available at www.sciencedirect.com

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

Article

Integrating non-precious-metal cocatalyst Ni_3N with $\text{g-C}_3\text{N}_4$ for enhanced photocatalytic H_2 production in water under visible-light irradiation

Jianhua Ge ^{a,b,*}, Yujie Liu ^a, Daochuan Jiang ^b, Lei Zhang ^b, Pingwu Du ^{b,#}^a School of Earth and Environment, Anhui University of Science & Technology, Huainan 232001, Anhui, China^b CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), University of Science and Technology of China (USTC), Hefei 230026, Anhui, China

ARTICLE INFO

Article history:

Received 9 October 2018

Accepted 14 December 2018

Published 5 February 2019

Keywords:

Photocatalysis

 Ni_3N

Cocatalyst

Hydrogen evolution

 $\text{g-C}_3\text{N}_4$

ABSTRACT

Photocatalytic H_2 production via water splitting in a noble-metal-free photocatalytic system has attracted much attention in recent years. In this study, noble-metal-free Ni_3N was used as an active cocatalyst to enhance the activity of $\text{g-C}_3\text{N}_4$ for photocatalytic H_2 production under visible-light irradiation ($\lambda > 420 \text{ nm}$). The characterization results indicated that Ni_3N nanoparticles were successfully loaded onto the $\text{g-C}_3\text{N}_4$, which accelerated the separation and transfer of photogenerated electrons and resulted in enhanced photocatalytic H_2 evolution under visible-light irradiation. The hydrogen evolution rate reached $\sim 305.4 \mu\text{mol h}^{-1} \text{g}^{-1}$, which is about three times higher than that of pristine $\text{g-C}_3\text{N}_4$, and the apparent quantum yield (AQY) was $\sim 0.45\%$ at $\lambda = 420 \text{ nm}$. Furthermore, the $\text{Ni}_3\text{N/g-C}_3\text{N}_4$ photocatalyst showed no obvious decrease in the hydrogen production rate, even after five cycles under visible-light irradiation. Finally, a possible photocatalytic hydrogen evolution mechanism for the $\text{Ni}_3\text{N/g-C}_3\text{N}_4$ system is proposed.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

In 2009, Wang and coworkers reported a novel metal-free polymeric semiconductor photocatalyst, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), for H_2 evolution [1]. Since then, many studies have been published concerning the use of $\text{g-C}_3\text{N}_4$ for solar energy conversion and environmental applications, mainly because of its facile synthesis, appealing bandgap ($E_g = 2.7 \text{ eV}$), suitable electronic structure, and high physicochemical stability. Nevertheless, bulk $\text{g-C}_3\text{N}_4$ has a low surface area and the photogenerated charges recombine rapidly, which reduces the

photocatalytic performance [2]. Hence, many efforts have been made to improve the performance of $\text{g-C}_3\text{N}_4$, for example, by doping with nonmetals and metals [3–9], protonation by strong acids [10], the introduction of porosity [11–13], and the fabrication of heterojunction composites [14–16]. Among the various strategies, the loading of moderate amounts of cocatalysts onto the surface of $\text{g-C}_3\text{N}_4$ is believed to be an ideal strategy to increase the separation of photogenerated electron-hole pairs and provide active sites for photocatalytic H_2 production via water splitting [17].

More recently, considering the practical applications, atten-

* Corresponding author. Tel/Fax: +86-554-6668430; E-mail: gejianhua13@163.com

Corresponding author. Tel/Fax: +86-551-63606207; E-mail: dupingwu@ustc.edu.cn

This work was financially supported by the National Key Research and Development Program of China (2017YFA0402800), the National Natural Science Foundation of China (51772285, 21473170, 51878004), the Natural Science Fund of Anhui Province (1808085ME139), and the Fundamental Research Funds for the Central Universities.

