide semiconductors, such as TiO_2 , are the most extensively applied photocatalysts for hydrogen generation from water splitting [5–8]. Nevertheless, these semiconductors exhibit some intrinsic disadvantages, such as low quantum yield and poor visible light harvesting, which largely restrict their practical implementation [8,9]. Efforts have been devoted to explore visible light H_2 generation photocatalysts by the modification of traditional wide band gap semiconductors or searching for new visible light semiconductors [2,5,8,10–14].

Recently, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) as a metal-free visible light semiconductor has been demonstrated for photocatalytic H_2 evolution [15–19], CO_2 reduction [16,20–25] and pollutant degradation [26–30] where it showed superior properties, such as high chemical stability, easy fabrication, low cost, excellent absorption properties, and a suitable band gap and position [15,21,24,31]. However, several challenges due to $\text{g-C}_3\text{N}_4$ itself, such as the rapid recombination of electron and hole pairs, and insufficient surface area and active sites leading to sluggish surface reaction kinetics and moderate oxidation ability gave a low photocatalytic H_2 evolution efficiency [21]. Therefore, various modification strategies, such as constructing Type II heterojunctions/Z-Scheme systems with other semiconductors, loading catalysts, fabricating nanostructures, and coupling with nanocarbons and their combinations have been employed to improve the visible light H_2 generation photoactivity of $\text{g-C}_3\text{N}_4$ photocatalysts [21,32–39]. Among these, the two interesting strategies of constructing Z-scheme systems [40–44] and loading catalysts [13,21,45–48] have effectively improved the thermodynamic oxidation ability and reduction kinetics of $\text{g-C}_3\text{N}_4$ photocatalysts, respectively.

Compared to traditional Type II heterojunctions, the artificial heterogeneous all solid state Z-Scheme photocatalytic systems without redox pairs simultaneously feature higher spatial charge separation efficiency and stronger redox ability by combining two narrow band gap semiconductors with enhanced visible light absorption [2,24,49]. In the past several years, various semiconductors with weak reduction ability of photo-generated electrons, such as TiO_2 [44], Bi_2WO_6 [40], WO_3 [41,50–53], Bi_2MoO_6 [42], Ag_3PO_4 [54,55] and ZnO [43], have been extensively employed to fabricate artificial $\text{g-C}_3\text{N}_4$ -based Z-scheme photocatalytic systems for different applications. Among these, the $\text{WO}_3/\text{g-C}_3\text{N}_4$ Z-scheme photocatalysts have attracted particular attention [41,50–53]. In this Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ photocatalytic system, the photo-generated electrons in the CB of WO_3 and the photo-generated holes in the VB of $\text{g-C}_3\text{N}_4$ are readily recombined, which retain the higher oxidation and reduction activity of WO_3 and $\text{g-C}_3\text{N}_4$, respectively, thus achieving significantly improved photocatalytic activity. For example, Cui et al. [41] synthesized Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts by a facile one-step simultaneously heating procedure. The results indicated that the Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ composites with 25 wt% WO_3 achieved the highest photo-degradation activity of Rhodamine B under visible light irradiation due to excellent surface properties, enhanced charge separation/migration rate and visible light absorption.

Similarly, the Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts prepared by ball milling and heat treatment exhibited greatly increased photocatalytic degradation activity towards methylene blue (MB) and fuchsin (BF) under visible light illumination. It was proposed that the photo-generated electrons and holes in $\text{g-C}_3\text{N}_4$ and WO_3 enhanced the formation rate of $\cdot\text{O}_2^-$ and active $\cdot\text{OH}$ radicals, respectively, thus leading to significantly enhanced Z-scheme photoactivity [51,53]. In another example, Ohno et al. [52] demonstrated that the Z-scheme $\text{g-C}_3\text{N}_4\text{-WO}_3$ composite photocatalysts fabricated by the planetary milling of $\text{g-C}_3\text{N}_4$ and WO_3 mixed powders exhibited the highest photocatalytic activity for multi-electron reduction of CO_2 to CH_3OH . The loading of Au catalysts on the hybrid Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ photocatalyst achieved 1.7 times higher photocatalytic activity, as compared to that of the hybrid photocatalyst without Au loading [52]. More interestingly, the Z-scheme reaction mechanism was also revealed by double beam photoacoustic spectroscopy, which further indicated the favorable charge separation and enhanced photocatalytic oxidation/reduction activity [52]. Katsumata et al. [50] synthesized Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite H_2 -evolution photocatalysts by simple calcination of the ground mixture of commercially available WO_3 nanoparticles and $\text{g-C}_3\text{N}_4$. The resulting 10 wt% $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite with 2 wt% Pt catalyst showed the highest photocatalytic H_2 production rate of 110 $\mu\text{mol}/(\text{h}\cdot\text{g})$, which was 2 times higher than that of pure $\text{g-C}_3\text{N}_4$. It was believed that the formation of $\text{WO}_3/\text{g-C}_3\text{N}_4$ Z-scheme junctions efficiently promoted charge separation, thus achieving enhanced photocatalytic H_2 evolution activity [50]. Clearly, in these Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts, the noble metals, such as Pt, Ag and Au, were utilized as catalyst to boost the photocatalytic reduction activity of the hybrid Z-Scheme systems [50,52]. However, their high cost and low natural abundance will significantly limit their practical large scale application. Although significant research efforts have been devoted to enhancing photocatalytic H_2 evolution over $\text{g-C}_3\text{N}_4$ decorated with non-noble metal catalysts [56], including nanocarbons, Ni, NiS, $\text{Ni}(\text{OH})_2$, WS_2 , MoS_2 and their composites [13,16,19,32,48,57–59], there have been scarce investigations on the surface deposition of suitable readily available catalysts on a hybrid Z-Scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ system for photocatalytic H_2 evolution. We believe that robust composite photocatalysts can be simply constructed by combining cheap and abundant H_2 evolution catalysts and favorable Z-Scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ systems.

In this study, the combined effects of cheap and abundant $\text{Ni}(\text{OH})_x$ as electron catalyst and WO_3 with strong oxidation activity were utilized to synergistically maximize the photocatalytic H_2 evolution activity of pure $\text{g-C}_3\text{N}_4$ nanosheets. The robust Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ photocatalyst was first fabricated by direct calcination of ammonium tungstate hydrate and thiourea, thus achieving intimate interfacial contact. Subsequently, the robust $\text{Ni}(\text{OH})_x$ nanoparticles as cocatalyst [60] were loaded onto the Z-scheme composites by in situ photo-deposition to further boost the Z-scheme charge separation and photocatalytic H_2 evolution kinetics. The fabrication of the hybrid composite is illustrated in Scheme 1. The H_2 evolution activity of the hybrid

$\text{WO}_3/\text{g-C}_3\text{N}_4/\text{Ni}(\text{OH})_x$ Z-scheme photocatalysts under visible light irradiation was investigated using an aqueous solution containing triethanolamine as electron donor. The results revealed that the hybrid $\text{WO}_3/\text{g-C}_3\text{N}_4/\text{Ni}(\text{OH})_x$ Z-scheme photocatalysts exhibited significantly enhanced photocatalytic H_2 evolution activity compared to bulk $\text{g-C}_3\text{N}_4$ and binary hybrids of $\text{WO}_3/\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{Ni}(\text{OH})_x$. It was proposed that the promoted Z-scheme charge separation and transfer between $\text{g-C}_3\text{N}_4$ and WO_3 as well as accelerated H_2 evolution kinetics on $\text{Ni}(\text{OH})_x$ nanoparticles played key roles in the photocatalytic enhancement mechanism for enhanced H_2 evolution activity over the composites. It is expected that the loading of readily available cocatalysts on Z-scheme $\text{WO}_3/\text{g-C}_3\text{N}_4$ nanocomposites can provide more insight into boosting the activity of robust heterojunction materials for photocatalytic applications.

