INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–12

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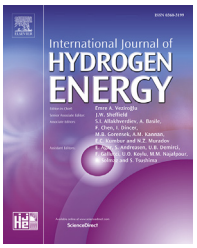

Efficient hydrogen production over MOFs (ZIF-67) and g-C_3N_4 boosted with MoS_2 nanoparticles

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ARTICLE INFO

Article history:
Received 13 March 2018
Received in revised form
10 May 2018
Accepted 14 May 2018
Available online xxx

Keywords:
g-C_3N_4/MOF/MoS_2 photocatalyst
ZIF-67
Hydrogen production
MoS_2 nanoparticles
MOFs

ABSTRACT

MOFs (ZIF-67) and g-C_3N_4 catalyst-modified MoS_2 nanoparticles are prepared by means of doping g-C_3N_4 in the process of ZIF-67 formation and then introducing MoS_2 nanoparticles on the surface of collaborative structure between MOFs and g-C_3N_4. The MOFs (ZIF-67) and g-C_3N_4 catalyst-modified MoS_2 photocatalyst exhibits efficient hydrogen production with about 321 μmol under visible light irradiation in 4 h, which is almost about 30 times higher than that of over the pure g-C_3N_4 photocatalyst. A series of characterization studies such as SEM, XRD, TEM, EDX, XPS, UV–vis DRS, FTIR, transient fluorescence and electro-chemistry show that the novel structure of g-C_3N_4 and MOF is formed, the more active sites appears and the efficiency of photo-generated charge separation is improved. MoS_2, as a narrow band semiconductor, is grafted on the surface of g-C_3N_4/MOF, which could effectively harvest visible light and swift charge separation. The results are well mutual corroboration with each other. In addition, a eosin Y-sensitized reaction mechanism is introduced.

Introduction

With the deterioration of global warming, the demands for low-carbon and clean energy structures are imminent. There are several possible ways to reduce emissions of carbon dioxide: (1) coupling hydrogen plants with CO_2 capture and storage systems, (2) dissociation of hydrocarbons to hydrogen and carbon, and (3) integrating hydrogen production processes with non-carbon energy sources such as nuclear and solar energy [1,2]. Photocatalyst emerges as the times required. The development of advanced materials will significantly improve the performance of photocatalyst and promote the conversion of solar energy [3].

In recent years, the metal organic frame structure has become the hotspot materials because of the excellent structures and performances [4–6]. It has great potential for MOF materials to improve the properties of photocatalyst. At the same time, the photocatalysts or photosensitizers which have been reported are mostly noble metals (Ag, Pt, Pd, Au and so on) or noble metal-based complexes among the three-component hydrogen systems. Their limited reserves have restricted the extensive application in these photocatalytic hydrogen production systems [6,7]. It's important to set a new photocatalytic hydrogen reaction system with good practicality for hydrogen production by reducing the costs and improving the hydrogen production efficiency.

Since Liu A. Y. and Cohen M. L proposed covalent crystal of beta carbon nitride (β-C_3N_4) in theory in 1989, the fine characteristics of the carbonitriding compound have been paid attention [8]. Due to favorable self-semiconductor structure band gap value and stability, graphitic carbon nitride (g-C_3N_4) has been used in the area of generation of hydrogen since the

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https://doi.org/10.1016/j.ijhydene.2018.05.099

first time in 2009 [3]. Compared with conventional inorganic photocatalysts, such as TiO_2, WO_3, CdS and Bi_2O_3, this metal-free polymeric material has showed a good performance in various applications including water splitting, degradation of pollutants and other aspects [3,9,10]. It usually uses thermal condensation of melamine or other triazine derivatives to synthesize bulk g-C_3N_4 [9–11]. However, its low carrier mobility and insufficient sunlight absorption limit the energy conversion efficiency. Although bulk g-C_3N_4 has a fractional visible light response (460 nm absorption edge), its wide bandgap restricts its further applications. To improve its photocatalytic performance, various strategies including morphology control, combining with other materials, ion doping, and noble metal deposition have been adopted [12,13]. It is little doubt that doping methods, especially non-metal doping, are worth focussing on due to their effectiveness in broadening the optical response range and economy. Thus, non-metal elements, such as B, C, N, O, F, P, and S, have been introduced to g-C_3N_4 and broadened its light absorption [6,7,11,14]. However, the bandgap is still too wide for efficient absorption of light energy because of the limitation of single atom doping. In the meantime, this method is troublesome and consumes a vast amount of hydrogen peroxide. Therefore, co-doping concept was proposed and it was applied to modify g-C_3N_4.

