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Enhancing reactive oxygen species generation and photocatalytic performance via adding oxygen reduction reaction catalysts into the photocatalysts

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ABSTRACT

In this work, a novel Ag_3PO_4@$CoFe_2O_4$ composite photocatalyst was synthesized via a phosphate salts alkalinity adjustment strategy. Structure, morphology, and chemical component analysis indicated that the magnetic $CoFe_2O_4$ nanoparticles (NPs) were evenly decorated on the surface of Ag_3PO_4 particles, forming a sesame ball like structure. This unique structure ensures that the Ag_3PO_4@$CoFe_2O_4$ composites could be totally separated by the magnet field. Photocatalytic water disinfection and organic pollutants degradation were employed to evaluate the photocatalytic performance of the as-prepared magnetic photocatalysts. The results showed that the optimum 3% Ag_3PO_4@$CoFe_2O_4$ composite could completely inactivate $1{*}10^7$ cfu/mL of Escherichia coli within 40 min, much faster than the pristine Ag_3PO_4. Meanwhile, the 3% Ag_3PO_4@$CoFe_2O_4$ composite also showed a dramatic enhancement of photocatalytic activities for the organic pollutants degradation. The reactive oxygen species yield measurements, O_2 control photocurrents experiments, O_2-TPD tests and photoluminescence spectra analysis indicate that the surface modification of $CoFe_2O_4$ NPs could facilitate the O_2 adsorption and O—O bond activation/cleavage/oxide removal and accelerate the two-electron oxygen reduction reaction for H_2O_2 generation on the surface of Ag_3PO_4, and thus more ROSs were generated. In addition, due to the acceleration of electrons consumption, more holes will be left for the organic pollutants oxidation, and the photocatalytic activities as well as stability of Ag_3PO_4 therefore have been greatly improved.

1. Introduction

Photocatalytic solar-energy conversion is being drawn increasing attention due to its robust new methods for water purification and environmental protection at lower cost and energy consumption [1,2]. Commercial TiO_2 has been recognized as efficient photocatalysts for water disinfection and organic pollutant degradation [3]. However, the large value of its bandgap results in the requirement of ultraviolet irradiation, which limit its practical utility for photocatalytic applications [4]. Therefore, the development of visible-light-driven (VLD) photocatalysts is considerably needed. Besides the VLD, reactive oxygen species (ROS), such as the hydroxyl radical, singlet oxygen superoxide, and their generation efficiency also should be involved in the photocatalysts designation because ROS govern the water purification ability [5–8]. Furthermore, the recyclability and stability of a photocatalyst need to be considered in the concept of "green chemistry" [9]. Upon gathering the above information, to seek novel photocatalysts which possess specific features including large visible light response, high ROS produce ability, easy recyclability and superior stability is extremely attractive.

Silver phosphate (Ag_3PO_4), with a suitable band gap of 2.45 eV and can absorb light that wavelength shorter than ca. 530 nm, has aroused increasing attention due to its excellent quantum efficiency in many photocatalytic fields, such as O_2 evolution from water splitting [10–12], organic pollutants elimination, CO_2 reduction [13] and so on. Up to now, various strategies for improving the activity of Ag_3PO_4 include morphology control to expose high energy surface [14,15], chemical modification to extend the absorption region [16,17], and band alignment by coupling with other semiconductors and co-catalysts to improve the electron–hole separation [18–23]. Despite the growing number of works exploring

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these strategies, the literatures have mainly focused on expending the light absorption and charge transfer of Ag_3PO_4. The researches of improving the surface/interface catalytic reaction efficiency (such as dissolved oxygen reduction and charge consumption) on the surface of Ag_3PO_4 are very rare. While on the one hand, the surface/interface catalytic reaction is an indispensable step of photocatalysis process and it plays a key role in ROS generation [24]. On the other hand, most semiconductor materials are nonspecific in catalyzing ROS production. Therefore, materials specific in catalyzing ROS production need to be combined into Ag_3PO_4 to further promote the photocatalytic activity. As some photocatalysis systems have verified that the introduction of electrocatalysis active materials could boost the ROS generation. For example, Liu et al. [25] showed that with additional catalysts (Cu or Au) were deposited onto the MoS_2 films, the ROS production abilities of FLV-MoS_2 were greatly enhanced and achieved a rapid water disinfection. And the reasons behind it were the high oxygen active abilities of Cu and Au. Therefore, adding oxygen active materials in Ag_3PO_4 may be an alternative strategy to improve the surface/interface catalytic reaction efficiency. Besides that, the problem of the easy loss of the suspended particulate catalysts in the process of photocatalytic reaction and separation has rarely addressed.

Spinel ferrite $CoFe_2O_4$ possesses unique magnetic, electric, physical, and chemical properties [26,27], which render it as an ideal candidate of magnetically recoverable catalyst supports [28–34], active material for batteries [35], and biomedicinal devices [36]. Especially, the recent reports on $CoFe_2O_4$ for oxygen reduction reaction (ORR), have attracted considerable attention due to their high abundance, low cost and environmental friendliness [37–39]. It is no doubt that the $CoFe_2O_4$ is an active and robust catalyst for O—O bond activation/cleavage and oxide removal. Accordingly, these superiorities of $CoFe_2O_4$ motivate us to fabricate $CoFe_2O_4/Ag_3PO_4$ magnetic photocatalysts with the hope of improving the dissolved oxygen reduction catalytic reactions of Ag_3PO_4 and promoting the production of ROS, as well as recycling the photocatalysts easily. Although, the work about Ag_3PO_4@$CoFe_2O_4$ magnetic photocatalysts that could enhance the photocatalytic activities towards organic dyes degradation dramatically has been reported [40], the discussion of the possible Ag_3PO_4@$CoFe_2O_4$ core-shell structure formation mechanisms, the photocatalytic disinfection performance and the specific catalyzing ROS production features of $CoFe_2O_4$ in the Ag_3PO_4@$CoFe_2O_4$ composites were firstly discussed in the present literature.