DOI: S1872-2067(19)63283-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 2, February 2019

tion has focused on low-cost and earth-abundant materials as replacements for noble metal cocatalysts for photocatalytic H₂ evolution systems [18]. These non-noble-metal catalysts include Co [19], CoP [17], Ni₂P [20], NiS [21], Ni(OH)₂ [22], Cu₃P [23], Fe₂P [24], MoP [25], and NiS [21]. Meanwhile, transition metal nitrides have received considerable attention because of their good electrical conductivity and flexible (electro)catalytic properties [6,26,27]. For example, Xu et al. [28] first reported metallic Ni₃N nanosheets as efficient oxygen evolution reaction (OER) electrocatalysts. Shalom et al. [26] fabricated Ni₃N on Ni foam for electrocatalytic applications, which exhibited an extremely low overpotential, high current density, and excellent stability for the hydrogen evolution reaction (HER) in alkaline solution. Our group reported that the use of Ni₃N as a cocatalyst on CdS nanorods for the photocatalytic HER can enhance the rate by more than 10 times [6]. However, from a literature survey, the use of a noble-metal-free Ni₃N as a cocatalyst on g-C₃N₄ for photocatalytic H₂ production has received little attention.

Motivated by the above results, we present the use of low-cost, noble-metal-free Ni₃N as an active cocatalyst for g-C₃N₄ via modification of the semiconductor surface. These Ni₃N/g-C₃N₄ hybrids present an enhanced visible-light-driven H₂ production rate of 305.4 μmol g⁻¹ h⁻¹, which is about three-times higher than that of bulk g-C₃N₄, and the apparent quantum yield (AQY) was ~0.45% at 420 nm. In addition, the photoluminescence (PL) spectra and photoelectrochemical characterization revealed that Ni₃N is an efficient cocatalyst for photocatalytic H₂ evolution. Furthermore, a photocatalytic hydrogen evolution mechanism based on Ni₃N/g-C₃N₄ is proposed and discussed in detail.

2. Experimental

2.1. Materials

All reagents (analytical grade) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China) and used directly without further purification.

2.2. Preparation

The g-C₃N₄ was prepared by thermal pyrolysis based on a previously reported method [29].

In a typical process, calculated amounts of Ni(NO₃)₂·6H₂O (29.079, 58.158, 145.395, and 203.553 mg) and hexamethylenetetramine (HMT, 8.038, 56.076, 140.19, and 196.266 mg) were dissolved in 40 mL H₂O with vigorous magnetic stirring for 0.5 h. Then, 0.5 g of g-C₃N₄ was added to the solution with vigorous stirring. The resulting suspension was transferred to a 50-mL Teflon-lined, stainless-steel autoclave and maintained at 120 °C for 12 h. After cooling to room temperature, the precipitates were collected by centrifugation and washed with ethanol and distilled water three times each and dried under vacuum overnight. After that, the precipitates were annealed at 380 °C for 3 h under a flow of NH₃ gas. The obtained samples were labeled Ni₃N/g-C₃N₄#1, Ni₃N/g-C₃N₄#2, Ni₃N/g-C₃N₄#3,

and Ni₃N/g-C₃N₄#4. For comparison, pristine Ni₃N nanoparticles were also prepared using the same method in the absence of g-C₃N₄.

2.3. Characterization

All the prepared photocatalyst samples were systematically investigated using powder X-ray diffraction (PXRD, D/max-TTR III, 5° min⁻¹ from 10° to 70° in 2θ), scanning electron microscopy (SEM, SIRION200 equipped with electron diffraction), transmission electron microscopy (TEM, JEM-2010, acceleration voltage of 200 kV), UV-Vis spectrometry (UV-Vis, SOLID 3700), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250).