Metal–organic frameworks (MOFs) are crystalline porous solids consisting of a three-dimensional (3D) network of metal ions held in place by multidentate organic molecules. The spatial organization of these structural units leads to a system of channels and cavities in the nanometer length scale, analogous to that found in zeolites [5,15,16]. Based on this structural feature, it's ideal to improve the performance of the photocatalyst by application of MOFs. Therefore, we selected ZIF-67 from a large number of different MOFs, which show excellent stability. However, the light activity of MOFs is poor because they cannot respond effectively to visible light [5,15]. At the meanwhile, it's also an urgent work to improve the visible light response range of MOFs for enhancing the photocatalytic efficiency.

MoS_2 materials have typical layered structure characteristics with the structure of S-Mo-S in each unit. It is connected with covalent bonds together in the layers and attracted by weak van der Waals force between every layers [17]. MoS_2 is well matched with the solar spectrum with the characteristic whose guide band and valence band have high edge potential. Those lead that there are many unsaturated bonds causing high catalytic activity. MoS_2 materials have fast carrier migration rate capacity, so the separation efficiency of electron-hole pairs is better than that of traditional catalyst such as TiO_2 [18,19]. As a kind of semiconductor materials with capacity of high efficient optical response, the researches are mainly from the nanostructures of constant stoichiometric ratio and the stoichiometric ratio of composite materials. MoS_2 materials not only own large specific surface area and strong adsorption ability, nanostructured MoS_2 are also easy to form the stoichiometric ratio of compound (MoS_x) with a closed structure of zero dimension and one dimensional nanotubes, which can expose more catalytic activity and higher reactivity [19–22]. On the one hand, MoS_2 composite photocatalyst can act the synergistic effect of MoS_2 and second phase by increasing the absorption of visible light through the adjustment of bandgap; On the other hand, it can improve the conductivity, increase the electron transport rate and reduce the compound probability of the electron-hole pairs by the compound of the second phase of the conductive phase. The study shows that the combination of MoS_2 with other semiconductors (such as MoS_2/g-C_3N_4 and MoS_2/CdS) can significantly improve the activity of photocatalyst, which can catalyze photocatalytic degradation or hydrogen evolution [21,22].

Because of restrictions on photocatalytic process, in this work, we aimed to improve the performance by increasing the catalyst itself absorbance, preventing electron-hole recombination in photocatalytic reaction and expanding the specific surface area [3,7,10,11]. Firstly, g-C_3N_4/MOF is synthesized by traditional hydrothermal method to synthesize. It can provide bigger specific surface area compared with pure g-C_3N_4. Then, the product is modified with MoS_2 to inhibit recombination of electron-hole. At last, the absorption spectrum is expanded by sensitization of eosin Y. Finally, the structure and effects are characterized and tested, which provides a meaningful reference for improvement of photocatalyst.

Experimental

Photocatalyst preparation

Preparation of the g-C_3N_4

Urea (15 g) was placed in a crucible and heated at 550 °C for 4 h in a muffle furnace. The product was took out and grinded. Then it was heated at 500 °C for 2 h again [3,12,24,25].

Preparation of the graphitic carbon nitride/metal–organic framework (g-C_3N_4/MOF)

The graphitic carbon nitride/metal-organic framework (g-C_3N_4/MOF) was prepared by traditional solvothermal method. All the chemicals used in this work were analytical grade and used as received without further purification. $Co(NO_3)_2 \cdot 6H_2O$ (1.21 g) and 2-Methylimidazole (1.366 g) were respectively dispersed into 35 mL of methanol in beakers. Graphitic carbon nitride (0.090 g) was added into methanol solution of $Co(NO_3)_2 \cdot 6H_2O$. Then, all the solution was ultrasonically dispersed in methanol. Stopped ultrasound when solution obtained was clear and transparent. The most important, solution of 2-Methylimidazole was needed to be rapidly added into the other mixed solution. The new mixed solution was then transferred to a 80 mL autoclave with material of polytetrafluoroethylene inside. It was kept in oven at 120 °C for 12 h [26–28]. After that, it was naturally cooled to room temperature. The liquid product was centrifuged and washed several times with ethanol to ensure that the useless substances were removed. Then, it was dried at 80 °C for 4 h.

Synthesis of the g-C_3N_4/MOF/MoS_2 composite photocatalyst

Composite photocatalyst (g-C_3N_4/MOF/MoS_2) was prepared by a hydrothermal method as follows. g-C_3N_4/MOF (0.25 g) was added to 30 mL deionized water and then stirred for 30 min until homogeneous g-C_3N_4/MOF was dispersed in the solution.

Please cite this article in press as: Wang Z, et al., Efficient hydrogen production over MOFs (ZIF-67) and g-C_3N_4 boosted with MoS_2 nanoparticles, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.099