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

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Abstract

Monoclinic structure silver vanadate Ag3VO4 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 Ag3VO4 for the decolorization azodye acid red B under visible irradiation were investigated. The Ag3VO4 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 Ag0 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 Ag3VO4 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

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 TiO2, 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 H2 and O2 evolution in a stoichiometric amount over the NiO/In0.9Ni0.1TaO4 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
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 H₂ and O₂. 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 O₂ must be involved in the photocatalytic system. Active oxygen radicals that are generated through the reaction of electron and holes with water or O₂ 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-AgVO₃, β-AgVO₃, Ag₄V₂O₇ and Ag₃VO₄) by precipitation and solid-state reactions and further investigated the photocatalytic activity for O₂ evolution. All silver vanadates showed intense absorption bands in the visible-light region due to band gap transitions. However, among them, only Ag₃VO₄ possessed a photocatalytic activity for O₂ evolution from an aqueous silver nitrate solution under visible-light irradiation. It indicated that its valence band is more positive than the O₂/H₂O 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 contaminants by the Ag₃VO₄ under visible-light irradiation. Based on the previous statement, it is necessary to investigate the performance of Ag₃VO₄ 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, Ag₃VO₄ 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 Ag₃VO₄ were investigated. Moreover, the photocatalytic activity of Ag₃VO₄ prepared at different conditions was evaluated by the photodegradation of acid red B (ARB) under visible-light irradiation. The highest activity of Ag₃VO₄ 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

Ag₃VO₄ powders were synthesized through hydrothermal process. All chemicals used were analytic grade reagents without further purification. Starting materials were V₂O₅, NaOH and AgNO₃. In a typical procedure, NaOH and V₂O₅ powders were put into a beaker with 20 ml distilled water, and magnetically stirred. Subsequently, the solution of AgNO₃ was added. Yellow precipitates appeared immediately. The chemical equation is shown as follows:

\[ \text{V}_2\text{O}_5 + 6\text{OH}^- \rightarrow 2\text{VO}_4^{3-} + 3\text{H}_2\text{O} \]

\[ 3\text{Ag}^+ + \text{VO}_4^{3-} \rightarrow \text{Ag}_3\text{VO}_4 \]

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 Ag₃VO₄ by an impregnation method in a similar manner as described elsewhere [19]. 0.5 g of the Ag₃VO₄ powder and appropriate amount of Ni(NO₃)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 Ni²⁺ to the total amount of the dosage of Ag₃VO₄ and NiO (Ni²⁺ was expected to be NiO).
2.2. Characterization

Powder X-ray diffraction (XRD) of catalyst was recorded on a Scintag-XDS-2000 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Morphologies and structures of the prepared samples were observed using a Hitachi S-3000N scanning electron microscopy (SEM). UV–vis diffuse reflectance spectra of the samples were recorded on a UV–vis spectrophotometer (Hitachi UV-3010) with an integrating sphere attachment. The analyzed range was 250–800 nm, and BaSO4 was the reflectance standard. Electron spin resonance (ESR) spectra were obtained using a Bruker model ESP 300E electron paramagnetic resonance spectrometer equipped with a quanta-ray Nd:YAG laser system as the irradiation light source (λ = 532 nm). The settings were center field, 3480.00 G; microwave frequency, 9.79 GHz; and power, 5.05 mW.

2.3. Photocatalytic experiments

The photocatalytic activities of the synthesized powders were evaluated by photocatalytic decomposition of ARB in Ag3VO4 aqueous suspension under visible-light irradiation. The light source for photocatalysis was a 350-W Xe arc lamp (Shanghai Photoelectron Device Ltd.). Light passed through a water filter and a UV cutoff filter (λ > 420 nm, Shanghai Seagull Coloured Optical Glass Co. Ltd.) and then was focused onto a 100-ml beaker. The average light intensity was 2.5 mWcm⁻². The reaction temperature was maintained at 25 °C. In a typical experiment, aqueous suspensions of ARB (60 ml, 50 ppm) and 0.1 g of catalyst powders were placed in the beaker. Prior to irradiation, the suspensions were magnetically stirred in dark for 30 min to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under room air equilibrated conditions. At given irradiation time intervals, 3-ml aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) to remove the catalyst particulates for analysis. The filtrates were monitored with a 752N UV–vis spectrophotometer (Shanghai Precision & Scientific Instrument Co. Ltd., China).

