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Article (Special Issue of Photocatalysis for Solar Fuels)

Zinc-doped g-C₃N₄/BiVO₄ as a Z-scheme photocatalyst system for water splitting under visible light

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ARTICLE INFO

Article history:

Received 28 September 2017

Accepted 29 October 2017

Published 5 March 2018

Keywords:

g-C₃N₄BiVO₄

Z-scheme

Shuttle redox mediator

Water splitting

ABSTRACT

A two-step photocatalytic water splitting system, termed a “Z-scheme system”, was achieved using Zn-doped g-C₃N₄ for H₂ evolution and BiVO₄ for O₂ evolution with Fe²⁺/Fe³⁺ as a shuttle redox mediator. H₂ and O₂ were evaluated simultaneously when the doping amount of zinc was 10%. Moreover, Zn-doped (10%) g-C₃N₄ synthesized by an impregnation method showed superior active ability to form the Z-scheme with BiVO₄ than by in-situ synthesis. X-ray diffraction, UV-Vis spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy were used to characterize the samples. It was determined that more Zn–N bonds could be formed on the surface of g-C₃N₄ by impregnation, which could facilitate charge transfer.

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1. Introduction

As the dramatic increase in the development of industry proceeds with overuse of fossil fuels, environmental problems and energy crises may become ever more serious. To help alleviate this situation, water splitting using semiconducting photocatalysts has been shown, since the discovery of the Honda-Fujishima effect, to be a promising method to generate H₂, as an environmentally friendly energy source, directly from the sun [1].

A new type of metal-free semiconductor material, g-C₃N₄, has received attention because of its non-toxicity, visible light response, and thermal-chemical stability [2–5]. Its low cost and simple synthesis make g-C₃N₄ easily obtainable from calcining melamine, dicyandiamide, urea, or other raw materials [6–8]. However, because of the high binding energy of g-C₃N₄ and its low crystallinity, it is difficult to separate the photogenerated

electron-hole pair and it suffers from fast recombination of photoexcited charge carriers [9,10]. Researchers have been working on modifications to g-C₃N₄, and several metal-containing carbon nitride compounds have been reported to greatly improve the performance of g-C₃N₄ under visible light [2,4,5,11]. However, such doping modification cannot solve the problem of recombination. To solve that, coupling g-C₃N₄ with other materials to form a composite structure shows some promise [12]. Examples include CdS/g-C₃N₄ [13], TiO₂/g-C₃N₄ [14], WO₃/g-C₃N₄ [15], g-C₃N₄/Ag₃PO₄ [16], Cd_{0.5}Zn_{0.5}S/g-C₃N₄ [17], and CoTiO₃/g-C₃N₄ [18], but all of these works focused only on enhancing H₂ evolution and no O₂ was observed.

So called “Z-scheme” principled photocatalyst has stirred the interest of scientists because of its charge transport mechanism, similar to the natural green plant photosynthesis, and its Z-scheme charge transfer path. In this system, two different photocatalysts are combined using an appropriate shuttle re-

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This work was supported by the National Natural Science Foundation of China (21773153).

DOI: 10.1016/S1872-2067(17)62961-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

dox mediator [19]. Its unique energy gap, structure, and charge transfer mode make the electrons and holes separately spaced [20]. The Z-scheme method also makes it possible to combine photocatalysts for either water reduction or oxidation potential to the system [19]. For example, BiVO_4 , whose conduction band is 0.3 V versus NHE, and which has no ability to produce H_2 , is capable of oxidizing O^{2-} from a solution containing appropriate electron acceptors, as will be discussed *vide infra*. Some work to date has focused on using BiVO_4 to reinforce the oxidation capacity of g- C_3N_4 [21–25], whose conduction band (CB) is -1.42 V and valence band (VB) is 1.25 V versus NHE. However, most of these studies only formed a heterojunction that results in a more negative VB and more positive CB, which is undesirable for water splitting.

Herein, we report on the overall water splitting using Zn-doped g- C_3N_4 for H_2 evolution and BiVO_4 photocatalyst for O_2 , with $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple as an electron mediator. Our photocatalytic experiments indicate that g- C_3N_4 can be used in a typical Z-scheme water splitting system with both H_2 and O_2 gases evolved in a stoichiometric ratio ($\text{H}_2/\text{O}_2 \approx 2$).

2. Experimental

Urea (>99.0%), Ethanol (99.7%), NH_4VO_3 (>99%), ZnCl_2 (>98.0%), HCl (>36.0% to aqueous solution), dicyandiamide (>99%), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (>98%), HNO_3 (65%–68%), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (28% to aqueous solution), and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). FeCl_2 (>98%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (China). All reagents were used without further purification.

