available at www.sciencedirect.com

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

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

Step-scheme porous g-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composites for efficient and stable photocatalytic H₂ production

Feifei Mei^a, Zhen Li^a, Kai Dai^{a,*}, Jinfeng Zhang^{a,#}, Changhao Liang^{b,\$}^a College of Physics and Electronic Information, Anhui Key Laboratory of Energetic Materials, Huaibei Normal University, Huaibei 235000, Anhui, China^b Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, Anhui, China

ARTICLE INFO

Article history:

Received 8 April 2019

Accepted 1 May 2019

Published 5 January 2020

Keywords:

Pg-C₃N₄Zn_{0.2}Cd_{0.8}S

Diethylenetriamine

Photocatalysis

Step-scheme porous composite

ABSTRACT

In recent years, environmental pollution and energy crisis have become increasingly serious issues owing to the burning of fossil fuels. Among the many technologies, decomposition of water to produce hydrogen has attracted much attention because of its sustainability and non-polluting characteristic. However, highly efficient decomposition of water that is driven by visible light is still a challenge. Herein, we report the large-scale preparation of step-scheme porous graphite carbon nitride/Zn_{0.2}Cd_{0.8}S-diethylenetriamine (Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA) composite by a facile solvothermal method. It was found by UV-vis spectroscopy that 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA exhibited suitable visible absorption edge and band gap for water decomposition. The hydrogen production rate of 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composite was 6.69 mmol g⁻¹ h⁻¹, which was 16.73, 1.61, and 1.44 times greater than those of Pg-C₃N₄, CdS-DETA, and Zn_{0.2}Cd_{0.8}S-DETA, respectively. In addition, 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composite displayed excellent photocatalytic stability, which was maintained for seven cycles of photocatalytic water splitting test. We believe that 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composite can be a valuable guide for the development of solar hydrogen production applications in the near future.

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

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, a green and clean energy source is urgently sought owing to insufficient fossil fuel reserves and pollution problems [1–4]. Hydrogen (H₂) is an extremely clean energy source, and the only substance that burns in air is water vapor. Furthermore, solar energy is an inexhaustible source of energy. Therefore, photocatalytic H₂ evolution is a potential research field [5–9]. To date, many semiconductors such as metal

selenides [10–14], metal sulfides [15–19], carbon nitrides [20,21], and metal oxides [22–26] have been reported for photocatalytic H₂ production. It is worth noting that CdS is widely studied owing to its suitable band gap (about 2.4 eV) and band edge, which result in the material exhibiting good performances under visible light irradiation. However, a single layer of CdS displays a high carrier recombination rate under light irradiation [27], which results in serious photo-corrosion. In order to solve this problem of CdS, many methods have been developed,

* Corresponding author. Fax: +86-561-3803256; E-mail: daikai940@chnu.edu.cn

Corresponding author. E-mail: jfzhang@chnu.edu.cn

\$ Corresponding author. E-mail: chliang@issp.ac.cn

This work was supported by the National Natural Science Foundation of China (51572103, 51502106), the Distinguished Young Scholar of Anhui Province (1808085J14), the Foundation for Young Talents in College of Anhui Province (gxyqZD2017051), the Key Foundation of Educational Commission of Anhui Province (KJ2016SD53) and Innovation Team of Design and Application of Advanced Energetic Materials (KJ2015TD003).

DOI: S1872-2067(19)63389-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 1, January 2020

including the construction of heterojunctions with other semiconductors [28–30], formation of solid solutions [31,32], and deposition of precious metals [33–35].

Many isomorphous crystals produce homogeneous and variable composition solid solutions. When a wide band gap semiconductor and a narrow band gap semiconductor form a solid solution [36,37], a novel photocatalyst with a continuously varying band gap can be prepared. In recent years, solid solutions have been extensively studied because of their excellent performances under visible light irradiation [38–40]. Zinc sulfide (ZnS) exhibits good photocatalytic activity and stability owing to its high conduction band energy position [41,42]. However, ZnS has a wide band gap (of about 3.5 eV) and can only be excited with ultraviolet light. Therefore, introduction of Zn ions into CdS to form $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solutions can combine the photostability of ZnS and the photocatalytic activity of CdS. More importantly, the band structure can be adjusted by changing the molar ratio of Zn to Cd.

In recent years, organic-inorganic hybrid materials have played a huge role in photocatalysis. As a small organic molecule, diethylenetriamine (DETA) can be protonated by solvothermal reaction with water under high pressures to form positively charged amine ions [43]. The protonated amine ions form an organic-inorganic hybrid material by coordination with anions. Our group has synthesized $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ -DETA with different band gaps by a simple one-step solvothermal method [44]. The organic-inorganic hybrid material can not only adjust the morphology, but also improve their photocatalytic performance. Therefore, solid solutions have great research prospects in photocatalysis. Although the single solid solution improved the photocatalytic performance, its stability decreased after repeated cycles of experiments. In order to overcome this shortcoming, some researchers have previously constructed heterojunctions with other semiconductors, such as $\text{CdSe}/\text{Zn}_x\text{Cd}_{1-x}\text{S}$ [45], $\alpha\text{-Fe}_2\text{O}_3/\text{Zn}_{0.4}\text{Cd}_{0.6}\text{S}$ [46], and ZnCdS/CdS [47].