3. Results and discussion

3.1. Effects of excess silver and vanadium in the preparation of Ag₃VO₄ photocatalysts

Fig. 1 shows X-ray diffraction patterns of samples prepared under different conditions. Clearly, all samples showed similar peaks of the XRD patterns, which were readily indexed to a monoclinic phase Ag₃VO₄ (JCPDS No. 43-0542). The diffraction peaks intensities of the sample prepared in excess vanadium and in the stoichiometric ratio are stronger than the ones in the excess silver. This indicated that the crystallinity in stoichiometric ratio and in excess vanadium is

![XRD patterns](image)

Fig. 1. XRD patterns of samples prepared at 160 °C for 48 h: (a) in the presence of excess silver, (b) in a stoichiometric ratio, and (c) in the presence of excess vanadium.
better than that in excess silver. However, an 38.1° diffraction peak assigned to Ag⁰ was displayed in excess silver and vanadium samples. The differences in chemical composition of the materials prepared with more Ag, stoichiometric ratio, and more V, were analyzed by ICP-OES. According to chemical analysis, the atomic ratio of Ag to V in the sample prepared with excess silver, in stoichiometric ratio and with excess vanadium was 3.05, 2.79, 2.99, respectively. This indicates that precipitates of Ag₃VO₄ were dissolved and recrystallized during hydrothermal treatment process, resulting in the formation of Ag⁰ species in the samples prepared with excess silver or excess vanadium. This result also agrees with the XRD data. Fig. 2 shows SEM photographs of all the above samples. Compared with the SEM of Ag₃VO₄ prepared in a stoichiometric ratio (Fig. 2b), excess silver in the preparation decreased the crystal sizes of Ag₃VO₄, and there were a lot of grain boundaries shown in Fig. 2a. In contrast, Ag₃VO₄ powder prepared with excess vanadium shows large crystals with uniform and regular particle size (Fig. 2c). The well-crystallized Ag₃VO₄ with the excess vanadium suppressed the formation of grain boundaries.

3.2. Morphologies of the Ag₃VO₄ samples

To determine the effect of the heat treatment temperature for Ag₃VO₄, the powder precursor in excess vanadium was heat-treated for 48 h at different temperatures from 140 °C to 180 °C. The crystallinity and morphologies of the samples are strongly dependent on the hydrothermal temperature (Fig. 3). Before hydrothermal treatment, the starting precipitate precursors obtained by inorganic precipitate reaction were Ag₃VO₄ phase with lower crystallinity. With increasing temperature, the crystallinity of Ag₃VO₄ increased, and the highest degree of crystallization of Ag₃VO₄ was obtained at 160 °C. However, at 180 °C, not only the crystallinity decreased, but also there was an apparently
heterogeneous phase to appear at the diffraction peaks 38.1°, 44.2°, 64.4° and 77.4°, which were assigned to the silver-3c syn crystals. Although these diffraction peaks also were exhibited in the other two samples, the intensity of these peaks in the sample prepared at 160 °C was lowest among the three samples. Fig. 4 displays morphologies of the samples prepared at different temperature. The starting precipitates were smaller, irregular particles, and the sample was poorly crystallized (Fig. 4a). As for the two samples prepared at 140 °C and 180 °C, there were obvious impurity

Fig. 3. XRD pattern of Ag₃VO₄ obtained at different temperature for 48 h.

Fig. 4. Morphologies of temperature series Ag₃VO₄ samples: (a) precursor, (b) 140 °C, (c) 160 °C, and (d) 180 °C.
phase, which were the metallic state silver confirmed by XRD analysis, and the sample at 180 °C had much more metallic state silver (Fig. 4d). However, morphology of the samples at 160 °C exhibited the well-crystallized particle with smooth surface and regular shape. The formation of metallic state silver was almost suppressed.