2.1. Photocatalyst preparation

The photocatalyst of g- C_3N_4 was synthesized according to the procedure presented in Ref. [26]. Typically, 16 g urea was heated to 873 K at a heating rate of 2.5 K/min in an alumina crucible with aluminum foil as a cover. After naturally cooling to room temperature, the light-yellow-colored g- C_3N_4 was obtained without further treatment.

The as-prepared g- C_3N_4 (1 g) was then mixed with 10 mL of ethanol and different proportions of ZnCl_2 (e.g. 0.1 g ZnCl_2 for CN-10-U, where U represents use of urea as the precursor) were added to the mixed solution. A few drops of HCl (36%) were added to avoid hydrolysis of ZnCl_2 . This solution was heated and stirred at 353 K to remove ethanol. It was then heated to 673 K at a rate of 5 K/min under nitrogen flow and kept at this temperature for 4 h. Zinc-containing g- C_3N_4 was then produced after naturally cooling in a nitrogen atmosphere.

Different methods have been used to realize Zn doping. Wang's group [4] used dicyandiamide and ZnCl_2 as precursors, combined with a polycondensation process at elevated temperatures. Meanwhile, Ye's group [22] mixed as-prepared g- C_3N_4 with ZnCl_2 and then dried this under nitrogen flow. In the Wang and Ye work, the materials used are the same and the only difference is the synthetic method employed. Our research uses the same synthetic method as Ye's work except that we

use urea instead of dicyandiamide. Three different types of g- C_3N_4 doped with zinc (10%) were synthesized and denoted as CN-10-D2, CN-10-D1, and CN-10-U.

BiVO_4 catalyst was synthesized using a hydrothermal method [27] as follows. First, 3 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 3 mmol NH_4VO_3 were dissolved in 40 mL HNO_3 (2 mol/L) with vigorous stirring. The pH was then adjusted to 2.0 using ammonia and dilute nitric acid to form a yellowish suspension that was kept under stirring for 1 h. Then, the resulting suspension was transferred into a Teflon recipient, which was performed at 473 K for 24 h.

2.2. Characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were measured on a D8 DA VINCE (Bruker) X-ray diffractometer using $\text{Cu K}\alpha$ radiation under 40 kV and 40 mA. The scanning speed was $6^\circ/\text{min}$ and $2\theta = 10^\circ\text{--}80^\circ$. The morphologies of the samples were revealed by scanning electron microscopy (SEM, JEOL JSM-6380LV). The XPS patterns were measured on an AXIS UltraDLD electronic energy spectrometer (Kratos group) at 300 W using $\text{Mg K}\alpha$ X-rays as the excitation source.

2.3. Photocatalytic experiment for water splitting

The photocatalytic activities were evaluated in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Particulate Pt was photodeposited onto the photocatalyst samples as a water reduction cocatalyst as the reaction progressed. Specifically, 1.8 g FeCl_2 was dissolved in 80 mL deionized water and 1 wt% Pt (1 mg Pt for 0.1 g CN- x -U, for example) was added into this solution. 0.1 g of CN- x -U ($x = 0, 5, 10$, or 20) and 0.05 g of BiVO_4 was then suspended in the solution. The suspension was thoroughly degassed and irradiated by a 300 W Xe-arc lamp. The amount of H_2 and O_2 was analyzed every hour using online gas chromatography.

The photodeposition method was also used to load Pt co-catalyst onto g- C_3N_4 doped with Zinc. An aqueous solution of H_2PtCl_6 (containing 1 wt% Pt) was added to 80 mL aqueous solution suspended in the CN-10-U powder, and then the solution was irradiated using a Xe lamp (300 W). The Pt cocatalyst was deposited in metallic form according to previous descriptions [28].

3. Results and discussion

3.1. Characterization of as-prepared samples

The diffraction patterns for the Zn-doped g- C_3N_4 with different amounts of zinc, as can be seen in Fig. 1(a), shows two peaks at 13.4° and 27.4° , corresponding to the (100) and (002) diffraction planes, respectively [3,21,29]. The main peak at 27.4° can be indexed as the distance of 0.681 nm between nitride pores in C_3N_4 , which indicates a two-dimensional carbon nitride structure both in the modified and unmodified samples [2,4,22]. Its intensity gradually decreases as the Zn content increases, and the same trend can be observed in the peak at

Fig. 1. XRD patterns of (a) the CN-*x*-U catalyst samples with different *x* values and pristine g-C₃N₄ and (b) BiVO₄ JCPDS 14-0688.