2.4. Photocatalytic H₂ production testing

The photocatalytic activity reactions were performed in a 50-mL flask with magnetic stirring using A 300-W xenon lamp as the irradiation source. The lamp was equipped with a UV cut-off filter (λ > 420 nm). Photocatalytic H₂ production was quantified by gas chromatography (GC, SP6890, thermal conductivity detector (TCD) detector, high purity nitrogen as a carrier gas, and 5 Å molecular sieve column). To investigate the long-term photocatalytic H₂ production stability under visible-light irradiation, 5.0 mg of the sample was ultrasonically dispersed in a 20 vol% aqueous solution of triethanolamine (TEOA) in a 250-mL flask. The apparent quantum efficiency was calculated using a 300-W Xe lamp with a band-pass filter (λ = 420 nm). The AQY was calculated using the following equation.

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\% \end{aligned}$$

3. Results and discussion

3.1. XRD analysis

The crystalline phases of pristine g-C₃N₄ and the pristine Ni₃N nanoparticles, together with those of the Ni₃N/g-C₃N₄ hybrid composites, were analyzed by XRD. As shown in Fig. 1, the characteristic peaks at 13.08° and 27.4° correspond to the (100) and (002) crystalline planes, respectively, for g-C₃N₄ with a graphitic structure (JCPDS#87-1526) [30]. The characteristic peaks at 38.9°, 42.5°, 44.5°, and 58.6° can be indexed to the (110), (002), (111), and (112) planes, respectively, for hexagonal Ni₃N (JCPDS#89-5144) [27]. Meanwhile, the Ni₃N/g-C₃N₄ hybrid composites samples display similar XRD patterns to both pristine g-C₃N₄ and pristine Ni₃N nanoparticles. With increasing Ni₃N content, the peak intensities of Ni₃N gradually become stronger, and no other impurities were detected, indicating that there are no obvious changes to g-C₃N₄ after modification with Ni₃N nanoparticles under a flow of NH₃ gas.

3.2. SEM and EDX analysis

Fig. 1. Powder XRD patterns of pristine Ni_3N , pristine $\text{g-C}_3\text{N}_4$, and $\text{Ni}_3\text{N/g-C}_3\text{N}_4$ composites with different amounts of Ni_3N .

The morphologies and material compositions of pristine $\text{g-C}_3\text{N}_4$ and the $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ hybrid composite were further analyzed using SEM, TEM, and energy-dispersive X-ray (EDX) measurements. As shown in Fig. 2(a), $\text{g-C}_3\text{N}_4$ has a typical lamellar structure of multilayer $\text{g-C}_3\text{N}_4$ nanosheets, and the $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ sample has a structure where the nanoparticles are closely anchored to the surface of the $\text{g-C}_3\text{N}_4$ nanosheets (Fig. 2(b)). As shown in the TEM image of the $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ hybrid composite (Fig. 2(c)), the Ni_3N nanoparticles were deposited on $\text{g-C}_3\text{N}_4$ surface. In addition, the elemental mapping and EDS spectra (Fig. 3) clearly reveal the existence of Ni and N, as well as Cu from the sample base, suggesting that Ni_3N nanoparticles had been successfully loaded onto the $\text{g-C}_3\text{N}_4$ surface. Thus, these characterization results further show that the Ni_3N nanoparticles were successfully loaded onto surface of the $\text{g-C}_3\text{N}_4$.

3.3. XPS Analysis

The chemical states and surface composition of the $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ hybrid composite photocatalyst were further investigated using XPS. The survey XPS scan spectrum shown in Fig. 4(a) clearly reveals the presence of Ni, C, O, and N, as well as C, which was used as the reference, and O from the absorbed gaseous molecules and oxidized Ni species [6]. In the high-resolution C 1s XPS spectrum (Fig. 4(b)), two peaks were

Fig. 3. Ni (a), C (b), and N (c) mapping of $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$, and EDS of $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ (d).

deconvoluted into peaks at 284.8, 286.1, and 288.3 eV; these correspond to graphitic C–C bonds, C–O bonds, and sp^2 -hybridized carbon in N-containing aromatic ring (N-C=N), respectively, thus confirming the presence of $\text{g-C}_3\text{N}_4$. In the Ni 2p region, four peaks are seen at 856.2, 874.3, 861.3, and 880.3 eV (Fig. 4(d)), which are ascribed to the $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ peaks and oxidized Ni species (NiO) [26,28]. In addition, N 1s peaks are located at 398.8, 399.9, and 401.1 eV (Fig. 4(c)); these Ni and N peaks are consistent with the characteristics of Ni_3N and are characteristic of C–N–C, tertiary nitrogen N-(C)_3 groups, and the tertiary nitrogen N-(C)_3 groups, respectively [31].