2. Experimental

2.1. Materials

Ammonium tungstatehydrate ($(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$), sodium hypophosphite (NaH_2PO_2), nickel chloride (NiCl_2) and triethanolamine (TEOA) were reagent grade and used without further purification.

2.2. Synthesis methods

2.2.1. Synthesis of $\text{WO}_3/\text{g-C}_3\text{N}_4$

The $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite was prepared by in situ heating ammonium tungstate hydrate and thiourea. In a typical synthesis, an amount of ammonium tungstate hydrate and 10 g of thiourea were dissolved in 30 mL deionized water. The homogeneous solution was continuously stirred at 80 °C until almost all the water has evaporated. The resulting $\text{WO}_3/\text{g-C}_3\text{N}_4$ powders with different amounts of WO_3 were heated to 550 °C for 2 h in a muffle furnace at a heating rate of 4 °C/min. The product

was collected and ground into a light yellow powder. The mass ratios of WO_3 in the binary $\text{WO}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts were 5%, 10%, 20% and 40%. The corresponding samples were denoted as CW5, CW10, CW20, and CW40, respectively.

2.2.2. Synthesis of $\text{WO}_3/\text{g-C}_3\text{N}_4/\text{Ni}(\text{OH})_x$

The $\text{WO}_3/\text{g-C}_3\text{N}_4/\text{Ni}(\text{OH})_x$ composite was synthesized by a photo-deposition method in a previous report [61]. In a typical synthesis for the $\text{WO}_3/\text{g-C}_3\text{N}_4/4.8\%\text{Ni}(\text{OH})_x$ samples (with an optimum content of 4.8% $\text{Ni}(\text{OH})_x$ in the CW20 nanocomposites; detailed data shown in Table 1), 100 mg of $\text{WO}_3/\text{g-C}_3\text{N}_4$ powders, 21 mL of NaH_2PO_2 (0.1 mol/L aqueous solutions), 3 mL of NiCl_2 (0.1 mol/L aqueous solutions), 30 mL of triethanolamine (TEOA) and 46 mL water were successively added into a 100 mL flat-bottom flask at room temperature, and flushed by nitrogen for 30 min. After the mixture was exposed to UV-Vis light for 30 min, the black sample obtained was washed with deionized water to remove any remaining reagent.

2.3. Characterization

The X-ray diffraction (XRD) patterns were obtained using a MSAL-XD2 diffractometer at room temperature with $\text{Cu K}\alpha$ radiation (operated at 36 kV and 30 mA, $\lambda = 0.15406$ nm). The base pressure was 0.3 uPa. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG ESCALAB250 surface analysis system using a monochromatized Al X-ray source (300 W, 5 mA, and 15 kV). The base pressure was 0.3 uPa. The binding energy shift due to surface charging was corrected for using the C 1s level at 284.6 eV as an internal standard. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area. The pore size distribution was derived from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. UV-vis absorption was measured by a Shimadzu spectrophotometer (model 2501 PC). Photoluminescence (PL) spectra were measured using an LS50B apparatus (Perkin Elmer, Inc., USA) with an excitation wavelength of 385 nm at room temperature. Transmission electron microscopy (TEM) images were acquired on an F20 S-TWIN electron microscope (Tecnai G2, FEI Co) with the accelerating voltage of 200 kV. Lattice fringe measurements were collected on high resolution transmission electron microscopy (HRTEM) (Tecnai G2, FEI Co.) images. Mapping and the energy dispersive X-ray peaks (EDX) measurements were analyzed by an F20 S-TWIN electron microscope (200 kV accelerating voltage). Electron spin resonance (ESR) signals of radicals spin-trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were recorded at room temperature on a JES FA200 spectrometer.

Table 1

Preparation conditions for $\text{WO}_3/\text{g-C}_3\text{N}_4/\text{Ni}(\text{OH})_x$ samples.

Sample	NiCl_2 (0.1 mol/L)/mL	NaH_2PO_2 (0.1 mol/L)/mL	H_2O /mL	Average H_2 -production rate ($\mu\text{mol}/(\text{g}\cdot\text{h})$)
(A)CW20/ $\text{Ni}(\text{OH})_x$	2	14	54	285
(B)CW20/ $\text{Ni}(\text{OH})_x$	3	21	46	576
(C)CW20/ $\text{Ni}(\text{OH})_x$	4	28	38	289

Other conditions: 100 mg $\text{g-C}_3\text{N}_4$, 30 mL TEOA and 30 min UV irradiation.

2.4. Photocatalytic reaction

Photocatalytic water splitting was measured in a 100 mL Pyrex flask sealed with a silicone rubber septum at room temperature and atmospheric pressure (a 300 W Xe lamp). In a typical photocatalytic experiment, 50 mg of sample was suspended in an aqueous solution (80 mL) containing 15% triethanolamine. Prior to irradiation, all air in the reactor was removed by nitrogen bubbling for 30 min to completely remove dissolved oxygen to ensure anaerobic conditions. Afterwards, the suspension solution was irradiated while under continuous stirring (300 W Xe lamp, UV cut-off filter ($\lambda > 400$ nm)). 0.4 mL gas was intermittently sampled through the septum and analyzed by a gas chromatograph (GC-7900, TCD, nitrogen carrier gas and 5 Å molecular sieve column) after 1 h of illumination. The reaction was continued for 3 h.

2.5. Photoelectrochemical measurements

The working electrodes were prepared as follows: 5 mg photocatalyst powder was put into 2 mL of ethanol containing 20 μ L of 0.25% Nafion solution to make a slurry. Then, the powder was uniformly dispersed by ultrasonication. 500 μ L of the solution was deposited on a fluorine-doped tin oxide (FTO) glass substrate (2 cm $\times$ 6 cm). The resulting electrodes were calcined for 1 h at 150 $^{\circ}$ C (N_2 carrier gas). Transient photocurrent experiments were performed on an electrochemical analyzer (BAS100 Instruments) in a standard three-electrode system using the as-prepared electrodes as the working electrodes, a Pt plate as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode. A Xe lamp (300 W) with a UV cut-off filter ($\lambda > 420$ nm) was used as light source. The electrochemical impedance spectra (EIS) of the working electrodes in the three-electrode system were also recorded by a computer controlled IM6e impedance measurement unit (Zahner Elektrik, Germany) over a frequency range of 0.01–105 Hz with an AC amplitude of 0 mV in the dark or under visible light. Na_2SO_4 (0.1 mol/L) aqueous solution was used as the electrolyte.

2.6. Electrocatalytic hydrogen evolution

Electrocatalytic hydrogen evolution was tested using a three-electrode cell. Linear sweep voltammetry with a 5 mV/s scan rate was performed in H_2SO_4 electrolyte solution (0.5 mol/L) using a Pt plate as the counter electrode, and Ag/AgCl (saturated KCl) as reference electrode. The working electrodes were prepared as follows: 6 mg photocatalyst powder was ultrasonically dispersed in 2 mL deionized water (for > 2 h) and then deposited on the glassy carbon electrode with 3 μ L of the solution. After drying, 3 μ L of 0.5% Nafion solution (containing 10 vol% ethanol) was then added on top of the catalyst layer.

