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Full Length Article

The triple-component Ag_3PO_4-$CoFe_2O_4$-GO synthesis and visible light photocatalytic performance

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ABSTRACT

This paper introduces a novel triple-component silver phosphate-cobalt ferrite-graphene oxide (Ag_3PO_4-$CoFe_2O_4$-GO) photocatalyst, illustrates its synthetic principle of adjusting the pH value, elaborates on its dual-channel reaction mechanism and reveals its advantages. Morphology and elementary analyses revealed that the magnetic $CoFe_2O_4$ nanoparticles (NPs) and the GO were uniformly adorned on the Ag_3PO_4 particles' surface, forming a spherical structure. Because of this particular structure, not only could the Ag_3PO_4-$CoFe_2O_4$-GO composite be thoroughly removed with magnet field from treated water, but the photocatalytic activity and stability had been greatly improved to pure Ag_3PO_4. The effects of different samples were also evaluated, in terms of the efficiencies in inactivation and degradation. The reactive oxygen species (ROSs) yield measurements and photoluminescence spectra analysis indicated that O_2 adsorption could be promoted by the $CoFe_2O_4$ and the GO. Upon visible light irradiation, a part of motivated electrons of the Ag_3PO_4 were consumed by the $CoFe_2O_4$, and others were transferred to the GO. The effective electron-hole separation is due to the dual transfer channel existing in the Ag_3PO_4-$CoFe_2O_4$-GO composite. Hence, the dual transfer channel is the major reason for enhancing photocatalytic activity and stability.

1. Introduction

With the development of novel photocatalyst for solar-energy conversion, more and more articles pay much attention to the highly efficient and lower-cost photocatalyst in purifying water and protecting the environment under light irradiation [1–4]. In the past, TiO_2 based semiconductors had been considered as a clearly superior option, on account of the high stability, non-toxicity and high electron mobility [5–7]. Though these semiconductors are effectual, we can't ignore a problem of TiO_2 possessing a relatively large value of band gap [8]. It means that only the ultraviolet (UV) light irradiation can activate these semiconductors, and the relatively low solar-light-harvesting capability is one of the major reasons for the practical utility of photocatalytic applications [9]. In this case, discovering a novel kind of solar-light-motivated photocatalyst, which has higher light energy conversion efficiency, takes on even more importance. On this subject, Ag_3PO_4 has been regarded as an outstanding candidate for the photocatalyst, on account of exhibiting extremely high quantum efficiency and low band gap (2.45 eV) in many photocatalytic fields [10]. Nonetheless, researchers also suffer from many disadvantages of using Ag_3PO_4. The slight solubility of Ag_3PO_4 prevents it from being employed under long-time light irradiation, influencing its repeated use [11]. The appropriate heterojunction which is formed through combining with another semiconductor can reduce the solubility of Ag_3PO_4 [12–14]. The heterojunction raises photoexcited charges separation efficiency, hindering the recombination to improve the stability of Ag_3PO_4. At the same time, in the photocatalyst designation, the generation of ROSs, which could govern the water purification process, should also be considered [15].

Spinel ferrite $CoFe_2O_4$ with unique electric, physical, and chemical properties has come to the attention for environmental remediation [16]. Such incredible advantages have driven the researchers to employ $CoFe_2O_4$ as support for photocatalyst [17,18]. Especially, recent reports

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concentrating on oxygen reduction reaction (ORR) of $CoFe_2O_4$ have been discussed due to high abundance and stability of $CoFe_2O_4$ [19,20]. Beyond all questions, $CoFe_2O_4$ is an effective and vigorous catalyst for oxide removal. Accordingly, these features of $CoFe_2O_4$ propel us to combine Ag_3PO_4 and $CoFe_2O_4$, improving the catalytic reduction reaction for dissolved oxygen and increasing the ROSs' generation. Besides, a more convenient method is also an improvement for recycling the photocatalyst. More importantly, $CoFe_2O_4$ is a magnetic substance, which is easily separated from treated water by using a simple magnetic strategy [21].