It is well known that human health drinking water must be free of pollutants such as pathogenic bacteria and organics. Usually, the wastewater is complex with different kinds of pollutants [41]. Accordingly, it is urgent to develop a novel photocatalyst that can be used to remove different pollutants simultaneously. Our previous works have developed some magnetic photocatalysts, which have been used for simultaneous bactericidal and organic pollutants removal [32,34,42]. For the purpose of further understanding the photocatalytic mechanism and developing more efficient photocatalysts, in this study, we tactfully utilized the surface-electric properties of the $CoFe_2O_4$ that can be tuned by the pH adjustment [43]. Taking the strong alkali salt Na_3PO_4 as the source of $PO_4{}^{3-}$ simultaneously to tune the surface-electric properties of the $CoFe_2O_4$ negative enough to catch Ag^+. As a result, the $CoFe_2O_4$ NPs can attach on the surface of Ag_3PO_4 particles evenly. The followed simple hydrothermal treatment produced uniformed and highly crystallized sesame ball like Ag_3PO_4@$CoFe_2O_4$ composites. The as-prepared Ag_3PO_4@$CoFe_2O_4$ composites combined the VLD and excellent photocatalytic activities of Ag_3PO_4, oxygen active abilities and magnetic property of $CoFe_2O_4$, which displayed superior photocatalytic activities in both rapid water disinfection and organic pollutants degradation. By using colorimetric N, *N*-diethyl-*p*-phenylenediamine (DPD) method and ESR analysis, it concludes that the $CoFe_2O_4$ NPs in the $CoFe_2O_4$@Ag_3PO_4 composites can act as a specific component in catalyzing ROS (especially H_2O_2 and hydroxyl radical) production. More important, the $CoFe_2O_4$@Ag_3PO_4 composites can be easily separated via a magnetic field.

2. Experimental section

2.1. Synthesis of $CoFe_2O_4$ NPs

The $CoFe_2O_4$ NPs were prepared by a hydrothermal treatment method. In a typical process, 2.304 g $FeCl_3{\cdot}6H_2O$ and 1.010 g $CoCl_2{\cdot}6H_2O$ were dissolved in 30 mL ethanol solution (ethanol: $H_2O = 3:1$). Then, a certain amount of 28% concentrated ammonia aqueous solution were added slowly into the above solution to make the pH > 9, followed by 0.5 h stirring. After that, the suspensions were transferred to a 50 mL stainless steel autoclave with a Teflon liner and kept at 180 °C for 20 h. Subsequently, the stainless steel autoclaves were allowed to cool to room temperature and the precipitates were washed with deionized water until the pH = 7. The obtained $CoFe_2O_4$ NPs were then redispersed in deionized water. Part of $CoFe_2O_4$ NPs were centrifuged and dried at 60 °C for characterization.

2.2. Synthesis of Ag_3PO_4@ $CoFe_2O_4$ composite material

The Ag_3PO_4@ $CoFe_2O_4$ composites were prepared via an in suit precipitation process followed by a simple hydrothermal strategy. Typically, 0.4 g $AgNO_3$ was dissolved in 30 mL deionized water. Then, a certain amount of above prepared $CoFe_2O_4$ (0.004 g mL^{-1}) suspensions were added and stirred for 0.5 h. Subsequently, 3 mL Na_3PO_4 solution (1 g mL^{-1}) were added into the mixture drop by drop and kept stirring for 1 h. It should be noted that the whole experiments were kept at 60 °C with a circulating water system. After the precipitation process, the suspension was transferred to several 25 mL Teflon-lined stainless-steel autoclaves and kept for 2 h at 120 °C. After cooling to room temperature, these obtained precipitates were washed with distilled water and ethanol for several times, and then dried at 60 °C in a vacuum oven overnight. The final products were named as 1% Ag_3PO_4@ $CoFe_2O_4$, 3% Ag_3PO_4@ $CoFe_2O_4$ and 5% Ag_3PO_4@ $CoFe_2O_4$ according to the mass fraction of $CoFe_2O_4$ in the weight of $AgNO_3$.

The Ag_3PO_4 (Na_2HPO_4) and $CoFe_2O_4/Ag_3PO_4$ composite (Na_2HPO_4) were prepared via a similar method except using Na_2HPO_4 instead of Na_3PO_4 and the mass fraction of $CoFe_2O_4$ in the weight of $AgNO_3$ was 5%.

The Ag_3PO_4 and Ag_3PO_4@$CoFe_2O_4$ composites without hydrothermal treatment were remarked as Ag_3PO_4 (Na_3PO_4) and Ag_3PO_4@$CoFe_2O_4$ composites (Na_3PO_4), respectively.

2.3. Photocatalytic disinfection performance

Escherichia coli (*E. coli*) was used as the target bacterium to evaluate the photocatalytic disinfection performance in this study. Before experiment, all glass apparatuses and culture medium solution used in the experiments were autoclaved at 121 °C for 20 min. The bacterial cells were grown in nutrient broth at 37 °C for 20 h under agitating at 200 rpm to yield a cell count of approximately 10^9 colony forming units (cfu)/mL. Subsequently, the sample was washed three times with bacterial phosphate buffered saline (PBS) solution by centrifugation for 10 min. Then the cell pellet was resuspended in the PBS solution. After that, the cell suspension was added into the pyrex glass reactor which contained 20 mL bacterial PBS solution and the photocatalyst concentration at 10 μg/mL. The final cell concentration in the test was adjusted to 10^7 cfu/mL.