3. Results and discussion

3.1. Structure and composition of the photocatalysts

The phase structure of the samples was identified by powder XRD measurement. Fig. 1 presents the comparison of the XRD patterns of different samples. As shown in Fig. 1(a), g- C_3N_4 photocatalysts exhibited two main diffraction peaks at 27.4° and 13.0° , which were indexed as the (002) and (100) diffraction planes of layered g- C_3N_4 [JCPDS, No. 87-1526] [62]. The diffraction peaks located at 27.4° and 13.0° corresponded to the distance of 0.325 and 0.681 nm, which were assigned to the interlayer stacking of the aromatic system and in-planar-s-triazine structural packing motif composed of the tris-s-triazine units (ca. 0.73 nm), respectively [13,21,46,48,63]. The diffraction peaks of the WO_3 sample are consistent with those of orthorhombic WO_3 [JCPDS, No. 20-1324]. Further observation showed that the strong diffraction peaks of g- C_3N_4 decreased gradually with increasing contents of WO_3 (Fig. 3(b)), confirming the inhibited crystal structure diffraction of g- C_3N_4 by the hybrid WO_3 on its surface to some extent [53]. The g- C_3N_4 /4.8%Ni(OH) $_x$ composites in Fig. 1(b) exhibited a diffraction peak at 44.5° , which was attributed to the (111) and (220) diffraction planes of rhombohedral Ni [JCPDS, No. 87-0721] and Ni(OH) $_2$ [JCPDS, No. 87-0647], respectively, indicating the presence of facet-exposed Ni and Ni(OH) $_2$ nano-

Fig. 1. Powder XRD patterns of (a) g- C_3N_4 (1), WO_3 (2), CW20 (3) and (b) g- C_3N_4 /4.8%Ni(OH) $_x$ and hybrid WO_3 /g- C_3N_4 /4.8%Ni(OH) $_x$ samples.

crystals in the nanocomposites. Notably, there was no significant shift or decrease of the strong characteristic diffraction peaks of g-C₃N₄ and WO₃ after deposition of Ni(OH)_x nanoparticles, implying that the Ni(OH)_x nanoparticles were deposited on the surface of g-C₃N₄, rather than doped into the lattices of g-C₃N₄ and WO₃. All the results clearly confirmed that WO₃/g-C₃N₄ composites have been successfully constructed and that Ni(OH)_x nanoparticles were highly dispersed on the surface of the WO₃/g-C₃N₄ composites.

The composition and chemical state of the CW20/4.8%Ni(OH)_x composites were further measured by XPS. The XPS broad spectrum of the CW20/4.8%Ni(OH)_x composites revealed the existence of Ni, W, C and N (Fig. 2(a)). There were three nickel peaks in the Ni 2*p* spectrum (Fig. 2(b)) at binding energies of 852.6, 855.6 and 862.1 eV. The peak at 852.6 eV was assigned to trace metallic nickel [61], while the other two peaks with the binding energies of 855.6 and 862.1 eV match well the reported values of nickel hydroxide [59]. The W 4*f* XPS peak (Fig. 2(c)) was fitted into four peaks. Clearly, the two stronger peaks at 37.6 eV and 35.5 eV corresponded to the W 4*f*_{5/2} and W 4*f*_{7/2} states of W⁶⁺, while the two weaker peaks at 34.3 eV and 36.3 eV were assigned to the W 4*f*_{5/2} and W 4*f*_{7/2} states of W⁵⁺, indicating the generation of oxygen vacancies during the manufacturing process [64]. The two carbon species binding energies in the C 1*s* spectrum (Fig. 2(d)) were 288.1 and 284.6 eV, which were ascribed to *sp*²-bonded carbon (N–C=N) and *sp*² C–C bonds, respectively. The N 1*s* spectra in Fig. 2(e) showed four peaks at 404.4, 401.4, 400.3 and 398.7 eV, which were assigned to π -excitation, amino functional groups with a hydrogen atom (C–N–H), tertiarynitrogen (N–(C)₃) and *sp*²-hybridized nitrogen (C=N–C) involved in triazine rings, respectively [13, 21]. Additionally, it was found by XPS that the total mass content of Ni(OH)_x nanoparticles was 4.8 wt%. Further observation also revealed that these Ni(OH)_x nanoparticles

were composed of 97.4 mol%Ni(OH)₂ and 2.6 mol%Ni⁰, indicating that Ni(OH)₂ was the main active catalyst in our studied systems. In summary, the XPS measurements further confirmed that Ni(OH)_x nanoparticles (4.8 wt%) with 97.4 mol%Ni(OH)₂ and 2.6 mol%Ni⁰ were successfully loaded onto the surface of the Z-scheme g-C₃N₄/WO₃ nanophotocatalysts.

The morphology and microstructure of WO₃ and Ni(OH)_x in the composites were investigated by TEM measurements. Fig. 3(a–d) illustrate the TEM micrographs of CW20-4.8%Ni(OH)_x. As observed from Fig. 3(a) and 3(b), the g-C₃N₄ photocatalysts exhibited a 2D nanosheet morphology and that WO₃ nanorods with diameters of 20–40 nm were deposited on the surface of the g-C₃N₄ nanosheets with high dispersion, in good agreement with reported results in the literature. In fact, it was observed from Fig. 3(b) that some monodisperse Ni(OH)_x nanoparticles with sizes from 20 to 50 nm were well dispersed on the surface of the 2D g-C₃N₄ nanosheets [65]. The HRTEM images are displayed in Fig. 3(c) and 3(d). From Fig. 3(c), it can be readily observed that the interplanar *d*-spacing of 0.263 nm is consistent with the spacing of the (220) plane of orthorhombic WO₃. Fig. 3(d) displays the ordered lattice fringes with the interplanar *d*-spacing of 0.2034 nm, which was ascribed to the (111) crystallographic plane of rhombohedral Ni NPs [61], while the interplanar spacing of 0.226 nm corresponded to the interplanar distance of the (111) plane of Ni(OH)₂ [66]. Clearly, the intimate interface contact between Ni(OH)_x, WO₃ and g-C₃N₄ can be easily identified in Fig. 3(d), which was believed to favor the charge transfer/separation between them, thus prolonging the lifetime of charge carriers and facilitating photoactivity. Fig. 2(e–j) show the SEM and corresponding EDX mapping images of the CW20/4.8%Ni(OH)_x sample. The EDX mapping results further confirmed the existence of Ni, W, C, N and O in the CW20/4.8%Ni(OH)_x sample, suggesting the successful formation of hybrids of g-C₃N₄, WO₃ and Ni(OH)_x NPs.

Fig. 2. XPS broad spectrum (a), high resolution XPS spectra of the Ni 2*p* (b), W 4*f* (c), C 1*s* (d) and N 1*s* (e) of the CW20/4.8%Ni(OH)_x sample.

Fig. 3. (a, b) TEM images, (c, d) HRTEM image of CW20/4.8%Ni(OH)_x and (f–j) corresponding EDX mapping of CW20/4.8%Ni(OH)_x of the region shown in (e).

All these results further confirmed the successful photo-deposition of Ni(OH)_x NPs on the Z-Scheme CW20 composites.

The BET surface area and pore structure of typical composite photocatalysts were investigated using nitrogen adsorption isotherms. Nitrogen adsorption isotherms and the corresponding pore size distribution curves (inset) of g-C₃N₄, CW20, g-C₃N₄/4.8%Ni(OH)_x and CW20/4.8%Ni(OH)_x samples are shown in Fig. 4. Clearly, the four different samples exhibited similar Type V isotherms with H3 hysteresis loops, showing the existence of mesoporous structure in the four samples [67]. In general, the H3 loop is formed by non-rigid aggregates of plate-like g-C₃N₄ particles or a pore network consisting of incompletely filled macropores with pore condensate [67]. The corresponding pore size distribution curves of the four samples showed broad peaks at 2–200 nm, further confirming the existence of mesopores and macropores (inset in Fig. 4). The surface and texture properties of the four products are summa-

rized in Table 2. As shown in Table 1, the BET surface area of g-C₃N₄, CW20, g-C₃N₄/4.8%Ni(OH)_x and CW20/4.8%Ni(OH)_x samples were 12.80, 30.85, 8.40 and 18.18 m²/g, respectively. Clearly, the WO₃ sample exhibited the largest BET surface area, whereas the g-C₃N₄/4.8%Ni(OH)_x sample possesses the smallest *A*_{BET} values. It was also observed from Table 2 that all four samples displayed mean mesopore diameters between 27 and 30 nm [68]. Notably, compared to the g-C₃N₄ sample, the g-C₃N₄/4.8%Ni(OH)_x photocatalyst showed a significant decrease in pore volume and BET specific surface, but a small increase in pore diameter, which was due to the filling of the micropores in g-C₃N₄ by Ni(OH)_x nanoparticles [69]. It should be also noted that the pore volume and surface area of the binary CW20 and CW20/4.8%Ni(OH)_x hybrids were much higher than those of the pure g-C₃N₄ sample, suggesting that the addition of WO₃ with well-developed meso/macroposity played an important role in enhancing the surface area and pore volume of g-C₃N₄. All these results indicated that the improvements in the pore volume and surface area of CW20/4.8%Ni(OH)_x are beneficial for boosting its photocatalytic H₂-evolution activity.