Graphite carbon nitride ($\text{g-C}_3\text{N}_4$), as a two-dimensional material, is widely studied because it is cheap, non-toxic, and displays good photostability [48–50]. Metal-free $\text{g-C}_3\text{N}_4$ can be excited with visible light because of its suitable band gap (about 2.83 eV), and its conduction band position is sufficiently negative (−1.28 eV) [51–54]. Based on the above points, $\text{g-C}_3\text{N}_4$ has great research prospects in the field of photocatalytic H_2 production [55,56]. The shortcoming is that the photogenerated carriers of single $\text{g-C}_3\text{N}_4$ can easily recombine, which hinders its practical application. Some strategies such as doping other elements [57,58], loading cocatalysts [59–61], tuning the morphology, and forming heterojunctions with other semiconductors have been developed to address this issue [62–66]. We obtained porous $\text{g-C}_3\text{N}_4$ ($\text{Pg-C}_3\text{N}_4$) by thermal decomposition of thiourea and urea. Compared with that of $\text{g-C}_3\text{N}_4$, $\text{Pg-C}_3\text{N}_4$, with a porous structure, exhibits a larger specific surface area. In addition, these pores provide internal channels that accelerate the carrier migration. This offers the possibility of practical application of $\text{Pg-C}_3\text{N}_4$.

In our work, we successfully developed a heterojunction between $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA by an in-situ sol-

vothermal method. The H_2 evolution activity of $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA composite was also studied. The results show that the $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA composites display enhanced H_2 production activities and stabilities, compared to those of other catalysts. Among them, 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA shows the best photocatalytic activity and stability. Specifically, it maintains its excellent activity after seven cycles. The improvement in the photocatalytic activity is attributed to the formation of a step-scheme heterojunction between $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA.

2. Experimental

2.1. Materials

Urea, zinc chloride (ZnCl_2), sulfourea, sodium sulfide (Na_2S), sublimed sulfur (S), chloroplatinic acid (H_2PtCl_6), and DETA were obtained from Sinopharm (P.R. China). Absolute ethyl alcohol, sodium sulfate (Na_2SO_4), polyethylene glycol, cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$), Nafion, and sodium sulfite (Na_2SO_3) were provided by Shanghai Chemical Reagent Co. Ltd (P.R. China). Deionized water (DW; 18.25 M Ω) was used in the experiments.

2.2. Preparation of $\text{Pg-C}_3\text{N}_4$

First, urea and thiourea were mixed in mortar at the ratio of 3:1 and continuously ground. Thereafter, the mixture was placed in a muffle furnace and heated to 550 °C for 2 h. Then, the sample was naturally cooled to room temperature, and finally, $\text{Pg-C}_3\text{N}_4$ was obtained.

2.3. Preparation of $X\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA composites

$X\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA ($X = 5, 10$, and 15) composites were synthesized by an in-situ growth method. First, different grades of $\text{Pg-C}_3\text{N}_4$ were added to the reactor, followed by the addition of 0.0489 g ZnCl_2 , 0.328 g CdCl_2 , 24 mL DETA, and 12 mL DW. Thereafter, 0.256 g S was added to the mixed liquid and stirred well for 3 h; then, the reaction kettle was placed in an oven and heated at 80 °C for 48 h. After cooling, the composite was washed several times with DW, and the $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA system was obtained by freeze drying.

2.4. Characterization

The crystal structures of $\text{Pg-C}_3\text{N}_4$, $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA system, and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ -DETA were investigated by XRD (Rigaku D/MAX 24000). TEM (JEM-2100 electron microscope) was used to determine the particle sizes and structures of the samples. The chemical compositions of the samples were determined by XPS (Thermo ESCALAB 250) and Fourier transform infrared spectroscopy (FT-IR NICOLET 6700). Moreover, UV-vis diffuse reflectance spectroscopy (DRS) measurements were performed by using a PerkinElmer Lambda 950 UV-vis spectrophotometer. The PL spectra of $\text{Pg-C}_3\text{N}_4$, 15% $\text{Pg-C}_3\text{N}_4/$

$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ were acquired by FLS920 combined fluorescence life time measurements. The photoelectrochemical measurements were performed on a Shanghai Chenhua CHI-660D electrochemical system. The electrolyte solution was 1.0 mol/L Na_2SO_4 . In addition, 0.05 g of the catalyst samples was mixed with 50 μL 5% Nafion and 0.5 mL ethyl alcohol to form a slurry. The slurry was injected into a 1.0 cm^2 ITO conductive glass electrode and dried for 30 min at 60 $^\circ\text{C}$.

2.5. Evaluation of the photocatalytic activity

The photocatalytic H_2 production experiment was carried out in a 250 mL flask with three necks. First, 50 mg of a sample, 100 mL of 0.25 mol/L Na_2SO_3 , and a solution mixed with 0.35 mol/L Na_2S and 300 μL H_2PtCl_6 (0.6 wt%) were placed in the flask with three necks. Then, the mixture was dispersed by ultrasound for 30 min and stirred for another 30 min. The system was bubbled with nitrogen for 30 min under dark conditions. Finally, a 300 W Xe lamp with a 420 nm cut-off filter was used for the irradiation. The distance between the Xe lamp and the reactor was 5 cm. The amount of H_2 produced by illumination was measured by gas chromatography (GC-7900).

