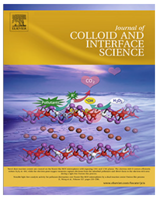
Journal of Colloid and Interface Science 529 (2018) 375–384

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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



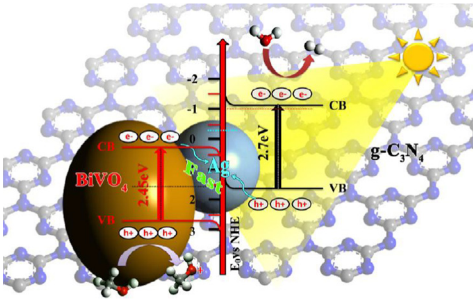
Switching charge transfer process of carbon nitride and bismuth vanadate by anchoring silver nanoparticle toward cocatalyst free water reduction

Meiting Song, Yuhang Wu, Xiaojing Wang, Mengqing Liu, Yiguo Su [*]

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, Inner Mongolia 010021, PR China

GRAPHICAL ABSTRACT

A ternary catalyst was constructed which exhibit superior H_2 production rate with co-catalyst free under visible light irradiation.



ARTICLE INFO

Article history:
Received 24 April 2018
Revised 13 June 2018
Accepted 14 June 2018
Available online 18 June 2018

Keywords:
$g-C_3N_4/Ag/BiVO_4$
Cocatalyst free
Water splitting
Z-scheme photocatalysis

ABSTRACT

With the aim of exploring and modulating the interfacial charge kinetics, a ternary $g-C_3N_4/Ag/BiVO_4$ was constructed with excellent photocatalytic performance and preferable stability toward H_2 evolution in absence of cocatalyst. Both density functional theory (DFT) and experimental results implied that the type II $g-C_3N_4/BiVO_4$ composite can be switched to Z-scheme via Ag nanoparticles as the electron shuttle. The optimal photocatalytic H_2 yield rate achieved for $g-C_3N_4/Ag/BiVO_4$ was 57.4 $\mu mol \cdot g^{-1} \cdot h^{-1}$, being far surpassed the H_2 harvest rate of $g-C_3N_4/BiVO_4$, $Ag/g-C_3N_4$ and $g-C_3N_4$, which is 2.9, 14.8 and 1.7 $\mu mol \cdot g^{-1} \cdot h^{-1}$, respectively. The apparent quantum efficiency of $g-C_3N_4/Ag/BiVO_4$ photocatalyst was also determined to be 1.23%. Besides, the photocatalytic performance of $g-C_3N_4/Ag/BiVO_4$ well preserved over 5 runs in 50 h. The improved H_2 production performance is considered as the consequence of promoted segregation of photoexcited charge carriers and SPR effects of Ag nanoparticles. In combination with photocurrent measurement, examination of active species and DFT calculation, it is found that Ag nanoparticles as an electron mediator can highly promote the Z-scheme carrier migration that electrons come from conduction band of $BiVO_4$ will quickly assemble with the photo-induced holes from valence band of $g-C_3N_4$, leaving electrons in the conduction band of $g-C_3N_4$ and holes in valence band of $BiVO_4$ that could greatly enhance the charge separation efficiency.

---

[*] Corresponding author.
E-mail address: cesyg@imu.edu.cn (Y. Su).

https://doi.org/10.1016/j.jcis.2018.06.029

1. Introduction

Semiconductor photocatalysis for hydrogen production provides an important environmental benign strategy toward sustainable energy conversion [1–5]. To meet the flexible industrial processing ability, the development of efficient photocatalytic system with high solar energy conversion efficiency is demanded. However, the bottlenecks of photocatalysts, such as low visible light absorption and poor quantum efficiency, are still of hindrance for practical applications, in spite of great efforts have been dedicated, including band gap engineering, surface modification and semiconductor heterojunction [6–8]. Recently, heterostructured materials by combining two semiconductors with band alignment are found effective photocatalysts to improve catalytic activity. However, traditional heterojunctions meet weakened reduction and oxidation ability of photoinduced charge carriers, which fall short of the requirement of high redox potential of H^+/H_2 for hydrogen production [9]. The Z-scheme photocatalytic systems possessing excellent redox driving force and charge separation efficiency have garnered much research attention for enhanced photocatalytic performance [10,11]. Using a redox shuttle or electron mediator, a Z-scheme charge transfer can be modulated to achieve spatial isolation of photoinduced charge carriers for more positive valence band potential and more negative conduction band potential [12]. Hence, it's highly desirable to modulate the interfacial charge kinetics to develop Z-scheme photocatalysts for improving photocatalytic activity.