3.2. Optical properties of the photocatalysts

The optical properties of the photocatalysts were determined by UV-Vis diffuse reflectance spectroscopy. Fig. 5(a) shows the absorption spectra of the WO₃/g-C₃N₄/Ni(OH)_x, WO₃/g-C₃N₄, g-C₃N₄/Ni(OH)_x, g-C₃N₄ and WO₃ photocatalysts. As shown in Fig. 5(a), all composite samples exhibited absorption edges at 450 nm corresponding to a band gap of 2.7 eV. Increasing the content of WO₃ led to a slight red shift of the

Fig. 4. Nitrogen adsorption isotherms and the pore size distribution curves (inset) of g-C₃N₄, CW20, g-C₃N₄/4.8%Ni(OH)_x and CW20/4.8%Ni(OH)_x samples.

Table 2

Pore structure parameters of different samples.

Photocatalyst	<i>A</i> _{BET} (m ² /g)	Mean pore diameter (nm)	Pore volume (cm ³ /g)
g-C ₃ N ₄	12.80	27.86	0.134
CW20	30.85	37.38	0.258
g-C ₃ N ₄ /4.8%Ni(OH) _x	8.40	30.50	0.104
CW20/4.8%Ni(OH) _x	18.18	30.17	0.182

Fig. 5. (a) UV-Vis absorption spectra of the photocatalysts; (b) Tauc plots of the UV-Vis spectra.

absorption edge between 400 and 500 nm, due to the smaller band gap of WO₃. The band gaps of the photocatalysts can be calculated by the equation [2]:

$$\alpha = A(h\nu - E_g)^{n/2} / h\nu$$

where α , A , h , ν and E_g are the absorption coefficient, proportionality constant, Planck's constant, and frequency of the incident light and band energy, respectively, and n is 1 for the direct transition. The band gap energies of the different samples can be obtained by the intercept of the tangent on the horizontal axis in the corresponding Tauc plots of the $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$), shown in Fig. 5(b). The band gaps of WO₃ and g-C₃N₄ were determined to be 2.46 and 2.66 eV, respectively. Clearly, the band gap of WO₃ was obviously smaller than the reported value (2.7 eV), further indicating the existence of oxygen defects in the WO₃. Although the loading of Ni(OH)_x does not affect the band gap of g-C₃N₄, it was also observed that the deposition of Ni(OH)_x greatly enhanced the visible light absorption of g-C₃N₄, coincident with the color change of the samples from yellow to black. It was believed that the enhanced visible light absorption of CW20/4.8%Ni(OH)_x photocatalysts is beneficial for the formation of photo-generated electron-hole pairs, thus favoring improved photocatalytic H₂ production.

3.3. Activity and stability of the photocatalysts

The photocatalytic H₂ evolution activity over different nanocomposites was evaluated using 80 mL of deionized water containing 15 vol%TEOA as hole scavenger under visible light irradiation ($\lambda > 400$ nm). Fig. 6(a) shows the photocatalytic H₂ production rate over WO₃/C₃N₄/4.8%Ni(OH)_x loaded with different contents of WO₃ (0, 5 wt%, 10 wt%, 20 wt% and 40 wt%) under visible light irradiation. The photocatalytic H₂ evolution activity over bare g-C₃N₄ can be neglected due to the fast recombination of photo-generated charge carriers. The H₂ evolution rates over all of other photocatalyst systems linearly increased with increasing irradiation time, fully indicating the achievement of photocatalytic H₂ generation. As shown in Fig. 6(a), the H₂ production yield was 2.5, 53, 101, 145, 278, 576 and 247 $\mu\text{mol}/(\text{g}\cdot\text{h})$ for g-C₃N₄, CW20, g-C₃N₄/4.8%Ni(OH)_x,

CW5/4.8%Ni(OH)_x, CW10/4.8%Ni(OH)_x, CW20/4.8%Ni(OH)_x and CW40/4.8%Ni(OH)_x, respectively. The improvement in the photocatalytic H₂ evolution activity by two orders of magnitudes can be ascribed to the synergistic effects of Z-scheme charge separation and loaded Ni(OH)_x cocatalysts. Moreover, the optimal amount of Ni(OH)_x cocatalysts loaded on CW20 was found to be 4.8 wt%, shown in Table 1. Further increasing the content of Ni(OH)_x led to a decrease in the H₂ production rate, due to the inevitable mask effect [13,70]. The CW20/4.8%Ni(OH)_x sample showed the highest hydrogen production efficiency (576 $\mu\text{mol}/(\text{g}\cdot\text{h})$), which was 5.7, 10.8 and 230 times more than those of g-C₃N₄/4.8%Ni(OH)_x, CW20 and g-C₃N₄ photocatalysts, respectively (Fig. 6(b)). The results demonstrated that the superior photocatalytic hydrogen generation activity of CW20/4.8%Ni(OH)_x was associated with the formation of the Z-Scheme heterojunction and the loading of Ni(OH)_x cocatalysts.

Apart from the photoactivity, the stability of H₂ evolution photocatalyst is crucial for practical and large scale application. To examine the stability of the CW20/4.8%Ni(OH)_x samples, the recycled activity of CW20/4.8%Ni(OH)_x was performed under identical conditions. Fig. 6(c) illustrates the results of recycling tests of the CW20/4.8%Ni(OH)_x sample under visible light irradiation (> 400 nm). As observed from Fig. 6(c), after four consecutive runs under visible light illumination, 78% of the original photocatalytic H₂ evolution activity over our hybrid CW20/4.8%Ni(OH)_x photocatalyst was retained, indicating its excellent photostability. The slight loss of photocatalytic H₂ production activity was attributed to the slow fall-off of Ni(OH)_x NPs from the Z-Scheme CW20 heterojunction.

3.4. Charge separation performance of the photocatalysts

In order to study the improved charge separation of the hybrid photocatalysts, PL spectra analysis was employed to reveal the migration of the charges. PL spectra of g-C₃N₄, CW20, g-C₃N₄/4.8%Ni(OH)_x and CW20/4.8%Ni(OH)_x samples were measured and shown in Fig. 7(a). The emission peak of g-C₃N₄ nanosheets at 450–475 nm was attributed to the band-band PL

Fig. 6. (a) Comparison of photocatalytic H₂ production over g-C₃N₄ (1), CW20 (2), g-C₃N₄/4.8%Ni(OH)_x (3), CW5/4.8%Ni(OH)_x (4), CW10/4.8%Ni(OH)_x (5), CW20/4.8%Ni(OH)_x (6), CW40/4.8%Ni(OH)_x (7); (b) Rate of H₂ evolution over g-C₃N₄ (1), CW20 (2), g-C₃N₄/4.8%Ni(OH)_x (3), CW20/4.8%Ni(OH)_x (4); (c) Recycling tests of photocatalytic H₂ production over CW20/4.8%Ni(OH)_x. Measurement conditions: 50 mg catalyst; 68 mL distilled water; 12 mL TEOA; Light source: a 300 W Xe lamp with UV cut-off filter (> 400 nm).

corresponding to their band gap energy [71,72]. It is generally acknowledged that a weaker PL intensity represents more efficient charge separation [73]. As observed in Fig. 7(a), the emission peak of CW20/4.8%Ni(OH)_x sample was much lower than that of g-C₃N₄/4.8%Ni(OH)_x, indicating the more efficient charge separation and transport for the CW20/4.8%Ni(OH)_x photocatalyst [74]. It was also obvious that the PL emission intensity of CW20/4.8%Ni(OH)_x was relatively lower than that of CW20. This result indicated that the addition of Ni(OH)_x significantly inhibited charge-carrier recombination.