3.4. Optical bandgap analysis

The light harvesting properties of the pristine $\text{g-C}_3\text{N}_4$, pristine Ni_3N , and $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ composites were measured by UV-vis diffuse reflectance spectroscopy. As depicted in Fig. 5(a), no obvious bandgap absorption structure was observed for Ni_3N , indicating its typical metallic character, and there is no apparent difference in the bandgap absorption edge between the $\text{g-C}_3\text{N}_4$ and $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ hybrid composites, suggesting Ni_3N was not doped into the $\text{g-C}_3\text{N}_4$ crystal lattice, and, thus, there was no change in its bandgap, which can be estimated

Fig. 2. SEM images of pristine $\text{g-C}_3\text{N}_4$ (a) and $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ (b), and TEM image of $\text{Ni}_3\text{N/g-C}_3\text{N}_4\#3$ (c).

Fig. 4. XPS survey spectrum (a) and high-resolution XPS spectra of C 1s (b), N 1s (c), and Ni 2p (d) of the $\text{N}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ sample.

Fig. 5. UV-Vis spectra of Ni_3N , $\text{g-C}_3\text{N}_4$, and the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ sample.

based on the diffuse reflection spectral data. As shown in Fig. 5(b), the bandgaps of pristine $\text{g-C}_3\text{N}_4$ and the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ composite were estimated to be 2.55 eV, which is slightly smaller than the reported values [32].

3.5. Photoelectrochemical analysis

PL spectral analysis was used to determine the recombination rate of the photogenerated electron-hole pairs. A lower PL emission intensity is an indication of a lower recombination rate of the photogenerated electron-hole pairs [33]. Fig. 6(a) shows the PL spectra of the pristine $\text{g-C}_3\text{N}_4$ and $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4$ composite samples. As shown, the PL spectra of all samples have the same wide emission peak at about 450 nm under an excitation wavelength of 385 nm, which is ascribed to the

bandgap recombination of photoexcited electron-hole pairs in pristine $\text{g-C}_3\text{N}_4$. Moreover, the PL intensity of the samples decreases in order of pristine $\text{g-C}_3\text{N}_4 > \text{g-C}_3\text{N}_4(\text{NH}_3 \text{ treated}) > \text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#1 > \text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#2 > \text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#4 > \text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$, which demonstrates that the recombination rate of photogenerated electron-holes first decreased with increasing amount of Ni_3N and, then, increased when an excess amount of Ni_3N was incorporated. The excess Ni_3N may act as recombination centers covering the active sites on the $\text{g-C}_3\text{N}_4$ surface, thus lowering the charge separation efficiency.

The transient photocurrent response curves of the electrodes coated with pristine $\text{g-C}_3\text{N}_4$ and $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ hybrid composite were recorded for several on-off cycles in 0.5 mol L^{-1} Na_2SO_4 aqueous solution at 0.0 V vs. Ag/AgCl ($I-t$ curve, Fig. 6(b)) [34]. Both samples yield relatively low photocurrents

Fig. 6. PL spectrum and photoelectrochemical activity of the samples.

without light irradiation. Interestingly, an apparent increase in the photocurrent appears when the visible-light source was turned on. The working electrode coated with the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ hybrid composite exhibited a much higher photocurrent than that coated with $\text{g-C}_3\text{N}_4$. This can be ascribed to the Ni_3N nanoparticles on the $\text{g-C}_3\text{N}_4$ interface, which efficiently separated the photogenerated charge carriers and resulted in decreased photoinduced electron-hole recombination and an enhanced photocurrent.