13.4°. This peak can be ascribed to the interplanar distance of 0.326 nm, and this may indicate that there is a deterioration of crystallinity upon Zn doping and it may strongly impact the distance between g-C₃N₄ hosts [2,23]. No heterogeneous phase, such as zinc, its oxide or chloride, was observed from the XRD data [5]. The phase and purity of the synthesized BiVO₄ can be observed from Fig. 1(b), which were consistent with JCPDS card No. 14-0688 (pure phase monoclinic point group).

For the purpose of studying the optical absorption of the as-prepared g-C₃N₄ based samples, the UV-Vis absorption spectra are provided in Fig. 2. The light absorption edges of the CN-*x*-U with different Zn contents gave a small change to the short wavelength range compared to the pristine g-C₃N₄ (the maximum light absorption edge was obtained with the CN-10-U samples).

3.2. Overall water splitting by Z-scheme photocatalysis system

Fig. 3 shows the changes in photocatalytic activity as various amounts of Zn was doped into g-C₃N₄. It has been revealed previously that the hydrogen yield is a non-monotonic function of the Zn content [11]; therefore, the overall water splitting was

only obtained when 10% of Zn was loaded. This can be explained from when there is too much doped Zn, they may unite as reaction sites for the recombination of photoelectric electron-hole pairs, resulting in a decrease in the redox ability of g-C₃N₄ [20].

To make sure that the CN-10-U was combined with BiVO₄ through a shuttle redox mediator, Fig. 4 shows the photocatalytic activity of the different components in aqueous FeCl₂ solution. Overall water splitting (H₂ and O₂ gases generated in a stoichiometric ratio) was only observed when both CN-10-U and BiVO₄ was added to the aqueous FeCl₂ solution with a certain amount of H₂PtCl₄.

However, there is another theory which purports that Pt nanoparticles would be formed and play a key role in overall water splitting when H₂PtCl₆ is added to the original solution and deposited as the reaction progresses [30]. To ascertain whether the overall water splitting actually contributed to g-C₃N₄ doped with zinc and BiVO₄, pre-photodeposited g-C₃N₄ was tested and the results can be seen in Fig. 5. As the picture shows, stoichiometric H₂ and O₂ gases can be observed in the Z-scheme system built by both pre-photodeposited (CN-10(Pt)/BiVO₄) and when it is photodeposited during the

Fig. 2. UV-Vis diffuse reflectance spectra (DRS) of CN-*x*-U (*x* = 5, 10, 15, or 20) and g-C₃N₄ samples.

Fig. 3. Photocatalytic activity of CN-*x*-U/Pt/BiVO₄ Z-scheme systems (*x* = 0, 5, 10 or 20).

Fig. 4. Photocatalytic activity of catalyst CN-10-U/Pt, BiVO₄/Pt, and Z-scheme CN-10-U/Pt/BiVO₄.

Fig. 5. Photocatalytic activity of Z-scheme system with CN-10-U (Pt)/BiVO₄ for pre-photodeposited Pt and CN-10-U/Pt/BiVO₄ for Pt photodeposited as the reaction proceeds.

reaction (CN-10/Pt/BiVO₄). The formation of a complex is supported by TEM images (Fig. 6(b)) of the CN-10/Pt example.

These results indicate that CN-10-U can be applied to a typical Z-scheme water splitting system as H₂-evolving photocatalysts via a shuttle redox mediator. A typical SEM image of the suspension of CN-10-U and BiVO₄ (2:1; 12 h), as illustrated in Fig. 6(a), also supports this. CN-10-U and BiVO₄ are separated in this mixture without any obvious form of heterojunction.

The stability of the as-prepared Z-scheme system can be observed in Fig. 7. We can see that the system retains a stable stoichiometric H₂ and O₂ production over a long time period. Under visible light the H₂ production was very low, and this may be due to the poor activity of g-C₃N₄ decomposed by urea, which was also shown by the UV DRS data (Fig. 2). There is no obvious difference in O₂ production over the initial two hours, which can be attributed to the high capability of BiVO₄ under visible light. However, after six hours of radiation, the production of O₂ using aqueous NaNO₂ as a light filter slowly decreased. This can be explained by the low production of H₂, which influences the interchange of the Fe³⁺/Fe²⁺ redox couple. The low production of H₂ might also lead to an accumulation of ferrous ion, a potential competitor to the oxidation reaction.