The interfacial charge-hole separation effect of the WO₃/g-C₃N₄ composites was further characterized by electrochemical impedance spectra (EIS) analysis. EIS analysis is a useful tool to investigate interfacial charge-carrier transfer and migration [32,75,76]. A smaller radius of the arc on the EIS spectra reveals more efficiently improved interfacial charge migration mobility and decreased solid state layer resistance. Fig. 7(b) shows the EIS Nyquist plots of the CW20/4.8%Ni(OH)_x, WO₃/g-C₃N₄, g-C₃N₄/4.8%Ni(OH)_x and C₃N₄ composites. It was obvious that the CW20/4.8%Ni(OH)_x composites exhibited the smallest semicircle in the mid-frequency region, compared with those of WO₃/g-C₃N₄, g-C₃N₄/4.8%Ni(OH)_x and C₃N₄ [77], indicating its fastest interfacial charge transfer due to the formation of the favorable

Z-Scheme and g-C₃N₄/Ni(OH)_x junction in the hybrids.

To further demonstrate the promoted separation efficiency of photo-induced charge carriers, the transient photocurrent response was also investigated in 0.5 mol/L Na₂SO₄ aqueous solution at 0.2 V vs Ag/AgCl under visible light irradiation. As indicated in Fig. 7(c), it is obvious that the photocurrent density of CW20/4.8%Ni(OH)_x was higher than those of g-C₃N₄, CW20 and g-C₃N₄/4.8%Ni(OH)_x, indicating that these photo-induced electrons and holes were quickly transported to the substrate and the electrolyte, respectively [78]. Especially, it should be noted that the photocurrent of g-C₃N₄/4.8%Ni(OH)_x sample is a little smaller than that of CW20, demonstrating that the Z-Scheme systems could achieve the efficient transfer of a larger quantity of photo-excited electrons to the back electrode, as compares to the g-C₃N₄/Ni(OH)_x composites, which might be due to the simultaneously effective excitation of WO₃ and g-C₃N₄ in Z-Scheme systems under visible light [52]. Nevertheless, these PEC results showed that the effectively inhibited recombination of photo-induced electrons and holes was simultaneously achieved by both Z-Scheme system and Ni(OH)_x cocatalyst loading.

3.5. Discussion of the mechanism

Fig. 7. (a) Room temperature PL spectra of $\text{g-C}_3\text{N}_4$ (1), CW20 (2), $\text{g-C}_3\text{N}_4/4.8\%\text{Ni}(\text{OH})_x$ (3) and $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$ (4); (b) Nyquist plots of $\text{g-C}_3\text{N}_4$ (1), CW20 (2), $\text{g-C}_3\text{N}_4/4.8\%\text{Ni}(\text{OH})_x$ (3) and $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$ (4) in 0.1 mol/L Na_2S and 0.02 mol/L Na_2SO_3 aqueous solution in the dark; (c) Transient photocurrent responses of $\text{g-C}_3\text{N}_4$ (1), CW20 (2), $\text{g-C}_3\text{N}_4/4.8\%\text{Ni}(\text{OH})_x$ (3) and $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$ (4) in 0.5 mol/L Na_2SO_4 aqueous solution at 0.2 V vs Ag/AgCl under visible light irradiation; (d) Polarization curves of $\text{Ni}(\text{OH})_x$, WO_3 , $\text{g-C}_3\text{N}_4$, CW20 , $\text{g-C}_3\text{N}_4/4.8\%\text{Ni}(\text{OH})_x$ and $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$ measured at a scan rate of 5 mV/s in H_2SO_4 solution (0.5 mol/L).

The enhanced surface H_2 -evolution kinetics can be further identified by the polarization curves. Fig. 7(d) shows polarization curves of the $\text{g-C}_3\text{N}_4$, Ni , WO_3 , CW20 , $\text{g-C}_3\text{N}_4/4.8\%\text{Ni}(\text{OH})_x$ and $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$ composite photocatalysts. The cathodic current ranging from -0.4 to -1.5 V vs Ag/AgCl was attributed to electrocatalytic H_2 evolution. Clearly, the pure $\text{Ni}(\text{OH})_x$ nanoparticles exhibited the lowest electrocatalytic H_2 evolution over-potential among all the test catalysts, indicating the important roles of $\text{Ni}(\text{OH})_x$ as catalyst in promoting the electrocatalytic hydrogen evolution kinetics. More interestingly, it was also observed from Fig. 7(d) that the defective WO_3 Z-Scheme component exhibited a much better electrocatalytic H_2 evolution activity than $\text{g-C}_3\text{N}_4$, indicating that the defective WO_3 itself was a potential H_2 evolution cocatalyst. As a result, the combination effects of the defective WO_3 Z-Scheme component and $\text{Ni}(\text{OH})_x$ cocatalysts achieved significantly improved H_2 evolution over $\text{g-C}_3\text{N}_4$ through lowering the H_2 evolution over-potential.

To further confirm the Z-Scheme mechanism, the ESR spin-trapping technique of superoxide and hydroxyl radicals using DMPO as trapping agent was used to detect the change of the active oxidizing species in aqueous systems. The ESR signals of $\text{DMPO}\cdot\text{O}_2^-$ (Fig. 8(a)) and $\text{DMPO}\cdot\text{OH}$ (Fig. 8(b)) radicals are

displayed under the same conditions for $\text{g-C}_3\text{N}_4$, CW20 and $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$. As shown in Fig. 8, no ESR signal was displayed in the dark, whereas four-line ESR signals of $\cdot\text{O}_2^-$ (Fig. 8(a)) and $\cdot\text{OH}$ (Fig. 8(b)) radicals were clearly observed under visible light irradiation. Furthermore, the intensity of the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radical signals was greatly enhanced with increasing irradiation time, indicating the important role of light irradiation. Compared with the curves of $\text{g-C}_3\text{N}_4$, the CW20 sample exhibited significantly enhanced ESR signals of both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals, confirming the Z-scheme charge separation mechanism. More interestingly, the formation rates of both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals over the $\text{CW20}/4.8\%\text{Ni}(\text{OH})_x$ sample were faster than those of $\text{g-C}_3\text{N}_4$ and CW20 , indicating the excellent synergistic effect of Z-scheme charge separation and cocatalyst loading. It is believed that the $\text{Ni}(\text{OH})_x$ cocatalyst achieved the accelerated formation of $\cdot\text{O}_2^-$ driven by the photo-induced electrons of $\text{g-C}_3\text{N}_4$ and the promoted recombination of the hole and electron of $\text{g-C}_3\text{N}_4$ and WO_3 , respectively, thus leading to the significantly enhanced signals of both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals in the Z-scheme nanocomposites. Accordingly, the ESR spectra of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals provided strong evidence for the Z-scheme charge separation mechanism.