Among widely investigated oxides, nitrides, and oxyhalides, graphite-like carbon nitrides carries a more negative conduction band potential (~-1.1 V vs. NHE) with a strong redox capability, which has been widely applied for photocatalytic hydrogen production [13–16]. However, it still has some drawbacks, like the high rate of recombination for photoexcited charge carriers and strong reliance on co-catalysts. Building g-C_3N_4 based heterostructure can provide an effective way for overcoming these disadvantages. A great deal of g-C_3N_4 based Z-scheme heterojunctions, including g-C_3N_4/TiO_2, g-C_3N_4/SnS_2, g-C_3N_4/Ag_3PO_4, and so forth were developed [17–20]. For instance, the nanojunction of g-C_3N_4/TiO_2 resulted in the constitution of a settled electric field that can gather photoinduced electrons and holes in diverse face region and prolong the longevity about charge carriers with strong reductive and oxidative ability [10]. Since the band gap construction of g-C_3N_4 matches well with that of $BiVO_4$, the junction of g-C_3N_4 and $BiVO_4$ may predict spatial charge separation and improved photocatalytic reactivity. However, it is still controversial that the charge migration between g-C_3N_4 and $BiVO_4$ demonstrates type II or Z-scheme transfer process [21–25]. Moreover, binary component heterojunctions still have drawbacks of slower charge transfer rate and inefficient charge separation ratio. To solve these problems, semiconductor-metal-semiconductor (S-M-S) ternary component systems have been developed. As a model S-M-S system, CdS-Au-TiO_2 possessed a fast vertical electron transfer of CdS → Au → TiO_2, resulting in high photocatalytic activity toward methylviologen (MV^{2+}) reduction, which improved by a factor of 1.6, 1.8 and 2.3 times in comparison to Au/TiO_2, CdS/TiO_2 and bare TiO_2 [9,26]. Usually, noble metallic nanoparticles were adopted as the electron shuttle to construct S-M-S system for promotion of photoreactivity. Having these in mind, the construction of ternary g-C_3N_4-M-$BiVO_4$ system predicts efficient charge separation and the subsequent improved photocatalytic performance. Though some studies of g-C_3N_4-M-$BiVO_4$ photocatalytic systems have been reported about degradating organic pollutants and oxidizing NO [8,12], it is still highly necessary to explore the interfacial charge kinetics and its application in water reduction.

In this work, using g-C_3N_4/Ag/$BiVO_4$ ternary photocatalytic system as model, we found that the type II g-C_3N_4/$BiVO_4$ composite can be switched to Z-scheme via Ag nanoparticles as electron shuttle. The coupling effects of g-C_3N_4 and $BiVO_4$ nanoparticles with Ag modification were systematically investigated in attempt to shed light on the interfacial charge kinetics and possible reasons for significant enhancement of photocatalytic performance toward hydrogen evolution.

2. Experiment

2.1. Sample synthesis

Synthesis of Ag/g-C_3N_4 photocatalyst: All reagents used were of analytical grade purity none of re-distillation. Water used was ultrapure water. The synthetic procedure for Ag/g-C_3N_4 catalyst can be briefly depicted as follows: g-C_3N_4 was obtained by calcining melamine. In a typical synthesis, 2.38 g melamine (CP, Sinopharm Group chemical reagent Co. Ltd) was ground for 30 min and placed in a semiclosed alumina crucible with a lid and heated at a speed of 5 °C/min to 550 °C for 4 h, cooling and regrinding to obtain yellow powder of g-C_3N_4, and the g-C_3N_4 sample was used directly without any further washing treatment. For the second step, different quality (1.00 g, 0.98 g, 0.96 g, 0.94 g, 0.92 g, 0.90 g) of g-C_3N_4 was blended with the different quality (0 g, 0.03 g, 0.06 g, 0.09 g, 0.12 g, 0.15 g) of $AgNO_3$ (AR, Wind ship in tianjin chemical reagent Co. Ltd), and ground for 30 min, then kept at 550 °C for 4 h. Finally, they were allowed to cool to ambient temperature and reground to reach different Ag/g-C_3N_4 composite photocatalyst (Ag mass ratios 0%, 2%, 4%, 6%, 8%, 10%). They were marked as g-C_3N_4, AC1, AC2, AC3, AC4 and AC5, respectively.

Synthesis of $BiVO_4$ photocatalyst: 5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ (AR, Wind ship in tianjin chemical reagent Co. Ltd), was dissolved in 20 mL nitric acid (2 M) to obtain solution A. Meanwhile, 5 mmol of NH_4VO_3 (AR, Adamas Reagent Co. Ltd) was dissolved in 10 mL NaOH solution (2 M) to acquire solution B and was injected drop by drop into solution A under intense stirring to achieve a steady suspension. The suspension liquid was regulated to adjust pH value of 7 using 1 M NaOH solution with energetic stirring for 30 min. Then it was poured into 100 mL Teflon-lined stainless steel autoclaves and reacted at 180 °C for 12 h. The achieved outcome was washed with ultra-pure grade water for several times and maintained at 60 °C to obtain $BiVO_4$.

Synthesis of g-C_3N_4/Ag/$BiVO_4$ photocatalyst: Different quality of Ag/g-C_3N_4 (with Ag mass ratio of 8%) was mixed with the different quality of the $BiVO_4$ to synthesize the ternary g-C_3N_4/Ag/$BiVO_4$ heterojunction (with mass ratios of 9:1, 7:3, 5:5, 3:7, 1:9). The compound was calcined at 400 °C at a speed of 5 °C /min for 4 h to acquire different ratio compound semiconductor photocatalytic materials of g-C_3N_4/Ag/$BiVO_4$. They were marked as ACB1, ACB2, ACB3, ACB4 and ACB5, respectively. For the purpose of comparison, the g-C_3N_4/$BiVO_4$ (with mass ratio of 9:1) photocatalyst was prepared and marked as CB1.

2.2. Sample characteristic analysis

Phase purity of all catalysts was measured by X-ray diffraction (XRD) using Panalytical X-ray diffractometer with a copper target at 40 kV and 40 mA. The diffraction patterns were kept track in the scope of $2\theta = 5–80°$ at a scan speed of $1° \text{ min}^{-1}$. Particle dimension and morphologies of the catalyst were tested using transmission electron microscopy (TEM) on a FEI TECNAI F20 S-Twin with an acceleration voltage of 200 kV. The Fourier transform infrared (FT-IR) spectra of all catalysts were taken on a Perkin–Elmer IR spectrophotometer at a resolution of 4 cm^{-1} using the KBr pellet skill. The UV–Vis absorption spectra were recorded on a UVIKON XL/XS diffuse reflectance spectrophotometer in the wavelength