3. Results and discussion

Fig. 1 shows the synthetic process of 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. First, a certain amount of urea and thiourea were mixed in mortar for grinding. The ground mixture was placed in a crucible, which was then transferred to the muffle furnace and annealed at 550 $^\circ\text{C}$ for two hours to produce $\text{Pg-C}_3\text{N}_4$. Thereafter, a certain amount of $\text{Pg-C}_3\text{N}_4$ was added to polytetrafluoroethylene liner, and specific amounts of DETA, sublimed S, cadmium chloride, and zinc chloride were added. After the mixture was stirred in a Teflon liner for 3 h, the liner was transferred to a stainless steel reactor and placed in an oven for 48 h at a temperature of 80 $^\circ\text{C}$, and finally, 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ was obtained.

In order to further investigate the phases of the synthesized photocatalysts, we performed XRD on all the photocatalysts. The XRD patterns of $\text{Pg-C}_3\text{N}_4$ and $X\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ are shown in Fig. 2. Furthermore, the phases of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ and $\text{Pg-C}_3\text{N}_4$ have been identified by previous work, and are shown in Fig. 2. It is easy to see that 5% $\text{Pg-C}_3\text{N}_4/$

Fig. 1. Schematic diagram of the formation of 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ composite.

Fig. 2. XRD patterns of $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, and $\text{Pg-C}_3\text{N}_4$.

$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, and 25% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ all exhibit the peaks of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, which indicate that all the composites contain $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. In addition, the main (002) peak of $X\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ gradually grows and resembles that of $\text{Pg-C}_3\text{N}_4$ with the increase in X value, which indicates that $\text{Pg-C}_3\text{N}_4$ is present in the composite. From this, it can be concluded that $X\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ contains both $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$.

To further explore the micromorphology of each photocatalyst, we also investigated the samples by means of TEM, HRTEM, EDS mapping, and SEM. As can be seen clearly in Fig. 3a, $\text{Pg-C}_3\text{N}_4$ is an ultrathin porous nanosheet with a hole of 20–50 nm. In Fig. 3b, $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ exhibits a nanoflower structure with a size of about 300 nm, and the petals of the nanoflowers exist in an ultrathin state. It can be clearly seen from Fig. 3c that the surface of the ultrathin and porous $\text{Pg-C}_3\text{N}_4$ is filled with $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ nanoflowers. It can also be seen from Fig. 3d that the spacings of $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ are 0.33 and 0.35 nm, respectively. Additionally, in Fig. 3d, the red curve on the left side clearly shows the heterojunction formed between $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. This indicates that the 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ material we synthesized is a result of the combination of $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, and not a mixture of two pure substances. Fig. 3e is a SEM image of 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. Fig. 3f shows the EDS pattern of 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. The EDS pattern shows that the composites we synthesized contain only C, N, O, Zn, Cd, and S elements, and no other impurities. The elemental maps are shown in Fig. 3g–3l. It is obvious that the 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ composite contains C, N, O, Zn, Cd and S elements and that the elements are evenly distributed.

The XPS patterns are shown in Fig. 4. Fig. 4a reveals the measured spectra of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, $\text{Pg-C}_3\text{N}_4$, and 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ shows the presence of C 1s, O 1s, N 1s, Zn 2p, Cd 3d, and S 2p elements without other impurities. $\text{Pg-C}_3\text{N}_4$ reveals the presence of C 1s, N 1s, and O 1s elements, and no other elements were detected. Among them, the O element found in $\text{Pg-C}_3\text{N}_4$ may have origi-

Fig. 3. TEM images of (a) $\text{Pg-C}_3\text{N}_4$, (b) $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, and (c) $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$; (d) HRTEM image of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$; (e) SEM image and (f) EDS pattern of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$; (g–l) Elemental mapping images of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ corresponding to C, N, O, Zn, Cd, and S.

Fig. 4. XPS spectra of the as-prepared photocatalysts. (a) Overview; (b) C 1s; (c) N 1s; (d) Zn 2p; (e) Cd 3d; (f) S 2p.

nated from the oxygen in the air. $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ shows the presence of C 1s, O 1s, N 1s, Zn 2p, Cd 3d, and S 2p elements, and no other impurities were detected, which indicate the purity of the substance. High-resolution XPS C 1s patterns are shown in Fig. 4b. $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ displays two main peaks, which are due to the inclusion of $\text{Pg-C}_3\text{N}_4$ [67]. However, the peak on the right side is larger, which is attributed to the high content of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. Moreover, the main peak of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$

was shifted relative to that of $\text{Pg-C}_3\text{N}_4$. Fig. 4c shows the high-resolution XPS N 1s spectra. Among them, $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ exhibits a larger peak on the left side and a smaller peak on the right side, which is due to the higher content of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. However, the peak intensity on the right side of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ is higher than that of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, which is ascribed to the small amount of $\text{Pg-C}_3\text{N}_4$ in the composite [68]. In addition, the main peak of the composite reveals a different degree of shift com-

pared with that of the main peak of the pure substance. From the changes in the C 1s and N 1s binding energies, it can be seen that the current density of Pg-C₃N₄ is increased, and it is concluded that electrons flow from Zn_{0.2}Cd_{0.8}S-DETA to Pg-C₃N₄ [69]. Fig. 4d shows a high-resolution XPS Zn 2p spectra. The two main peaks of 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA are shifted by about 0.27 eV relative to those of Zn_{0.2}Cd_{0.8}S-DETA. Fig. 4e is high-resolution XPS Cd 3d spectra. The two main peaks of 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA are shifted by about 0.06 eV relative to those of Zn_{0.2}Cd_{0.8}S-DETA. As shown in Fig. 4f, the S 2p pattern can be fitted with two main peaks, and the two main peaks of 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA are shifted by about 0.22 eV with respect to those of Zn_{0.2}Cd_{0.8}S-DETA. This further proves the conclusion made above. In Fig. 4b–4f, the main peaks of the 15%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composite reveal different degrees of shift relative to those of pure Pg-C₃N₄ or Zn_{0.2}Cd_{0.8}S-DETA, which suggest that the composite we synthesized is not a simple mixture of two pure substances.