As everyone knows, the catalytic activity of $CoFe_2O_4$ is blocked by low electronic conductivity [22]. Besides, strengthening the charge transfer in the application of solar photocatalysis is an effective method to eliminate emerging contaminants [23]. The electrically conductive substrate, such as carbon, is essential for improvement of electronic conductivity [24]. In the latest studies of carbonaceous material, the achievements of graphene being used as the adsorbent, conductive, carrier and photocatalytic material have been elaborated, as its large specific surface and charge mobility are the first two reasons [25–27]. The electron transfer and charge separation are expedited by addition of GO. It is noteworthy that GO, which absorbs visible light and acts as a transport channel for photogenerated electrons, is a compatible coating material for photocatalytic sterilization and degradation, enhancing the utilization efficiency of visible light and impeding the recombination of photogenerated charges [28]. Even more remarkable, the addition of the GO not only changes the conductivity of the Ag_3PO_4-$CoFe_2O_4$ but provides an absorber of bacteria and organic pollutants. Previous researches suggested that graphene sheets of broad conjugated sp^2 carbon network and the high specific surface area can immediately form lipopolysaccharide bridging to connect with surfaces of microbial cells and attract organic pollutants owing to GO sheets superior conductivity [29,30].

For attaining the objective of comprehending the photocatalytic mechanism and designing a more efficient photocatalyst, in the article, the structure of the Ag_3PO_4-$CoFe_2O_4$-GO composite was tactfully assembled through utilizing the surface-electric property of $CoFe_2O_4$. $CoFe_2O_4$ could reverse in different pH environment [31]. Subsequently, physico-chemical properties of the Ag_3PO_4-$CoFe_2O_4$-GO composite were comprehensively analyzed. Besides, the sterilization and degradation tests under Xenon illumination were used to appraise the photocatalysis capability of the Ag_3PO_4-$CoFe_2O_4$-GO. The Ag_3PO_4-$CoFe_2O_4$-GO composite's visible photocatalysis capability, which was higher than pure Ag_3PO_4, had been substantiated in the experiment results. Therefore, the enhanced photocatalysis mechanism of the Ag_3PO_4-$CoFe_2O_4$-GO was expounded and listed in detail.

2. Experimental

2.1. Materials and characterization

All chemical reagents were of analytical grade and were purchased from commercial suppliers such as Beijing Chemical, Shanghai Zhanyun Chemical, Shanghai Lingfeng, Suzhou Tanfeng Tech and Siopharm Chemical Reagent Co., Ltd. All chemicals would be directly utilized without further purification.

X-ray diffraction (XRD) analyses were achieved with a D/max-2550 diffractometer (Rigaku, Japan) employing Cu-Ka radiation. The composites' morphologies were inspected by Field emission scanning electron microscopy (FE-SEM; JEOL JSM-5600LV), the distribution and content of elements were examined by associated energy dispersive X-ray spectroscopy (EDS; Oxford IE 300 X). An Agilent Technologies 7800 inductively coupled plasma mass spectroscopy (ICP-Mass) would be utilized to probe the actual contents of essential elements in the Ag_3PO_4-$CoFe_2O_4$-GO composite, comparing them with the expected contents. Chemical compositions of the Ag_3PO_4-$CoFe_2O_4$-GO composite were characterized by using a PHI 5000C ESCA high-resolution X-ray photoelectron spectroscopy (XPS). The Raman scattering spectra which further proved the existence of the GO were drawn on a dispersive Raman spectrometer (Jobin Yvon XploRA). Ultraviolet–visible (UV–vis) diffuse reflectance absorption spectra were drawn on a UV–vis spectrophotometer using an integrating sphere of the $BaSO_4$ reflectance standard (PerkinElmer Lambda 35). The magnetic experiments were studied by using a vibrating sample magnetometer (VSM) at 20 K. A PQSTA 128 N electrochemical workstation, which equipped the working electrode of Pt plate, the counter electrode of saturated calomel and the reference electrode, was employed to acquire the transient photocurrent density response and electrochemical impedance spectroscopy (EIS) images of composites. And the supporting electrolyte was $0.2\ mol\cdot L^{-1}$ of sodium borate solution. Photoluminescence (PL) spectra were drawn by Edinburgh FLS 920 fluorescence spectrophotometer. Before Brunauer-Emmett-Teller (BET) surface area tests, the composites were placed in releaser at 110 °C for 10 h, and tests were conducted at 77 K.