By considering all the above results of charge separation,

Fig. 8. DMPO spin-trapping ESR spectra of g-C₃N₄, CW20 and CW20/4.8%Ni(OH)_x. (a) DMPO·O₂⁻; (b) DMPO·OH.

charge utilization and photocatalytic H₂ evolution activity, we can suggest the Z-scheme charge separation mechanism from the charge kinetics (Scheme 2). The reduction potential of Ni²⁺ (Ni²⁺ + 2e⁻ → Ni(s)) and Ni(OH)₂ (Ni(OH)₂ + 2e⁻ → Ni(s) + 2OH⁻) are -0.257 and -0.72V versus NHE at pH = 0 and pH = 14 [11], respectively, which are more negative than the CB potential (0.3 V vs NHE at pH = 0) of WO₃ [21], indicating that Ni⁰ is selectively deposited on the reduction sites of g-C₃N₄, and not on WO₃. Furthermore, WO₃ cannot achieve photocatalytic H₂ generation due to its unsuitable CB potential. More importantly, the CW20/4.8%Ni(OH)_x sample exhibited a 5.7 times higher H₂-evolution activity than that of g-C₃N₄/4.8%Ni(OH)_x, clearly indicating the key roles of Z-scheme charge separation in enhancing photocatalytic H₂ generation. Accordingly, it was proposed that the oxidation and reduction sites are located at WO₃ and Ni(OH)_x in the hybrid, corresponding to a typical Z-scheme charge-separation mechanism. Scheme 2 displays a schematic of the photo-induced charge separation process in the WO₃/g-C₃N₄/Ni(OH)_x composite photocatalysts. Both g-C₃N₄ and WO₃ components can be excited under visible light, thus leading to the formation of photo-induced electron/hole pairs. According to previous reports, the CB of WO₃ is close to the VB of g-C₃N₄, which is beneficial for the fast recombination of photo-generated electrons in the CB of WO₃ and the pho-

to-generated holes in the VB of g-C₃N₄ upon visible light illumination, thus achieving the interesting Z-scheme charge separation. The leaving electrons on the CB of g-C₃N₄ can be readily injected into the Ni(OH)_x cocatalyst to drive the surface water reduction reaction, achieving the significantly enhanced photocatalytic H₂ evolution on the surface active sites of Ni(OH)_x NPs. Meanwhile, the photo-generated holes in the VB of WO₃ with a stronger oxidation ability participate in the oxidation of TEOA as a hole scavenger. As a result, the combination of Z-scheme and catalyst loading greatly suppressed fast electron-hole recombination in g-C₃N₄ and improved H₂ evolution and TEOA oxidation kinetics, thus leading to enhanced hydrogen production.

4. Conclusions

We fabricated high quality WO₃/g-C₃N₄/Ni(OH)_x nanocomposites by a two-step strategy of high temperature calcination and in situ photo-deposition. In the synergistic system, the photo-generated electrons and holes of g-C₃N₄ were simultaneously separated and utilized by the Ni(OH)_x cocatalysts and WO₃ Z-scheme component, respectively. The Ni(OH)_x cocatalyst effects were demonstrated by the polarization curves, while the Z-scheme charge separation mechanism was revealed by the electron spin resonance spectra of ·O₂⁻ and ·OH radicals. As a result, the Ni(OH)_x cocatalysts and Z-scheme charge separation achieved enhancement in photocatalytic H₂ evolution driven by the photo-generated electrons and TEOA oxidation driven by the photo-generated holes. The optimum WO₃/g-C₃N₄/Ni(OH)_x hybrid photocatalytic system with WO₃ mass content of 20% showed the highest hydrogen production rate of 576 μmol/(g·h), which is 5.7, 10.8 and 230 times higher than those of g-C₃N₄/4.8%Ni(OH)_x, 20%WO₃/C₃N₄ and g-C₃N₄ photocatalysts, respectively. The combination effects of Z-scheme (WO₃/g-C₃N₄) and Ni(OH)_x cocatalysts loading effectively inhibit the recombination of the photoexcited electron-hole pairs of g-C₃N₄ and improve H₂ evolution and TEOA oxidation kinet-

Scheme 2. Schematic of the photo-induced charge separation process in the WO₃/g-C₃N₄/Ni(OH)_x composite photocatalysts.

Graphical Abstract

Chin. J. Catal., 2017, 38: 240–252 doi: 10.1016/S1872-2067(17)62759-1

Enhanced visible light photocatalytic H₂ production over Z-scheme g-C₃N₄ nanosheets/WO₃ nanorods nanocomposites loaded with Ni(OH)_x cocatalysts

Kelin He, Jun Xie, Xingyi Luo, Jiuqing Wen, Song Ma, Xin Li*, Yueping Fang, Xiangchao Zhang
South China Agricultural University; Changsha University

The synergistic effects of Z-scheme heterojunctions (g-C₃N₄ nanosheets/WO₃ nanorods) and loaded cocatalyst (Ni(OH)_x) were demonstrated, which boosted visible light photocatalytic H₂ production over g-C₃N₄ nanosheets.

ics, thus achieving enhanced photocatalytic H₂ generation. It is expected that more robust multiple heterojunctions composed of readily available Ni(OH)_x cocatalysts and Z-scheme junctions can be fabricated for photocatalytic applications.