In order to investigate the light absorptions of the pure and composite materials, we conducted UV-vis DRS studies. As shown in Fig. 5a, the absorption edges of Zn_{0.2}Cd_{0.8}S-DETA and Pg-C₃N₄ are about 521 and 449 nm, respectively. A reduction in the light absorption at 320–380 nm can be observed in all the prepared samples. The reason is that the instrument is changing the light. The corresponding band gaps are 2.45 and 2.85 eV, respectively (Fig. 5b). In Fig. 5a, the absorption edge of 5%

Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA is similar to that of Zn_{0.2}Cd_{0.8}S-DETA. This is due to the low content of Pg-C₃N₄, which will not significantly affect the optical absorption properties of Zn_{0.2}Cd_{0.8}S-DETA. However, with the increase in Pg-C₃N₄ content, the absorption edge of Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composite shifts to blue wavelengths, which is attributed to the low absorption capacity of Pg-C₃N₄. Fig. 5b presents linear transformations of the Pg-C₃N₄ and Zn_{0.2}Cd_{0.8}S-DETA absorption curves. As can be seen from Fig. 5b, the band gaps of Pg-C₃N₄ and Zn_{0.2}Cd_{0.8}S-DETA are 2.83 and 2.48 eV, respectively. The conduction band (CB) and valence band (VB) energy levels are given by

$$E_{VB} = X - E^c + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

Here, the value of E^c is 4.5 eV, which is the energy of free electrons in the hydrogen scale. X is the absolute electronegativity, which is 4.64 and 5.21 eV for Pg-C₃N₄ and Zn_{0.2}Cd_{0.8}S-DETA, respectively. According to calculations, the CB energy levels of Pg-C₃N₄ and Zn_{0.2}Cd_{0.8}S-DETA are -1.28 and -0.53 eV, respectively, and the VB energy levels of Pg-C₃N₄ and Zn_{0.2}Cd_{0.8}S-DETA are 1.55 and 1.95 eV, respectively.

The N₂ adsorption-desorption curves of the prepared samples are shown in Fig. 6a. They correspond to type-IV, according to the classification of Brunauer-Deming-Deming Teller. This indicates the presence of mesopores in the prepared samples. The Brunauer-Emmett-Teller surface areas (S_{BET}) of the

Fig. 5. (a) UV-vis diffuse reflectance spectra of different photocatalysts; (b) plots of $(\alpha h\nu)^2$ versus energy ($h\nu$) for Zn_{0.2}Cd_{0.8}S-DETA and Pg-C₃N₄.

Fig. 6. (a) N₂ adsorption-desorption isotherms of Pg-C₃N₄, X%Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA, and Zn_{0.2}Cd_{0.8}S-DETA; (b) S_{BET} of the prepared samples.

prepared samples are displayed in Fig. 6b. It can be seen that $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ exhibits a larger S_{BET} ($150.3 \text{ m}^2 \text{ g}^{-1}$) than $\text{Pg-C}_3\text{N}_4$ ($52.7 \text{ m}^2 \text{ g}^{-1}$). As the content of $\text{Pg-C}_3\text{N}_4$ increases, the S_{BET} of the $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ composite decreases.

The rates of photocatalytic H_2 production of $X\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ ($X = 5, 15$, and 25) composite, CdS-DETA , and $\text{Pg-C}_3\text{N}_4$ are presented in Fig. 7. The photocatalytic performance of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ is better than that of pure CdS-DETA , which is attributed to the doping of Zn^{2+} that promotes the photocatalytic activity. However, the photocatalytic activity of pure $\text{Pg-C}_3\text{N}_4$ is very low. It can be clearly seen in Fig. 7 that the H_2 production rate of the $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ system is $6.69 \text{ mmol g}^{-1} \text{ h}^{-1}$, with an apparent quantum efficiency of 17.8% , which is much higher than those of pure $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ and $\text{Pg-C}_3\text{N}_4$, which indicates that the addition of appropriate amounts of $\text{Pg-C}_3\text{N}_4$ can significantly promote the photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. The main reason is that the addition of $\text{Pg-C}_3\text{N}_4$ can effectively promote the separation of the photo-generated electrons and holes in $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, thus improving the photocatalytic efficiency of the photocatalyst. However, the photocatalytic activity of $25\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ is much lower than those of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ and CdS-DETA . This suggests that excess $\text{Pg-C}_3\text{N}_4$ inhibits the photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. Therefore, an appropriate amount of $\text{Pg-C}_3\text{N}_4$ can effectively improve the activity of a photocatalyst, which presents a framework for increasing the activities of single photocatalysts.

In order to further explore the stabilities of the materials, we carried out seven cycles of 21 h experiments on $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. As shown in Fig. 8a, $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ maintains a good photocatalytic activity over the first three cycles under visible light irradiation, but its photocatalytic activity significantly decreases from the fourth cycle onwards, reaching only 67.7% of the initial value after the seventh cycle. Nevertheless, $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ maintains a high photocatalytic activity during the first six cycles, which decreases slightly after the seventh cycle. In addition, Fig. 8b shows the XRD patterns of the recycled and original samples. It can be seen that the main

Fig. 7. Photocatalytic H_2 production rates of various samples.

peaks of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ display no obvious shifts after the cycling. This indicates that the addition of an appropriate amount of C_3N_4 can not only improve the photocatalytic activity of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, but also significantly enhance its photocatalytic stability.

