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Preparation and visible-light activity of silver vanadate for the degradation of pollutants

Xuexiang Hu, Chun Hu [*], Jiuhui Qu

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, Beijing 100085, China

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Abstract

Monoclinic structure silver vanadate Ag_3VO_4 was prepared by hydrothermal process. The effects of the ratio of silver to vanadium in starting material, hydrothermal temperature on surface morphologies, structure and photoactivity of Ag_3VO_4 for the decolorization azodye acid red B under visible irradiation were investigated. The Ag_3VO_4 prepared in the excess vanadium at 160 °C for 48 h exhibited highest visible-light-driven activity. Excess vanadium in the preparation increased the crystallinity and suppressed the formation of grain boundaries, while the formation of Ag^0 on the surface of the catalyst promoting the electron–hole separation and interfacial charge transfer, resulting in an increase in the photocatalytic activity. Furthermore, the activity of the Ag_3VO_4 was increased by 11 times when NiO was loaded, which also shows high activities for the decomposition of phenol and aniline. It is possible due to the formation of a short-circuited microphotoelectrochemical cell enhancing the separation of photogenerated electron–hole pairs.

Keywords: A. Semiconductors; B. Chemical synthesis; C. Catalytic properties; C. Crystal structure

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1. Introduction

Numerous studies have attempted to develop visible-light-driven photocatalysts in order to utilize solar energy and indoor light efficiently [1–5]. There are usually two ways [6] to exploit photocatalysts responsive to visible-light irradiation: one way is to generate intermediate energy levels in UV-active photocatalysts, such as TiO_2, by doping other elements to turn them into visible-light photocatalysts. However, this way is not so effective because dopants will serve as sites for electron–hole recombination to decrease photocatalytic activity. Another way is to develop new materials with photocatalytic activity under visible-light irradiation. Since Zou et al. [7] introduced water splitting for H_2 and O_2 evolution in a stoichiometric amount over the $NiO_x/In_{0.9}Ni_{0.1}TaO_4$ photocatalyst under visible-light irradiation, many new visible-light-driven catalysts have also been reported [6,8–16]. However, only a few [6,14–16] have been investigated with the aim to eliminate organic pollutants in water so far. The mechanism of photocatalytic splitting water is different from that one of photocatalytic elimination pollutions, although both of them use the strong redox powder of photogenerated electron and hole. In the former situation, if the conduction band potential level of a

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[*] Corresponding author. Tel.: +86 10 62849171; fax: +86 10 62923541.
E-mail address: huchun@rcees.ac.cn (C. Hu).

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semiconductor is more negative than that of hydrogen evolution, and the valence band potential level is more positive than that of oxygen evolution, it is possible to decompose water molecules into H_2 and O_2. However, the photocatalytic decomposition of organic contaminants requires that the valence band of the photocatalyst must meet the potential level of oxidizing the organic contaminants and O_2 must be involved in the photocatalytic system. Active oxygen radicals that are generated through the reaction of electron and holes with water or O_2 absorbed on the surface mainly account for the oxidization of the organic compound. The difference of reaction mechanism determines the different demand to the structure and property of material. Since the reaction of photocatalysis occurs on the surface of the photocatalyst, various parameters in models predicting the conversion efficiency may be combined to characterize the surface on the photocatalyst in a solar photocatalysis system.

Konta et al. [17] prepared silver vanadates (α-$AgVO_3$, β-$AgVO_3$, $Ag_4V_2O_7$ and Ag_3VO_4) by precipitation and solid-state reactions and further investigated the photocatalytic activity for O_2 evolution. All silver vanadates showed intense absorption bands in the visible-light region due to band gap transitions. However, among them, only Ag_3VO_4 possessed a photocatalytic activity for O_2 evolution from an aqueous silver nitrate solution under visible-light irradiation. It indicated that its valence band is more positive than the O_2/H_2O potential level (1.23 V vs. SHE, pH 0). So, the photocatalyst with a strong oxidizing potential can be postulated and expected to be good candidate to decompose organic compounds [18]. Herein, we are interested in the photocatalytic decomposition of organic contaminants by the Ag_3VO_4 under visible-light irradiation. Based on the previous statement, it is necessary to investigate the performance of Ag_3VO_4 in the degradation of pollutants under visible-light irradiation, although its performance in water splitting has been studied before.

Obviously, the suitable synthetic approaches may give rise to differing photochemical properties due to possible variation of surface morphology and structure. Hydrothermal process could generate highly crystalline products with high purity, narrow size distribution, and low aggregation. More important, much higher efficiency of the photocatalyst synthesized by this method could be expected. In the present work, Ag_3VO_4 was synthesized via a hydrothermal treatment process. Effects of preparation factors, including the ratio of starting materials, hydrothermal treatment temperature on the structure properties of Ag_3VO_4 were investigated. Moreover, the photocatalytic activity of Ag_3VO_4 prepared at different conditions was evaluated by the photodegradation of acid red B (ARB) under visible-light irradiation. The highest activity of Ag_3VO_4 was obtained. The degradation of phenol and aniline was also investigated. The relationship between activity and structure was discussed.

2. Experimental

2.1. Synthesis of the samples

Ag_3VO_4 powders were synthesized through hydrothermal process. All chemicals used were analytic grade reagents without further purification. Starting materials were V_2O_5, NaOH and $AgNO_3$. In a typical procedure, NaOH and V_2O_5 powders were put into a beaker with 20 ml distilled water, and magnetically stirred. Subsequently, the solution of $AgNO_3$ was added. Yellow precipitates appeared immediately. The chemical equation is shown as follows:

$$V_2O_5 + 6OH^- \rightarrow 2VO_4{}^{3-} + 3H_2O$$

$$3Ag^+ + VO_4{}^{3-} \rightarrow Ag_3VO_4$$

The ratio of silver to vanadium in the starting materials was kept in a stoichiometric ratio (3:1) or in the presence of excess amounts of silver (6:1) or in the presence of excess amounts of vanadium (3:2). The slurry solution was transferred into a 50-ml Teflon-liner autoclave and filled up to 70% of the total volume. After that, the autoclave was sealed into a stainless steel tank and kept at different temperature from 140 °C to 180 °C for 48 h. Then the reactor was cooled to room temperature naturally. Resulting samples were collected and washed with deionized water and dried at 70 °C in air.

Subsequently, NiO was loaded on the surface of Ag_3VO_4 by an impregnation method in a similar manner as described elsewhere [19]. 0.5 g of the Ag_3VO_4 powder and appropriate amount of $Ni(NO_3)_2$ aqueous solution were put into a porcelain crucible. Water was evaporated at 70 °C. The suspension was stirred using a glass rod during the evaporation. The dried powder was calcined at 300 °C for 1 h in air using a muffle furnace. The weight percent of Ni was calculated by the ratio of the dosage of Ni^{2+} to the total amount of the dosage of Ag_3VO_4 and NiO (Ni^{2+} was expected to be NiO).