References

- [1] J. A. Turner, *Science*, **1999**, 285, 687–689.
- [2] X. Li, J. G. Yu, J. X. Low, Y. P. Fang, J. Xiao, X. B. Chen, *J. Mater. Chem. A*, **2015**, 3, 2485–2534.
- [3] X. B. Chen, S. H. Shen, L. J. Guo, S. S. Mao, *Chem. Rev.*, **2010**, 110, 6503–6570.
- [4] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [5] C. P. Sajjan, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, S.W. Cao, *Nano Res.*, **2016**, 9, 3–27.
- [6] Q. J. Xiang, J. G. Yu, M. Jaroniec, *J. Am. Chem. Soc.*, **2012**, 134, 6575–6578.
- [7] F. Y. Xu, W. G. Xiao, B. Cheng, J. Yu, *Int. J. Hydrogen Energy*, **2014**, 39, 15394–15402.
- [8] J. Q. Wen, X. Li, W. Liu, Y. P. Fang, J. Xie, Y. H. Xu, *Chin. J. Catal.*, **2015**, 36, 2049–2070.
- [9] S. Ma, J. Xie, J. Q. Wen, K. L. He, X. Li, W. Liu, X. C. Zhang, *Appl. Surf. Sci. B*, **2017**, 391, 580–591.
- [10] Q. Li, X. Li, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, *Adv. Energy Mater.*, **2015**, 5, 1500010.
- [11] X. Li, J. G. Yu, M. Jaroniec, *Chem. Soc. Rev.*, **2016**, 45, 2603–2636.
- [12] J. X. Low, J. G. Yu, W. K. Ho, *J. Phys. Chem. Lett.*, **2015**, 6, 4244–4251.
- [13] J. Q. Wen, X. Li, H. Q. Li, S. Ma, K. L. He, Y. H. Xu, Y. P. Fang, W. Liu, Q. Z. Gao, *Appl. Surf. Sci.*, **2015**, 358, 204–212.
- [14] Q. J. Xiang, B. Cheng, J. G. Yu, *Angew. Chem. Int. Ed.*, **2015**, 54, 11350–11366.
- [15] S. W. Cao, J. G. Yu, *J. Phys. Chem. Lett.*, **2014**, 5, 2101–2107.
- [16] S. Ye, R. Wang, M. Z. Wu, Y. P. Yuan, *Appl. Surf. Sci. A*, **2015**, 358, 15–27.
- [17] M. Wu, J. M. Yan, X. W. Zhang, M. Zhao, *Appl. Surf. Sci. A*, **2015**, 354, 196–200.
- [18] S. J. Liang, Y. Z. Xia, S. Zhu, S. H. Zheng, Y. H. He, J. H. Bi, M. H. Liu, L. Wu, *Appl. Surf. Sci. A*, **2015**, 358, 304–312.
- [19] M. S. Akple, J. X. Low, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, J. Zhang, *Appl. Surf. Sci. A*, **2015**, 358, 196–203.
- [20] X. Li, J. Q. Wen, J. X. Low, Y. P. Fang, J. G. Yu, *Sci. China Mater.*, **2014**, 57, 70–100.
- [21] J. Wen, J. Xie, X. Chen, X. Li, *Appl. Surf. Sci. B*, **2017**, 391, 72–123.
- [22] L. Yuan, Y. J. Xu, *Appl. Surf. Sci.*, **2015**, 342, 154–167.
- [23] Q. Huang, J. Yu, S. Cao, C. Cui, B. Cheng, *Appl. Surf. Sci.*, **2015**, 358, 350–355.
- [24] S. W. Cao, J. X. Low, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2015**, 27, 2150–2176.
- [25] J. X. Low, B. Cheng, J. G. Yu, M. Jaroniec, *Energy Stor. Mater.*, **2016**, 3, 24–35.
- [26] L. Pi, R. Jiang, W. C. Zhou, H. Zhu, W. Xiao, D. H. Wang, X. H. Mao, *Appl. Surf. Sci. A*, **2015**, 358, 231–239.
- [27] I. Papailias, T. Giannakopoulou, N. Todorova, D. Demotikali, T. Vaimakis, C. Trapalis, *Appl. Surf. Sci. A*, **2015**, 358, 278–286.
- [28] S. Fang, K. L. Lü, Q. Li, H. P. Ye, D. Y. Du, M. Li, *Appl. Surf. Sci. A*, **2015**, 358, 336–342.
- [29] B. Yuan, J. X. Wei, T. J. Hu, H. B. Yao, Z. H. Jiang, Z. W. Fang, Z. Y. Chu, *Chin. J. Catal.*, **2015**, 36, 1009–1016.
- [30] Y. J. Cui, *Chin. J. Catal.*, **2015**, 36, 372–379.
- [31] B. C. Zhu, P. F. Xia, W. K. Ho, J. G. Yu, *Appl. Surf. Sci.*, **2015**, 344, 188–195.
- [32] J. T. Zhang, F. Huang, *Appl. Surf. Sci. A*, **2015**, 358, 287–295.
- [33] H. G. Yu, F. Y. Chen, F. Chen, X. F. Wang, *Appl. Surf. Sci. A*, **2015**, 358, 385–392.
- [34] N. Tian, H. W. Huang, Y. H. Zhang, *Appl. Surf. Sci. A*, **2015**, 358, 343–349.
- [35] L. H. Tan, J. H. Xu, X. J. Zhang, Z. S. Hang, Y. Q. Jia, S. B. Wang, *Appl. Surf. Sci.*, **2015**, 356, 447–453.
- [36] Y. J. Sun, T. Xiong, Z. L. Ni, J. Liu, F. Dong, W. Zhang, W. K. Ho, *Appl. Surf. Sci. A*, **2015**, 358, 356–362.
- [37] Y. G. Su, Y. X. Zhao, Y. J. Zhao, J. Y. Lang, X. Xin, X. J. Wang, *Appl. Surf. Sci. A*, **2015**, 358, 213–222.
- [38] J. Y. Lang, M. Q. Liu, Y. G. Su, L. J. Yan, X. J. Wang, *Appl. Surf. Sci. A*, **2015**, 358, 252–260.
- [39] A. Akhundi, A. Habibi-Yangjeh, *Appl. Surf. Sci. A*, **2015**, 358, 261–269.
- [40] W. Chen, T. Y. Liu, T. Huang, X. H. Liu, J. W. Zhu, G. R. Duan, X. J. Yang, *Appl. Surf. Sci.*, **2015**, 355, 379–387.
- [41] L. F. Cui, X. Ding, Y. G. Wang, H. C. Shi, L. H. Huang, Y. H. Zuo, S. F. Kang, *Appl. Surf. Sci. B*, **2017**, 391, 202–210.
- [42] J. Lü, K. Dai, J. F. Zhang, L. Geng, C. H. Liang, Q. C. Liu, G. P. Zhu, C. Chen, *Appl. Surf. Sci. A*, **2015**, 358, 377–384.
- [43] W. L. Yu, D. F. Xu, T. Y. Peng, *J. Mater. Chem. A*, **2015**, 3, 19936–19947.
- [44] J. G. Yu, S. H. Wang, J. X. Low, W. Xiao, *Phys. Chem. Chem. Phys.*, **2013**, 15, 16883–16890.
- [45] Y. N. Zhang, X. H. Li, Y. Y. Cai, L. H. Gong, K. X. Wang, J. S. Chen, *RSC Adv.*, **2014**, 4, 60873–60877.
- [46] J. L. Yuan, J. Q. Wen, Y. M. Zhong, X. Li, Y. P. Fang, S. S. Zhang, W. Liu, *J. Mater. Chem. A*, **2015**, 3, 18244–18255.
- [47] Y. M. Zhong, J. L. Yuan, J. Q. Wen, X. Li, Y. H. Xu, W. Liu, S. S. Zhang,

- Y. P. Fang, *Dalton Trans.*, **2015**, 44, 18260–18269.
- [48] G. C. Bi, J. Q. Wen, X. Li, W. Liu, J. Xie, Y. P. Fang, W. W. Zhang, *RSC Adv.*, **2016**, 6, 31497–31506.
- [49] P. Zhou, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2014**, 26, 4920–4935.
- [50] H. Katsumata, Y. Tachi, T. Suzuki, S. Kaneco, *RSC Adv.*, **2014**, 4, 21405–21409.
- [51] S. F. Chen, Y. F. Hu, X. L. Jiang, S. G. Meng, X. L. Fu, *Mater. Chem. Phys.*, **2015**, 149, 512–521.
- [52] T. Ohno, N. Murakami, T. Koyanagi, Y. Yang, *J. CO₂ Util.*, **2014**, 6, 17–25.
- [53] S. F. Chen, Y. F. Hu, S. G. Meng, X. L. Fu, *Appl. Catal. B*, **2014**, 150–151, 564–573.
- [54] H. Katsumata, T. Sakai, T. Suzuki, S. Kaneco, *Ind. Eng. Chem. Res.*, **2014**, 53, 8018–8025.
- [55] S. G. Meng, X. F. Ning, T. Zhang, S. F. Chen, X. Fu, *Phys. Chem. Chem. Phys.*, **2015**, 17, 11577–11585.
- [56] J. R. Ran, J. Zhang, J. G. Yu, M. Jaroniec, S. Z. Qiao, *Chem. Soc. Rev.*, **2014**, 43, 7787–7812.
- [57] Y. Xu, R. Xu, *Appl. Surf. Sci.*, **2015**, 351, 779–793.
- [58] J. G. Yu, S. H. Wang, B. Cheng, Z. Lin, F. Huang, *Catal. Sci. Technol.*, **2013**, 3, 1782–1789.
- [59] X. Li, J. G. Yu, S. Wageh, A. A. Al-Ghamdi, J. Xie, *Small*, **2016**.
- [60] K. Kailasam, J. Schmidt, H. Bildirir, G. G. Zhang, S. Blechert, X. C. Wang, A. Thomas, *Macromol Rapid Commun.*, **2013**, 34, 1008–1013.
- [61] L. G. Kong, Y. M. Dong, P. P. Jiang, G. L. Wang, H. Z. Zhang, N. Zhao, *J. Mater. Chem. A*, **2016**, 4, 9998–10007.
- [62] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [63] F. Dong, Y. H. Li, Z. Y. Wang, W. K. Ho, *Appl. Surf. Sci. A*, **2015**, 358, 393–403.
- [64] J. He, H. L. Liu, B. Xu, X. Wang, *Small*, **2015**, 11, 1144–1149.
- [65] M. A. Gondal, A. A. Adesida, S. G. Rashid, S. Shi, R. Khan, Z. H. Yamani, K. Shen, Q. L. Xu, Z. S. Seddigi, X. F. Chang, *React. Kinet. Mech. Catal.*, **2015**, 114, 357–367.
- [66] H. J. Yin, S. L. Zhao, K. Zhao, A. Muqsit, H. J. Tang, L. Chang, H. J. Zhao, Y. Gao, Z. Y. Tang, *Nat. Commun.*, **2015**, 6, 6430.
- [67] 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.
- [68] K. I. Katsumata, R. Motoyoshi, N. Matsushita, K. Okada, *J. Hazard. Mater.*, **2013**, 260, 475–482.
- [69] X. Li, H. L. Li, S. Q. Huo, Z. Li, *Kinet. Catal.* **2010**, 51, 754–761.
- [70] J. L. Yuan, J. Q. Wen, Q. Z. Gao, S. C. Chen, J. M. Li, X. Li, Y. P. Fang, *Dalton Trans.*, **2015**, 44, 1680–1689.
- [71] J. G. Yu, L. F. Qi, M. Jaroniec, *J. Phys. Chem. C*, **2010**, 114, 13118–13125.
- [72] H. H. Xiao, W. Y. Wang, G. G. Liu, Z. M. Chen, K. L. Lü, J. J. Zhu, *Appl. Surf. Sci.*, **2015**, 358, 313–318.
- [73] L. Cai, X. L. Xiong, N. G. Liang, Q. Y. Long, *Appl. Surf. Sci.*, **2015**, 353, 939–948.
- [74] G. Lu, X. Y. Li, Z. P. Qu, Q. D. Zhao, H. Li, Y. Shen, G. H. Chen, *Chem. Eng. J.*, **2010**, 159, 242–246.
- [75] J. Li, E. Z. Liu, Y. N. Ma, X. Y. Hu, J. Wan, L. Sun, J. Fan, *Appl. Surf. Sci.*, **2016**, 364, 694–702.
- [76] L. Liu, Y. H. Qi, J. S. Hu, Y. H. Liang, W. Q. Cui, *Appl. Surf. Sci.*, **2015**, 351, 1146–1154.
- [77] M. Yang, S. Z. Hu, F. Y. Li, Z. P. Fan, F. Wang, D. Liu, J. Z. Gui, *Ceram. Int.*, **2014**, 40, 11963–11969.
- [78] P. Y. Kuang, Y. Z. Su, G. F. Chen, Z. Luo, S. Y. Xing, N. Li, Z. Q. Liu, *Appl. Surf. Sci. A*, **2015**, 358, 296–303.