To investigate the improvement in the carrier separation efficiency of $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$, we conducted a photocurrent-time test. As shown in Fig. 9, the light is turned on every 50 s . All the samples show enhanced current intensities when illuminated. The greater the magnitude of the photocurrent, the faster is the charge carrier separation and transmission in $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. Therefore, it can be seen that $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ exhibits the highest electron-hole pair separation and transmission efficiency. This result is consistent with its H_2 production performance.

Based on the above discussion, a possible charge transfer mechanism in photocatalysis is proposed. As shown in Fig. 10, the possible mechanism involves a step-scheme that is based on the change in the binding energy of each element in the XPS spectra (Fig. 4). When sunlight is absorbed, the photogenerated electrons are excited from the VBs of $\text{Pg-C}_3\text{N}_4$ and Zn-

Fig. 8. (a) Results of recycling tests for $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ for H_2 evolution; (b) XRD patterns of fresh and used $15\%\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ composites.

Fig. 9. Photocurrent-time responses of the prepared samples.

Fig. 10. The possible charge transfer mechanism.

$_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ to their CBs, which leave holes in their VBs. After $\text{Pg-C}_3\text{N}_4$ and $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ are combined, an internal electric field is formed between the two [70]. The unwanted electrons in the CB of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ recombine with the holes in the VB of $\text{Pg-C}_3\text{N}_4$ owing to the presence of an internal electric field [71]. Then, the electrons in the CB of $\text{Pg-C}_3\text{N}_4$ are transferred to Pt to undergo a reduction reaction with H^+ [72], and the holes in the VB of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ are oxidized with S^{2-} and SO_3^{2-} . In addition, S^{2-} and SO_3^{2-} can provide S for the catalyst and reduce photoetching of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. Through the S-scheme mechanism, the electron-hole pairs are separated in space to endow the $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ composites with a strong redox capacity. The space-separated holes and electrons undergo oxidation and reduction reactions, respectively. The electron-hole pairs are not enriched in the CB of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ and VB of $\text{Pg-C}_3\text{N}_4$, thereby reducing the photoetching of $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$. Therefore, the prepared catalyst can effectively suppress the recombination of electron-hole pairs, which results in excellent photocatalytic performance and photostability.

4. Conclusions

We have successfully prepared a step-scheme $\text{Pg-C}_3\text{N}_4/$

$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ system by a solvothermal method for photocatalytic H_2 evolution. 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ exhibits the best H_2 evolution performance ($6.69 \text{ mmol g}^{-1} \text{ h}^{-1}$). In addition, 15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ remains highly active after seven cycles of experiments. The improvement in the photocatalytic performance and photostability is attributed to the formation of a step-scheme heterojunction. The formation of the step-scheme heterojunction promotes the separation of carriers and the transmission efficiency and reduces the probability of recombination. We have provided possible strategies for solving the energy problems.

References

- [1] W. Yu, J. Zhang, T. Peng, *Appl. Catal. B*, **2016**, 181, 220–227.
- [2] Z. Li, X. Wang, J. Zhang, C. Liang, L. Lu, K. Dai, *Chin. J. Catal.*, **2019**, 40, 326–334.
- [3] X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem. Rev.*, **2019**, 119, 3962–4179.
- [4] R. Shi, Y. H. Cao, Y. J. Bao, Y. F. Zhao, G. I. N. Waterhouse, Z. Y. Fang, L. Z. Wu, C. H. Tung, Y. D. Yin, T. R. Zhang, *Adv. Mater.*, **2017**, 29, 1700803.
- [5] A. Meng, L. Zhang, B. Cheng, J. Yu, *ACS Appl. Mater. Interfaces*, **2019**, 11, 5581–5589.
- [6] 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.
- [7] B. Chai, C. Liu, C. Wang, J. Yan, Z. Ren, *Chin. J. Catal.*, **2017**, 38, 2067–2075.
- [8] B. Chai, M. Xu, J. Yan, Z. Ren, *Appl. Surf. Sci.*, **2018**, 430, 523–530.
- [9] Z. Qin, W. Fang, J. Liu, Z. Wei, Z. Jiang, W. Shangguan, *Chin. J. Catal.*, **2018**, 39, 472–478.
- [10] F. Mei, J. Zhang, K. Dai, G. Zhu, C. Liang, *Dalton Trans.*, **2019**, 48, 1067–1074.
- [11] M. F. Kuehnel, C. E. Creissen, C. D. Sahm, D. Wielend, A. Schlosser, K. L. Orchard, E. Reisner, *Angew. Chem. Int. Ed.*, **2019**, 58, 5059–5063.
- [12] T. Xie, Y. Liu, H. Wang, Z. Wu, *Appl. Surf. Sci.*, **2018**, 444, 320–329.
- [13] X. B. Fan, S. Yu, X. Wang, Z. J. Li, F. Zhan, J. X. Li, Y. J. Gao, A. D. Xia, Y. Tao, X. B. Li, L. P. Zhang, C. H. Tung, L. Z. Wu, *Adv. Mater.*, **2019**, 31, 1970048.
- [14] J. L. Andrews, J. Cho, L. Wangoh, N. Suwandarantne, A. Sheng, S. Chauhan, K. Nieto, A. Mohr, K. J. Kadassery, M. R. Popeil, P. K. Thakur, M. Sfeir, D. C. Lacy, T. L. Lee, P. H. Zhang, D. F. Watson, L. F. J. Piper, S. Banerjee, *J. Am. Chem. Soc.*, **2018**, 140, 17163–17174.
- [15] S. Wang, B. Zhu, M. Liu, L. Zhang, J. Yu, M. Zhou, *Appl. Catal. B*, **2019**, 243, 19–26.
- [16] T. Hu, K. Dai, J. Zhang, G. Zhu, C. Liang, *Appl. Surf. Sci.*, **2019**, 481, 1385–1393.
- [17] A. Lamouchi, I. B. Assaker, R. Chtourou, *Appl. Surf. Sci.*, **2019**, 478, 937–945.
- [18] R. Chen, P. F. Wang, J. Chen, C. Wang, Y. H. Ao, *Appl. Surf. Sci.*, **2019**, 473, 11–19.
- [19] M. Asadi, M. H. Motevaselian, A. Moradzadeh, L. Majidi, M. Esmailirad, T. V. Sun, C. Liu, R. Bose, P. Abbasi, P. Zapol, A. P. Khodadoust, L. A. Curtiss, N. R. Aluru, A. Salehi-Khojin, *Adv. Energy Mater.*, **2019**, 9, 1803536.
- [20] W. Yu, J. Chen, T. Shang, L. Chen, L. Gu, T. Peng, *Appl. Catal. B*, **2017**, 219, 693–704.
- [21] H. An, B. Lin, C. Xue, X. Q. Yan, Y. Z. Dai, J. J. Wei, G. D. Yang, *Chin. J. Catal.*, **2018**, 39, 654–663.
- [22] L. Guo, Z. Yang, K. Marcus, Z. Li, B. Luo, L. Zhou, X. Wang, Y. Du, Y. Yang, *Energy Environ. Sci.*, **2018**, 11, 106–114.