From the above results, it is interesting that the formation of metallic state silver in Ag₃VO₄ sample prepared in excess vanadium, as well as in excess silver, while starting precipitates are pure Ag₃VO₄ phase without impurity phase formation. However, with increasing hydrothermal treatment temperature, the intensity of diffraction peaks of the silver-3c syn crystals was increased. It indicates that precipitates of Ag₃VO₄ were dissolved and recrystallized during hydrothermal treatment process, resulting in the Ag⁰ species formation. This phenomenon was not observed by precipitation process. The results confirmed that the Ag⁰ species arose from hydrothermal process at higher temperature.

3.3. Optical properties of Ag₃VO₄

Optical absorption of the Ag₃VO₄ particles was measured by using an UV-vis spectrometer. Fig. 5A shows UV-vis diffuse reflectance spectra of the as-prepared samples prepared in different ratio of silver to vanadium. They absorbed in UV and visible-light region. The sample in the excess of silver has an absorption band 250–580 nm, while both the sample in the excess of vanadium and that one in a stoichiometric ratio present almost the same absorption edge around 600 nm. However, the spectra shape of samples powders prepared at 140 °C and 180 °C greatly changed (Fig. 5B),

![Fig. 5. UV-vis diffuse reflectance of Ag₃VO₄: (A) in different ratio of silver to vanadium at 160 °C and (B) at different temperature with excess vanadium.](image-url)
which is possible to be affected by the surface plasmon absorption of metallic silver. $\text{Ag}_3\text{VO}_4$ powders prepared at $140 \pm 8 \degree C$ exhibited visible-light absorption around $400–580 \text{ nm}$, whereas another one at $180 \pm 8 \degree C$ displayed $400–550 \text{ nm}$ absorption in visible region. The optical absorbance property of the starting precipitate precursors was also shown in Fig. 5B. The precursor displayed strong UV absorption and $400–520 \text{ nm}$ visible-light absorption.