Electrochemical impedance spectroscopy (EIS) measurements of the electrodes coated with pristine $\text{g-C}_3\text{N}_4$ and $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ hybrid composite were obtained in 0.5 mol L^{-1} Na_2SO_4 aqueous solution to investigate the electron transfer and combination of the semiconductor in solution. As shown in Fig. 6(c), the EIS results indicate that the impedance arc radius of the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ hybrid composite is smaller than that of the pristine $\text{g-C}_3\text{N}_4$, indicating that the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ composite shows enhanced photoexcited charge carrier separation efficiency compared to that of $\text{g-C}_3\text{N}_4$. This result indicates the Ni_3N efficiently facilitates the transport of photogenerated charge carriers and promotes hydrogen production activity [35].

3.6. Photocatalytic hydrogen production activity

Photocatalytic H_2 production experiments were carried out under visible-light irradiation in aqueous TEOA solution using pristine $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4$ treated with NH_3 , and pristine $\text{g-C}_3\text{N}_4$ loaded with different amounts of Ni_3N . As shown in Fig. 7(a), the hydrogen production rate increased initially and, subsequently, decreased with increasing ratio of loaded Ni_3N , indicating that Ni_3N is an efficient cocatalyst. However, excess Ni_3N may shield the incident light and may also block the active sites

responsible for hydrogen production. Pristine Ni_3N is not active for hydrogen evolution. In addition, the mechanically mixed sample of pristine $\text{g-C}_3\text{N}_4$ and Ni_3N exhibited a lower rate of hydrogen production than $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$, highlighting the importance of the close contact between pristine $\text{g-C}_3\text{N}_4$ and the Ni_3N cocatalyst. Meanwhile, the effect of the type and concentration of sacrificial electron donors was further investigated. As shown in Fig. 7(b), when $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ and TEOA were combined, the photocatalytic activity for hydrogen production increased sharply, and a maximum H_2 production rate of $\sim 305.4 \mu\text{mol h}^{-1} \text{g}^{-1}$ was obtained. The results are also shown in Fig. 7(c), which reveal that the rate of H_2 production slightly decreased when the TEOA concentration further increased, indicating that very high concentrations of the TEOA electron donor does not improve the photocatalytic activity beyond the optimal concentration.

The ability of the photocatalyst to remain active over multiple cycles is vital for practical applications [36]. As shown in Fig. 8(a), the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4\#3$ photocatalyst showed no obvious decrease in the hydrogen production rate after five cycles under visible-light irradiation, which indicate that the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4$ photocatalyst have good photocatalytic durability and stability. Furthermore, the hydrogen production rate reached $\sim 329.6 \mu\text{mol h}^{-1} \text{g}^{-1}$ upon irradiation with 420 nm monochromatic light for 7 h (Fig. 8(b)). After 4 h, the AQY was maintained at an average value of $\sim 0.45\%$.

Based on the above characterization, a possible photocatalytic mechanism for the enhanced photocatalytic activity of the $\text{Ni}_3\text{N}/\text{g-C}_3\text{N}_4$ hybrid composites has been proposed, as shown in Scheme 1. When pristine $\text{g-C}_3\text{N}_4$ was irradiated with visible light, the electrons in the valence band (VB) of $\text{g-C}_3\text{N}_4$ are excited to the conduction band (CB). The photogenerated electrons will either recombine with the holes or transfer to the

Fig. 7. Photocatalytic hydrogen production activity of the samples.

Fig. 8. Photocatalytic hydrogen production performance and AQY of Ni₃N/g-C₃N₄#3.

Scheme 1. Mechanism of photocatalytic H₂ production using the Ni₃N/g-C₃N₄ photocatalyst.

surface for photochemical hydrogen evolution reactions. As a metallic compound, Ni₃N nanoparticles will form a typical metal-semiconductor interface with g-C₃N₄, and the photogenerated electrons are able to transfer from the semiconductor photocatalyst g-C₃N₄ to the metallic cocatalyst, Ni₃N [6]. Thus, loading moderate amounts of Ni₃N onto g-C₃N₄ facilitates the separation of the photogenerated electron-hole pairs in g-C₃N₄, resulting in the improved photocatalytic activity.