Fig. 6. (a) SEM and (b) TEM images of the mixture obtained after the reaction on CN-10-U and BiVO₄ (2:1, 12 h).

Thus, we obtained a stable Z-scheme system for overall water splitting by combining Zn-doped (10%) g-C₃N₄ and BiVO₄ though a Fe³⁺/Fe²⁺ redox couple. Pt was used as a cocatalyst for H₂ revolution.

3.3. Possible function of zinc doped in g-C₃N₄

According to previous research [4,11], there are two different ways to realize doping with Zn. Specifically, Zn-doped g-C₃N₄ can be synthesized by an impregnation method (CN-10-U and CN-10-D1) or by in-situ synthesis (CN-10-D2). These three types of Z-scheme were constructed and tested, with the results shown in Fig. 8. Overall water splitting can be observed in the Z-scheme using both CN-10-U and CN-10-D1. The difference in the production between CN-10-U and CN-10-D1 may contribute to the introduction of pores in g-C₃N₄ by using urea as the precursor. The high surface area and continuous porosity, which can be active centers, are important requirements for catalysis [12].

The chemical state and surface chemical composition were characterized by XPS (Fig. 9). There are significant differences in the C 1s and N 1s peaks for Zn-doped g-C₃N₄ synthesized by the impregnation method (CN-10-D1) relative to the in-situ synthesized CN-10-D2, as discussed *vide infra*. A Zn 2p_{3/2} binding energy (BE) peak at 1020.3 eV in both Zn-doped samples is revealed in Fig. 9(d). This is lower than the 1021.9 eV value measured for Zn(II) in ZnCl₂, and there are no Cl peaks detected

Fig. 7. Photocatalytic activity of the CN-10-U/Pt/BiVO₄ Z-scheme system for 12 h. Visible light was used with aqueous NaNO₂ as a light filter.

Fig. 8. Photocatalytic activity of Z-scheme system using g-C₃N₄ with various methods to dope Zn and BiVO₄.

in either sample. Hence, it can be speculated that Zn(II) was successfully linked to the g-C₃N₄ framework in both samples through a Zn-N bond without Cl⁻ ions [11]. The reason for the different catalytic ability between the two types of Zn-doped g-C₃N₄ may be ascertained from the C 1s (Fig. 9(a)) and N 1s (Fig. 9(b)) peaks.

The C 1s and N 1s peaks of the two samples in Fig. 10 are both clear, but the ways in which they were modified by zinc differ. In Fig. 10(a) and (b), the C 1s peaks can be convoluted as several binding energies. The main peak at 287.7 eV (C1) cor-

responds to the triazine ring of the N=C-N group [4,30,31]. The peak at 285.4 eV (C3) can be assigned to the *sp*³ C-N bond, and the peak at 284.2 eV (C2) corresponds to the *sp*² C=C bond. The weak peak at 289.0 eV (C4) can be attributed to C-O groups caused by inevitable oxidation [11]. Zn-doped g-C₃N₄ obtained by in-situ synthesis shows a significantly weaker C2 peak than that obtained via impregnation. For the N 1s signal, a similar trend is observed, as shown in Fig. 8(c) and (d). The N 1s XPS peak can also be deconvoluted into three typical peaks. The dominant peak at 398.2 eV (N1) can be attributed to the C-N=C group, which is a manifestation of the triazine ring. The peak at 399.3 (N2) and 400.5 eV (N3) can be assigned, respectively, to the -N- and ≡N bonds [32]. Compared to CN-10-D1, the integral strength of the N 1s signal of the CN-10-D2 sample is reduced. From these observations, we conclude that Zn might be doped by forming Zn-N bonds, which promote carrier transport from Zn to the g-C₃N₄ bodies [4,31,33]. Also, by using the impregnation method, Zn can be combined more homogeneously without distorting the triazine ring. This method could be a way to better improve the redox ability of g-C₃N₄ to dope zinc and make it suitable for forming a Z-scheme water splitting system with bismuth vanadate.

4. Conclusions

A typical Z-scheme system composed of a Fe³⁺/Fe²⁺ redox mediator that splits water into H₂ and O₂ by using zinc-doped (10%) g-C₃N₄ for H₂ production and BiVO₄ as O₂-photocatalyst was reported. The Z-scheme system showed a stoichiometric

Fig. 9. XPS analysis of (a) C 1s, (b) N 1s, (c) O 1s, and (d) Zn 2p peaks. (1) CN-10-D1; (2) CN-10-D2.