2.2. Synthesis of $CoFe_2O_4$ NPs

There is a typical hydrothermal process of producing $CoFe_2O_4$ NPs. Especially, 4.61 g $FeCl_3\cdot 6H_2O$ and 2.02 g $CoCl_2\cdot 6H_2O$ were dissolved in 60 mL ethanol solution including 45 mL deionized water and 15 mL ethanol in a glass reactor that allowed the process of making the $pH > 9$ to occur by adding the certain amount of 30% concentrated ammonium hydroxide solution. 0.5 h's stirring was followed. The resultant mixture was heated to 180 °C for 20 h. The resultant solution including the $CoFe_2O_4$ NPs was cooled down to room temperature and centrifugated at 15,000 rpm for 10 min after the addition of deionized water until the $pH = 7$. This separation process was repeated three times after redispersing the $CoFe_2O_4$ NPs in deionized water. The final separations of the $CoFe_2O_4$ NPs were dispersed in deionized water and preserved for the characterization.

2.3. Synthesis of Ag_3PO_4-$CoFe_2O_4$ composite material

The Ag_3PO_4-$CoFe_2O_4$ composite was prepared in a 55 °C circulating water system. 0.8 g $AgNO_3$ was dissolved in 60 mL deionized water under gentle stirring. After stirring for 20 min, then the 0.02 g $CoFe_2O_4$ was added and was stirred for 1 h. 6 mL Na_3PO_4 solution ($1\ g\cdot mL^{-1}$) was dropwise added into the above dispersion under 1 h's stirring. The precipitation process was necessary before transfer. The 50 mL Teflon-lined stainless-steel autoclave was used to keep the suspension for 3 h at 150 °C. After cooling the hot product to room temperature, the acquired precipitates were collected by the washing of using ethanol and deionized water for repeated times. The product was then stoved until most of the water dried up at 60 °C. The obtained sample was labelled as the Ag_3PO_4-$CoFe_2O_4$ composite. The weight ratio between the $AgNO_3$ and the $CoFe_2O_4$ was set to 40:1, which was expected to get the weight ratio of the Ag_3PO_4 to the $CoFe_2O_4$ being 32:1 in the Ag_3PO_4-$CoFe_2O_4$ composite.

The pure Ag_3PO_4 was produced in the same hydrothermal treatment and was marked as the pure-Ag_3PO_4 without $CoFe_2O_4$.

2.4. Synthesis of Ag_3PO_4-$CoFe_2O_4$-GO composite material

The micro-sized Ag_3PO_4-$CoFe_2O_4$-GO spherical composite was in a typical synthesis. The Ag_3PO_4-$CoFe_2O_4$ composite and the GO were homogeneously dispersed in NaH_2PO_4 solution ($1\ g\cdot mL^{-1}$) assisted by ultrasonic treatment for 5 h. The weight ratio of the Ag_3PO_4-$CoFe_2O_4$ composite to the GO was set to 99:1. By a simple mechanical ultrasonic oscillation process, the Ag_3PO_4-$CoFe_2O_4$-GO mixture was prepared. Then, the mixture was centrifuged at a relative low revolving speed. Finally, the mixture was annealed at 500 °C for 2 h under an N_2 atmosphere to yield the Ag_3PO_4-$CoFe_2O_4$-GO composite. The final weight ratio among the Ag_3PO_4, the $CoFe_2O_4$ and the GO was 96:3:1.