4. Conclusions

In summary, we have successfully developed a novel Ni₃N/g-C₃N₄ hybrid composite photocatalyst by a facile thermal ammonolysis method. The photocatalytic activity for hydrogen production is enhanced after the loading of Ni₃N onto g-C₃N₄ under visible-light irradiation. The hydrogen evolution rate reached ~305.4 μmol·h⁻¹·g⁻¹, which is about three times higher than that of pristine g-C₃N₄, and the AQY was ~0.45% at λ = 420 nm. The characterization results indicated that Ni₃N, a noble-metal-free cocatalyst, can efficiently promote the separation of the photogenerated electron-hole pairs in g-C₃N₄. This

work demonstrates the potential of noble-metal-free Ni₃N as a cocatalyst comprising earth-abundant elements (Co and Ni) for photocatalysis.

References

- [1] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [2] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.* **2016**, 16, 159–7329.
- [3] 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.
- [4] Z. A. Lan, G. G. Zhang, X. C. Wang, *Appl. Catal. B*, **2016**, 192, 116–125.
- [5] G. G. Zhang, Z. A. Lan, L. H. Lin, S. Lin, X. C. Wang, *Chem. Sci.*, **2016**, 7, 3062–3066.
- [6] Z. J. Sun, H. L. Chen, L. Zhang, D. P. Lu, P. W. Du, *J. Mater. Chem. A*, **2016**, 4, 13289–13295.
- [7] S. W. Cao, Q. Huang, B. C. Zhu, J. G. Yu, *J. Power Sources*, **2017**, 351, 151–159.
- [8] F. Chen, H. Yang, X. F. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 296–304.

Graphical Abstract

Chin. J. Catal., 2019, 40: 160–167 doi: S1872-2067(19)63283-3

Integrating non-precious-metal cocatalyst Ni_3N with $\text{g-C}_3\text{N}_4$ for enhanced photocatalytic H_2 production in water under visible-light irradiationJianhua Ge^{*}, Yujie Liu, Daochuan Jiang, Lei Zhang, Pingwu Du^{*}

Anhui University of Science & Technology; University of Science and Technology of China

Noble-metal-free Ni_3N was used as an active cocatalyst to accelerate the separation and transfer of photogenerated charges. The resultant catalyst exhibited enhanced photocatalytic H_2 evolution, which was about three times higher than that of pristine $\text{g-C}_3\text{N}_4$.