Fig. 10. C 1s and N 1s XPS spectra of (a, c) CN-10-D1 and (b, d) CN-10-D2.

ratio (2:1) in the generation of H_2 and O_2 over a long time period when the zinc was doped by an impregnation method. This provides a homogeneous formation of Zn-N bonds without distorting the triazine ring.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 472–478 doi: 10.1016/S1872-2067(17)62961-9

Zinc-doped g-C₃N₄/BiVO₄ as a Z-scheme photocatalyst system for water splitting under visible light

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A two-step photocatalytic water splitting system, so called “Z-scheme system”, was achieved using Zn-doped g-C₃N₄ for H₂ evolution and BiVO₄ for O₂ evolution with Fe²⁺/Fe³⁺ as a shuttle redox mediator.

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基于掺Zn氮化碳和BiVO₄构建Z型光催化系统实现完全分解水

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摘要: 随着现代工业的迅猛发展和化石燃料的过量使用, 全球范围内能源和环境问题日益严峻, 因此利用丰富的太阳光能分解水来直接制取清洁的氢气具有诱人的应用前景。目前, 聚合物半导体石墨相氮化碳(g-C₃N₄)因其廉价、稳定、不含金属组分和独特的电子能带结构已被广泛应用于光解水产氢研究。然而, 氮化碳具有结晶度差、光生载流子易复合的缺点。众所周知, Z型体系可以很好地减少电子和空穴的复合问题。同时, 催化剂只需分别满足光解水过程的一端, 这使得半导体光催化剂的选择非常丰富, 可以大大拓宽材料体系。因此, 将g-C₃N₄运用到Z型体系中的研究得到了广泛关注。然而, 这些研究多集中在如何增强g-C₃N₄的产氢能力方面, 对实现水的完全分解的研究鲜见报道。

本实验设计了这样一种Z型体系: 使用掺Zn的g-C₃N₄作为产氢端, BiVO₄作为产氧端, Fe³⁺/Fe²⁺作为氧化还原对。实验结果表明, 该体系可以在全波段下实现水的完全分解(氢氧比为2:1), 并且保持相当高的稳定性。

实验所使用的氮化碳为固相法烧结尿素制得, Zn的掺杂采用浸渍法, 同时通过水热法合成BiVO₄, 使用Pt作为助催化剂。通过搭建含有不同组成成分的Z型体系, 将它们的性能和表征结果进行比较分析。

通过XRD, UV-Vis, SEM和XPS等测试手段对催化剂进行表征。XRD分析结果表明成功合成了掺杂Zn的石墨相氮化碳。UV-Vis则显示随着Zn浓度的提高, 吸收边发生变化。通过改变掺杂Zn的浓度, 得到了能够实现完全分解水的Z型体系, 其最佳掺杂比例为: ZnCl₂和氮化碳的质量比为1:10。为了排除单催化剂和Pt颗粒对完全分解水性能的影响, 分别作了单独产氢端、单独产氧端、预负载Pt和光沉积Pt的性能测试。从SEM中没有发现g-C₃N₄和BiVO₄的异质结结构。这些结果表明所搭建的是典型的利用氧化还原离子对为中间电子传输载体的Z型体系, 经长达12 h的持续测试证明其具有较高的稳定性。

为了研究Zn在构建Z型中所起的作用, 分别采用文献中报道的原位和浸渍法实现Zn的掺杂。对这两种掺杂方式的性能测试表明, 只有采用浸渍法时, 所构建的Z型体系具有完全分解水的能力。对这两种方法得到的掺Zn氮化碳进行表面化学组成和价态(XPS)的分析。结果显示, 两种掺杂方法都可以通过形成Zn=N键的形式实现Zn的掺杂, 但浸渍法使Zn在g-C₃N₄表面分布更均匀, 同时对氮化碳原本三嗪环的破坏较小, 因此具有更好的还原能力, 可以与BiVO₄匹配以构成Z型体系。

实验通过采用掺杂Zn的氮化碳作为产氢催化剂, BiVO₄作为产氧催化剂, Fe³⁺/Fe²⁺作为氧化还原中间体, 构建了典型的Z型体系。该体系在Zn的掺杂浓度为10%时能够实现长时间稳定的完全分解水。

关键词: 氮化碳; 钒酸铋; Z型; 氧化还原介质; 分解水

收稿日期: 2017-09-28. 接受日期: 2017-10-29. 出版日期: 2018-03-05.

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基金来源: 国家自然科学基金(21773153).

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