Graphical Abstract

Chin. J. Catal., 2020, 41: 41–49 doi: S1872-2067(19)63389-9

Step-scheme porous g-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composites for efficient and stable photocatalytic H₂ production

Feifei Mei, Zhen Li, Kai Dai*, Jinfeng Zhang*, Changhao Liang*
Huaibei Normal University, Hefei Institutes of Physical Science, Chinese Academy of Sciences

Step-scheme Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composites with enhanced photocatalytic activity and durability were successfully fabricated by a solvothermal method. Compared to those of Zn_{0.2}Cd_{0.8}S-DETA and Pg-C₃N₄, the photocatalytic H₂ production rate and stability of Pg-C₃N₄/Zn_{0.2}Cd_{0.8}S-DETA composites are high, which is attributed to the spatial separation of electron-hole pairs and improved transmission efficiency.

- [23] X. Zhao, J. Feng, J. Liu, J. Lu, W. Shi, G. Yang, G. Wang, P. Feng, P. Cheng, *Adv. Sci.*, **2018**, 5, 1700590.
- [24] S. Wang, C. Ren, H. Tian, J. Yu, M. Sun, *Phys. Chem. Chem. Phys.*, **2018**, 20, 13394–13399.
- [25] L. B. Liao, Q. H. Zhang, Z. H. Su, Z. Z. Zhao, Y. N. Wang, Y. Li, X. X. Lu, D. G. Wei, G. Y. Feng, Q. K. Yu, X. J. Cai, J. M. Zhao, Z. F. Ren, H. Fang, F. Robles-Hernandez, S. Baldelli, J. M. Bao, *Nat. Nanotechnol.*, **2014**, 9, 69–73.
- [26] Z. Y. Mao, J. J. Chen, Y. F. Yang, D. J. Wang, L. J. Bie, B. D. Fahlman, *ACS Appl. Mater. Interfaces*, **2017**, 9, 12427–12435.
- [27] J. Low, B. Dai, T. Tong, C. Jiang, J. Yu, *Adv. Mater.*, **2018**, 31, 1802981.
- [28] J. Lv, J. Zhang, J. Liu, Z. Li, K. Dai, C. Liang, *ACS Sustain. Chem. Eng.*, **2018**, 6, 696–706.
- [29] T. Hu, P. Li, J. Zhang, C. Liang, K. Dai, *Appl. Surf. Sci.*, **2018**, 442, 20–29.
- [30] B. Ma, R. Zhang, K. Lin, H. Liu, X. Wang, W. Liu, H. Zhan, *Chin. J. Catal.*, **2018**, 39, 527–533.
- [31] T. Di, Q. Xu, W. Ho, H. Tang, Q. Xiang, J. Yu, *ChemCatChem*, **2019**, 11, 1394–1411.
- [32] Q. Li, H. Meng, P. Zhou, Y. Q. Zheng, J. Wang, J. G. Yu, J. R. Gong, *ACS Catal.*, **2013**, 3, 882–889.
- [33] L. Ma, K. Chen, F. Nan, J.-H. Wang, D.-J. Yang, L. Zhou, Q.-Q. Wang, *Adv. Funct. Mater.*, **2016**, 26, 6076–6083.
- [34] J. Feng, C. An, L. Dai, J. Liu, G. Wei, S. Bai, J. Zhang, Y. Xiong, *Chem. Eng. J.*, **2016**, 283, 351–357.
- [35] L. Zhang, X. Fu, S. Meng, X. Jiang, J. Wang, S. Chen, *J. Mater. Chem. A*, **2015**, 3, 23732–23742.
- [36] F. Xu, J. Zhang, B. Zhu, J. Yu, J. Xu, *Appl. Catal. B*, **2018**, 230, 194–202.