- [9] J. Jiang, S. W. Cao, C. G. Hu, C. H. Chen, *Chin. J. Catal.*, **2017**, 38, 1981–1989.
- [10] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, A. R. Mohamed, *Nano Energy*, **2015**, 13, 757–770.
- [11] X. D. Sun, Y. Y. Li, J. Zhou, H. M. Cheng, Y. Wang, J. H. Zhu, *J. Colloid Interface Sci.*, **2015**, 451, 108–116.
- [12] K. K. Han, C. C. Wang, Y. Y. Li, M. M. Wan, Y. Wang, J. H. Zhu, *RSC Adv.*, **2013**, 3, 9465–9469.
- [13] B. Shen, Z. H. Hong, Y. L. Chen, B. Z. Lin, B. F. Gao, *Mater. Lett.*, **2014**, 118, 208–211.
- [14] Q. Yu, S. Guo, X. Li, M. Zhang, *Mater. Technol.*, **2014**, 29, 172–178.
- [15] Z. F. Jiang, W. M. Wan, H. M. Li, S. Q. Yuan, H. J. Zhao, P. K. Wong, *Adv. Mater.*, **2018**, 30, 1706108.
- [16] X. J. She, J. J. Wu, H. Xu, J. Zhong, Y. Wang, Y. H. Song, K. Q. Nie, Y. Liu, Y. C. Yang, M. T. F. Rodrigues, R. Vajtai, J. Lou, D. L. Du, H. M. Li, P. M. Ajayan, *Adv. Energy Mater.*, **2017**, 7, 1700025.
- [17] P. W. Du, R. Eisenberg, *Energy Environ. Sci.*, **2012**, 5, 6012–6021.
- [18] R. M. Irfan, D. Jiang, Z. J. Sun, D. P. Lu, P. W. Du, *Dalton Trans.*, **2016**, 45, 12897–12905.
- [19] D. C. Jiang, X. Chen, Z. Zhang, L. Zhang, Y. Wang, Z. J. Sun, R. M. Irfan, P. W. Du, *J. Catal.*, **2017**, 357, 147–153.
- [20] Z. J. Sun, H. F. Zheng, J. S. Li, P. W. Du, *Energy Environ. Sci.*, **2015**, 8, 2668–2676.
- [21] D. C. Jiang, L. Zhu, R. M. Irfan, L. Zhang, P. W. Du, *Chin. J. Catal.*, **2017**, 38, 2102–2109.
- [22] Z. P. Yan, Z. J. Sun, X. Liu, H. X. Jia, P. W. Du, *Nanoscale*, **2016**, 8, 4748–4756.
- [23] A. Rauf, M. Ma, S. Kim, M. S. A. Sher Shah, C. H. Chung, J. H. Park, P. J. Yoo, *Nanoscale*, **2018**, 10, 3026–3036.
- [24] Z. J. Sun, H. L. Chen, Q. Huang, P. W. Du, *Catal. Sci. Technol.*, **2015**, 5, 4964–4967.
- [25] Q. D. Yue, Y. Y. Wan, Z. J. Sun, X. J. Wu, Y. P. Yuan, P. W. Du, *J. Mater. Chem. A*, **2015**, 3, 16941–16947.
- [26] M. Shalom, D. Rössner, X. F. Yang, G. Clavel, T. P. Feller, M. Antonietti, *J. Mater. Chem. A*, **2015**, 3, 8171–8177.
- [27] M. Shalom, V. Molinari, D. Esposito, G. Clavel, D. Rössner, C. Giordano, M. Antonietti, *Adv. Mater.*, **2014**, 26, 1272–1276.
- [28] K. Xu, P. Z. Chen, X. L. Li, Y. Tong, H. Ding, X. J. Wu, W. S. Chu, Z. M. Peng, C. Z. Wu, Y. Xie, *J. Am. Chem. Soc.*, **2015**, 137, 4119–4125.
- [29] X. H. Li, X. C. Wang, M. Antonietti, *ACS Catal.*, **2012**, 2, 2082–2086.
- [30] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [31] P. Ye, X. L. Liu, J. Iocozzia, Y. P. Yuan, L. N. Gu, G. S. Xu, Z. Q. Lin, *J. Mater. Chem. A*, **2017**, 5, 8493–8498.
- [32] H. Wang, Y. Su, H. X. Zhao, H. T. Yu, S. Chen, Y. B. Zhang, X. Quan, *Environ. Sci. Technol.*, **2014**, 48, 11984–11990.
- [33] J. J. Xue, S. S. Ma, Y. M. Zhou, Z. W. Zhang, M. He, *ACS Appl. Mater. Interfaces*, **2015**, 7, 9630–9637.
- [34] J. H. Ge, X. T. Guo, X. Xu, P. P. Zhang, J. L. Zhu, J. B. Wang, *RSC Adv.*, **2015**, 5, 49598–49605.
- [35] W. H. Leng, Z. Zhang, J. Q. Zhang, C. N. Cao, *J. Phys. Chem. B*, **2005**, 109, 15008–15023.
- [36] S. M. Liu, J. L. Zhu, Q. Yang, P. P. Xu, J. H. Ge, X. T. Guo, *Photochem. Photobiol.*, **2015**, 91, 1302–1308.