利用Ni(OH)_x助催化剂修饰提高g-C₃N₄纳米片/WO₃纳米棒Z型纳米体系的可见光产氢活性的研究

何科林^{a,b,c}, 谢君^{a,b,c}, 罗杏宜^{a,b,c}, 温九青^{a,b,c}, 马松^{a,b,c}, 李鑫^{a,b,c,*}, 方岳平^a, 张向超^d

^a华南农业大学材料与能源学院, 广东广州510642

^b华南农业大学林学与风景园林学院, 广东广州510642

^c华南农业大学新能源与新材料研究所, 农业部能源植物资源与利用重点实验室,

广东省高校生物质能源重点实验室, 广东广州510642

^d长沙学院环境光催化应用技术省重点实验室, 湖南长沙市410022

摘要: 光催化技术是目前解决能源和环境问题最具前景的手段之一, 因此寻找高效光催化剂已成为光催化技术的研究热点。而在众多半导体催化剂中, 廉价、环保且性能稳定的g-C₃N₄光催化剂在太阳光开发利用方面尤其引人注目。然而, 由于g-C₃N₄的比表面小, 活性位点少, 以及光生电子/空穴对易复合等不足, 严重导致其较低的光催化量子效率。因此, 构造Z型体系和负载助催化剂等策略被广泛应用于提高g-C₃N₄光催化效率。在过去几年中, TiO₂, Bi₂WO₆, WO₃, Bi₂MoO₆, Ag₃PO₄和ZnO已经被成功证实可以与g-C₃N₄耦合而构造Z型光催化剂体系。其中, WO₃/g-C₃N₄光催化剂体系, 具有可见光活性的WO₃导带中的光生电子和g-C₃N₄价带中的光生空穴容易实现Z型复合, 从而保留了WO₃的强氧化能力和g-C₃N₄的高还原能力, 最终大幅度提高了整个体系的光催化活性。在g-C₃N₄的各种产氢助催化剂中, 由于常用的Pt, Ag和Au等贵金属的高成本和低储量等问题严重限制了它们的实际应用, 所以近年来各种非贵金属助催化剂(包括纳米碳, Ni, NiS, Ni(OH)₂, WS₂和MoS₂等)得到了广泛的关注。我们采取廉价且丰富的Ni(OH)_x助催化剂修饰g-C₃N₄/WO₃耦合形成的Z型体系, 开发出廉价高效的WO₃/g-C₃N₄/Ni(OH)_x三元产氢光催化体系。在该三元体系中, Ni(OH)_x和WO₃分别用于促进g-C₃N₄导带上光生电子和价带的光生空穴的分离及利用, 从而使得高能的光生电子在Ni(OH)_x富集并应用于光催化产氢, 而高能的光生空穴被应用于氧化牺牲剂三乙醇胺, 最终实现了整个体系的高效光催化产氢活性及稳定性。

我们通过直接焙烧硝酸铵和硫脲制备出WO₃纳米棒/g-C₃N₄, 并采用原位光沉积方法将Ni(OH)_x纳米颗粒负载到

WO₃/g-C₃N₄上。随后,我们采取X射线衍射(XRD)、高分辨透射电子显微镜(HRTEM)、X射线光电子能谱分析(XPS)和比表面和孔径分布等表征手段来研究光催化剂的结构与形貌;采取紫外-可见漫反射表征方法来研究其光学性能;采取荧光光谱,阻抗和瞬态光电流曲线等表征手段来测试光催化剂的电荷分离性能;采取极化曲线和电子自旋共振谱等表征手段来证明光催化机理;采取光催化分解水产氢的性能测试来研究光催化剂的光催化活性与稳定性。XRD, HRTEM和XPS表征结果,表明WO₃为有缺陷的正交晶系的晶体,直径为20–40纳米棒且均匀嵌入在g-C₃N₄纳米片上;Ni(OH)_x为Ni(OH)₂与Ni的混合物,其Ni(OH)₂与Ni的摩尔比为97.4 : 2.6, Ni(OH)_x粒径为20–50 nm且均匀分散在g-C₃N₄纳米片上, WO₃/g-C₃N₄/Ni(OH)_x催化剂界面之间结合牢固,其中WO₃和Ni(OH)_x均匀分布在g-C₃N₄上。紫外-可见漫反射表征结果表明,随着缺陷WO₃的负载量增加,复合体系的吸收边与g-C₃N₄相比产生明显的红移,而加入Ni(OH)_x助催化剂使得催化剂体系的颜色由黄变黑,明显地增加了可见光的吸收。荧光光谱,阻抗和瞬态光电流曲线结果表明,WO₃和Ni(OH)_x的加入能有效地促进光生电子/空穴的分离。极化曲线结果表明,掺入WO₃和Ni(OH)_x能降低g-C₃N₄的析氢过电位,从而提高光催化剂表面的产氢动力学。•O₂⁻和•OH电子自旋共振谱表明成功形成了WO₃/g-C₃N₄耦合Z型体系。光催化分解水产氢的性能测试表明,20%WO₃/g-C₃N₄/4.8%Ni(OH)_x产氢效率最高(576 μmol/(g·h)),分别是g-C₃N₄/4.8%Ni(OH)_x, 20%WO₃/g-C₃N₄和纯g-C₃N₄的5.7, 10.8和230倍。上述结果充分证明, Ni(OH)_x助催化剂修饰和g-C₃N₄/WO₃ Z型异质结产生了极好的协同效应,最终实现了三元体系的极高的光催化产氢活性。

关键词: 光催化产氢; 稳定的Ni(OH)_x催化剂; g-C₃N₄; Z型体系; 异质结

收稿日期: 2016-10-30. 接受日期: 2016-11-20. 出版日期: 2017-02-05.

*通讯联系人. 电话: (020)85282633; 传真: (020)85285596; 电子信箱: xinliscan@yahoo.com

基金来源: 国家自然科学基金(51672089); 广州市产学研协同创新重大专项(201508020098); 材料复合新技术国家重点实验室(武汉理工大学)开放基金(2015-KF-7); 环境与能源光催化湖南省高等学校“2011协同创新中心”(长沙学院环境光催化应用技术省重点实验室)开放课题(CCSU-XT-04).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).