- [37] C. Liu, B. Chai, C. Wang, J. Yan, Z. Ren, *Int. J. Hydrogen Energy*, **2018**, 43, 6977–6986.
- [38] F. Deng, X. Lu, Y. Luo, J. Wang, W. Che, R. Yang, X. Luo, S. Luo, D. D. Dionysiou, *Chem. Eng. J.*, **2019**, 361, 1451–1461.
- [39] S. Wepfer, J. Frohleiks, A.R. Hong, H.S. Jang, G. Bacher, E. Nannen, *ACS Appl. Mater. Interfaces*, **2017**, 9, 11224–11230.
- [40] W. Chen, Z.-C. He, G.-B. Huang, C.-L. Wu, W.-F. Chen, X.-H. Liu, *Chem. Eng. J.*, **2019**, 359, 244–253.
- [41] J. Zhang, G. Huang, J. Zeng, Y. Shi, S. Lin, X. Chen, H. Wang, Z. Kong, J. Xi, Z. Ji, *J. Am. Ceram. Soc.*, **2019**, 102, 2810–2819.
- [42] G. Naresh, P.-L. Hsieh, V. Meena, S.-K. Lee, Y.-H. Chiu, M. Madasu, A.-T. Lee, H.-Y. Tsai, T.-H. Lai, Y.-J. Hsu, Y.-C. Lo, M. H. Huang, *ACS Appl. Mater. Interfaces*, **2019**, 11, 3582–3589.
- [43] K. Dai, J. Lv, J. Zhang, G. Zhu, L. Geng, C. Liang, *ACS Sustain. Chem. Eng.*, **2018**, 6, 12817–12825.
- [44] J. Lv, J. Zhang, K. Dai, C. Liang, G. Zhu, Z. Wang, Z. Li, *Dalton Trans.*, **2017**, 46, 11335–11343.
- [45] S. Wei, Y. Liu, M. Ma, Y. Wu, L. Huanga, D. Pan, *J. Mater. Chem. C*, **2018**, 6, 11104–11110.
- [46] M. Imran, A. B. Yousaf, P. Kasak, A. Zeb, S. J. Zaidi, *J. Catal.*, **2017**, 353, 81–88.
- [47] Y. Zhang, Y.-Z. Lin, Z.-X. Wang, K. Li, T. Li, F.-T. Liu, *Catal. Sci. Technol.*, **2019**, 9, 583–587.
- [48] K. Dai, L. Lu, C. Liang, Q. Liu, G. Zhu, *Appl. Catal. B*, **2014**, 156–157, 331–340.
- [49] Y. Huo, J. Zhang, K. Dai, Q. Li, J. Lv, G. Zhu, C. Liang, *Appl. Catal. B*, **2019**, 241, 528–538.
- [50] Y. Zhang, C. Ren, Y. Zhang, W. Lin, K. Ding, *Appl. Surf. Sci.*, **2019**, 478, 119–127.
- [51] Y. Huo, Z. Wang, J. Zhang, C. Liang, K. Dai, *Appl. Surf. Sci.*, **2018**, 459, 271–280.
- [52] B. Zhu, L. Zhang, B. Cheng, J. Yu, *Appl. Catal. B*, **2018**, 224, 983–999.
- [53] X. Du, X. Yi, P. Wang, J. Deng, C.-C. Wang, *Chin. J. Catal.*, **2019**, 40, 70–79.
- [54] B. Chai, C. Liu, J. Yan, Z. Ren, Z.-J. Wang, *Appl. Surf. Sci.*, **2018**, 448, 1–8.
- [55] J. Fu, Q. Xu, J. Low, C. Jiang, J. Yu, *Appl. Catal. B*, **2019**, 243, 556–565.
- [56] Y. Liu, H. Liu, H. Zhou, T. Li, L. Zhang, *Appl. Surf. Sci.*, **2019**, 466, 133–140.
- [57] J. Fu, B. Zhu, C. Jiang, B. Cheng, W. You, J. Yu, *Small*, **2017**, 13, 1603938.
- [58] Y. Xu, F. Ge, Z. Chen, S. Huang, W. Wei, M. Xie, H. Xu, H. Li, *Appl. Surf. Sci.*, **2019**, 469, 739–746.
- [59] J. Ge, Y. Liu, D. Jiang, L. Zhang, P. Du, *Chin. J. Catal.*, **2019**, 40, 160–167.
- [60] S. Ma, X. Xu, J. Xie, X. Li, *Chin. J. Catal.*, **2017**, 38, 1970–1980.