非贵金属助催化剂 Ni_3N 修饰 $\text{g-C}_3\text{N}_4$ 用于可见光催化产氢的研究葛建华^{a,b,*}, 刘玉洁^a, 江道传^b, 张磊^b, 杜平武^{b,#}^a安徽理工大学地球与环境学院, 安徽淮南 232001^b中国科学技术大学化学与材料科学学院材料科学与工程系, 中国科学院能量转换材料重点实验室, 能源材料化学协同创新中心, 安徽合肥 230026

摘要: 近年来, 利用太阳光光解水制氢被认为是解决当前能源短缺和环境污染问题的重要途径之一。众所周知, 助催化剂

可以有效的降低光催化产氢反应的活化能, 提供产氢反应的活性位点, 有效的促进催化剂中光生载流子的传输与分离, 从而提高光催化剂产氢体系的反应活性和稳定性. 然而, 鉴于贵金属助催化剂(Pt, Au和Pd等)储量低、成本高, 极大地制约了其应用. 因而, 开发出适用于光催化水分解制氢的非贵金属助催化剂尤为重要.

石墨相氮化碳(g-C₃N₄)因其具有热稳定性、化学稳定性高以及制备成本低廉等优点, 成为光催化领域研究的热点. 然而, 由于g-C₃N₄的禁带宽度($E_g = 2.7$ eV)较宽, 致使其对可见光的响应能力较弱, 并且在光催化反应过程中其光生电子-空穴对易复合, 从而导致其光催化产氢活性较低. 因此, 如何开发出含非贵金属助催化剂的g-C₃N₄高效、稳定的太阳光催化分解水制氢体系引起了人们极大的关注.

本文通过水热法-高温氮化法首次将非贵金属Ni₃N作为助催化剂来修饰g-C₃N₄, 增强其可见光光催化性能($\lambda > 420$ nm). 采用XRD、SEM、EDS、Mapping、UV-Vis、XPS和TEM等手段对Ni₃N/g-C₃N₄光催化体系进行了表征. 结果表明, Ni₃N纳米颗粒成功的负载到g-C₃N₄表面且没有改变g-C₃N₄的层状结构. 此外, 采用荧光光谱分析(PL)、阻抗测试(EIS)和光电流谱进行表征, 结果显示, Ni₃N纳米颗粒可有效促进催化剂中光生载流子的传输与分离, 抑制电子-空穴对的复合. 同时, 将功率为300 W且装有紫外滤光片($\lambda > 420$ nm)的氙灯作为可见光源进行光催化产氢实验结果表明, 引入了一定量的Ni₃N可以极大提高g-C₃N₄的光催化活性, 其中, Ni₃N/g-C₃N₄#3的产氢量为 $\sim 305.4 \mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$, 大约是单体g-C₃N₄的3倍. 此外, 在450 nm单色光照射下, Ni₃N/g-C₃N₄光催化产氢体系的量子效率能达到 $\sim 0.45\%$, 表明Ni₃N/g-C₃N₄具有将入射电子转化为氢气的的能力. 循环产氢实验表明, Ni₃N/g-C₃N₄在光催化产氢过程中有着较好的产氢活性和稳定性. 最后, 阐述了Ni₃N/g-C₃N₄体系的光催化产氢反应机理. 本文采用的原料价格低廉, 性能优异, 制备简单, 所制材料在光催化制氢领域展现出重要前景.

关键词: 光催化; Ni₃N; 助催化剂; 产氢; g-C₃N₄

收稿日期: 2018-10-09. 接受日期: 2018-12-14. 出版日期: 2019-02-05.

*通讯联系人. 电话/传真: (0554)6668430; 电子信箱: gejianhua13@163.com

#通讯联系人. 电话/传真: (0551)63606207; 电子信箱: dupingwu@ustc.edu.cn

基金来源: 国家重点研发计划(2017YFA0402800); 国家自然科学基金(51772285, 21473171, 51878004); 安徽自然科学基金(1808085ME139); 中央高校基本业务费.

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>).