- [61] L. Kong, J. Yan, S. F. Liu, *ACS Sustain. Chem. Eng.*, **2019**, 7, 1389–1398.
- [62] Y. Huo, Y. Yang, K. Dai, J. Zhang, *Appl. Surf. Sci.*, **2019**, 481, 1260–1269.
- [63] P. Xia, M. Liu, B. Cheng, J. Yu, L. Zhang, *ACS Sustain. Chem. Eng.*, **2018**, 6, 8945–8953.
- [64] Y. Wei, Y. Zhu, Y. Jiang, *Chem. Eng. J.*, **2019**, 356, 915–925.
- [65] N. Mao, J.-X. Jiang, *Appl. Surf. Sci.*, **2019**, 476, 144–150.
- [66] X. Geng, S. Chen, X. Lv, W. Jiang, T. Wang, *Appl. Surf. Sci.*, **2018**, 462, 18–28.
- [67] J. Lv, K. Dai, J. Zhang, L. Geng, C. Liang, Q. Liu, G. Zhu, C. Chen, *Appl. Surf. Sci.*, **2015**, 358, 377–384.
- [68] Z. Wang, J. Lv, J. Zhang, K. Dai, C. Liang, *Appl. Surf. Sci.*, **2018**, 430, 595–602.
- [69] W. Liu, X. Wang, H. Yu, J. Yu, *ACS Sustain. Chem. Eng.*, **2018**, 6, 12436–12445.
- [70] R. He, D. Xu, B. Cheng, J. Yu, W. Ho, *Nanoscale Horiz.*, **2018**, 3, 464–504.
- [71] F. Xu, B. Zhu, B. Cheng, J. Yu, J. Xu, *Adv. Opt. Mater.*, **2018**, 6, 1800911.
- [72] S. Cao, H. Li, Y. Li, B. Zhu, J. Yu, *ACS Sustain. Chem. Eng.*, **2018**, 6, 6478–6487.

梯型多孔 $\text{g-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 复合材料的合成及其高效稳定光催化产氢性能

梅飞飞^a, 李真^a, 代凯^{a,*}, 张金锋^{a,#}, 梁长浩^{b,\$}

^a淮北师范大学物理与电子信息学院, 安徽含能材料重点实验室, 安徽淮北235000

^b中国科学院固体物理研究所, 材料物理重点实验室和安徽纳米材料和纳米技术重点实验室, 安徽合肥230031

摘要: 近年来, 化石燃料燃烧导致的环境污染问题和能源危机越来越严重. 在众多解决方案中, 光催化产氢由于其可持续性以及无污染等特点而受到广泛关注. 然而, 由于许多半导体光催化剂性能不理想, 光催化水分解研究进程缓慢. 本研究采用水热法成功制备了梯型 $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 复合材料用于光催化产氢. DETA(二亚乙基三胺)作为一种有机分子插入在 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ 的层中构成有机-无机杂化材料. 采用X射线衍射(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)、X射线光电子能谱(XPS)、紫外-可见光漫反射光谱(UV-vis)以及光电流研究了所制备样品的结构、形貌、元素组成以及光电特征, 并提出了可能的光催化机制.

XRD和XPS结果表明 $\text{Pg-C}_3\text{N}_4$ 和 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 复合在一起而不是机械混合. 通过TEM可以看出 $\text{Pg-C}_3\text{N}_4$ 是一种带有很多孔洞的纳米片, 而 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 类似于纳米花瓣, 在 $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 复合材料中 $\text{Pg-C}_3\text{N}_4$ 表面充满了 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 纳米花瓣. 经过元素分析得知所合成的复合材料没有杂质元素. UV-vis表明 $\text{Pg-C}_3\text{N}_4$ 和 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 具有良好的吸收带边以及带隙, 分别为2.83 eV和2.48 eV. 光电流和PL显示15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 具有很高的载流子分离及传输效率. 光催化性能测试显示15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 具有很好的产氢活性, 为 $6.69 \text{ mmol g}^{-1} \text{ h}^{-1}$, 分别是 $\text{Pg-C}_3\text{N}_4$ 和 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 的16.73和1.44倍. 在经过七次循环实验后15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 仍保持很优异的活性, 说明它具有很好的稳定性.

通过高分辨XPS中各元素结合能的变化可以看出构成异质结之后电子的流向, 从而看出光催化可能的机制为梯形. 光照射之后, $\text{Pg-C}_3\text{N}_4$ 和 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 中产生电子-空穴对, 电子迁移到导带并在价带留下空穴. 当 $\text{Pg-C}_3\text{N}_4$ 与 $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 复合之后, 在它们的接触处会形成内部电场, $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 导带上的电子和 $\text{Pg-C}_3\text{N}_4$ 价带上的空穴会在内部电场作用下复合. $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 价带上的空穴和 $\text{Pg-C}_3\text{N}_4$ 上的电子分别参与氧化还原反应. 梯形机制促使电子和空穴在空间上分离, 从而具有强氧化还原性. 梯形异质结的形成加快了15% $\text{Pg-C}_3\text{N}_4/\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S-DETA}$ 复合材料中电子-空穴对的分离效率, 并减少了电子-空穴对的复合, 从而使其具有很优异的光催化性能和稳定性.

关键词: $\text{Pg-C}_3\text{N}_4$; $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$; 二亚乙基三胺; 光催化; 梯形多孔复合物

收稿日期: 2019-04-08. 接受日期: 2019-05-01. 出版日期: 2020-01-05.

*通讯联系人. 传真: (0561)3803256; 电子邮箱: daikai940@chnu.edu.cn

#通讯联系人. 电子邮箱: jfzhang@chnu.edu.cn

\$通讯联系人. 电子邮箱: chliang@issp.ac.cn

基金来源: 国家自然科学基金(51572103, 51502106); 安徽省杰出青年基金(1808085J14); 安徽省高等学校省级优秀青年人才基金(gxyqZD201751); 安徽省教育厅重点项目(KJ2016SD53); 安徽省创新团队(KJ2015TD003).

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>).