3.4. Photocatalytic activities of various catalysts under visible-light irradiation

The photocatalytic activities of different $\text{Ag}_3\text{VO}_4$ samples were evaluated under visible-light irradiation. ARB is not degraded under visible-irradiation in the absence of photocatalyst. In contrast, it was degraded by different rates with various catalysts under otherwise identical conditions. The photocatalyst in excess vanadium showed highest activity, while the activity of another one in a stoichiometric ratio was higher than that one in excess of silver (Fig. 6). ARB had almost same adsorption (about $5\%$) on the three samples, indicating that difference of photodegradation of ARB was not due to the adsorption of dyes on the surface of photocatalysts. The photocatalytic activity greatly depended on the morphology and structure of $\text{Ag}_3\text{VO}_4$. Based on the results of XRD and SEM, $\text{Ag}_3\text{VO}_4$ prepared in excess vanadium had well crystallinity resulting in less grain boundaries. These grain boundaries serve as a recombination center between photogenerated electrons and holes [17]. Therefore, the decrease in the number of grain boundaries resulted in an increase in photocatalytic activity. In addition, the extra small particle on the surface of $\text{Ag}_3\text{VO}_4$ in excess vanadium contained $\text{Ag}^0$ species. According to the reported work [20–22], it is quite possible that appropriate amount of $\text{Ag}^0$ species on the surface of the catalyst mainly act as electron traps, enhancing the electron–hole separation, leading the higher photocatalytic activity. This point was further proved by the determination of photoluminescence of the samples. Fig. 7 showed that these catalysts exhibited different photoluminescence spectrum by excitation at $330 \text{ nm}$. When $\text{Ag}_3\text{VO}_4$ samples were excited by around UV light at $330 \text{ nm}$, an electron transfer was brought about from the valence band to the conduction band to form excited state. The observed photoluminescence spectrum is attributed to the radiative decay process from the excited state to the ground state. If the radiative process was suppressed, an available hole would be remained in the VB, taking part in the chemical reaction. Therefore, the effective quenching of photoluminescence can improve the photocatalytic efficiency. Obviously, the photoluminescence intensities of $\text{Ag}_3\text{VO}_4$ in excess vanadium were lower than those of the other two samples. Since $\text{Ag}$ particles deposited on photocatalyst could act as electron traps and transfer the trapped electron to adsorbed $\text{O}_2$ acting as an electron acceptor [22,23], the effective quenching of photoluminescence can be attributed to the photoexcited electron transfer from the excited state to $\text{Ag}^0$ while the holes remain in the $\text{Ag}_3\text{VO}_4$ species, resulting in the charge separation of electrons and holes. As for the sample in excess silver, there were a lot of grain boundaries although $\text{Ag}^0$ species also existed on the surface of the sample, therefore the recombination of the photogenerated electron and hole still was predominant, resulting in the lower photocatalytic activity.
Fig. 8 shows the degradation of ARB using samples prepared at different temperatures. The first-order linear relationship was revealed by the plots of the $\ln(C_0/C)$ versus irradiation time ($t$). The apparent reaction rate constant $k$ was 0.0098 min$^{-1}$, 0.0331 min$^{-1}$ and 0.0083 min$^{-1}$, respectively, for the 140 °C, 160 °C, 180 °C samples. Ag$_3$VO$_4$ prepared at 160 °C exhibited much higher activity than any other samples for the degradation of ARB under visible-light irradiation. Based on the data of XRD, SEM and UV–vis DRS, Ag$_3$VO$_4$ prepared at 160 °C were well-crystallized particles with appropriate Ag$^0$ species formation on its surface, enhancing the separation of generated electron–hole pair, causing the increase of photocatalytic efficiency. Nevertheless, excess Ag$^0$ species formed on the surface of the two samples prepared at 140 °C and 180 °C, served as recombination centers between photogenerated electrons and holes, causing the decrease of photocatalytic activity. In addition, the visible-light absorptions of the two samples were affected by plasmon absorption of metallic silver. It has been proved that plasmon absorption of metallic silver could not generate reactive oxygen species [24]. The precursor activity was also lower than the sample of 160 °C. The precursor with low crystallinity resulted in more grain boundaries leading to lower activity. Based on the above statement, the Ag$_3$VO$_4$ prepared in excess vanadium at 160 °C showed highest photocatalytic activity for the decolorization of ARB under visible-light irradiation. The stability of a photocatalyst is important to its application. Therefore, after the aqueous suspension of catalyst at optimum prepared conditions was irradiated by UV and visible light, the dried Ag$_3$VO$_4$ sample was characterized by XRD. In comparison with XRD patterns of the samples before
and after irradiation, the crystal structure of the Ag$_3$VO$_4$ photocatalyst was not changed. This result implies that Ag$_3$VO$_4$ is stable in aqueous solution and under irradiation. However, the activity of Ag$_3$VO$_4$ is still low considering the practical applications. To improve the photocatalytic activity, the catalyst prepared at optimum conditions was loaded a NiO cocatalyst by impregnation method. Fig. 9 shows the reaction constant $k$ as a function of Ni content in NiO/Ag$_3$VO$_4$ for the degradation of ARB under visible-light irradiation. The photocatalytic activity of Ag$_3$VO$_4$ was drastically increased with the amount of NiO loading and showed a maximum at 2.0 wt% for the amount of Ni loaded, and decreased upon further loading. The photoactivity of the Ni 2.0 wt%/Ag$_3$VO$_4$ is 11 times that of the bare Ag$_3$VO$_4$ sample. The temporal UV/vis spectra showed that the ARB characteristic band centered at 514 nm was decreased promptly upon light irradiation with Ni 2.0 wt%/Ag$_3$VO$_4$ (the insert of Fig. 9). The ARB was decolorized completely after 120 min of irradiation, indicating that at least the chromophoric structure of the dye was destroyed. After illumination for 12 h, about 90% of the total sulfur content was converted into SO$_4^{2-}$ ions. However, TOC measurements show almost no change in the total organic content before and after photooxidation. Phthalic acid, acetic acid, and 1,2-ethanediol are the main products of GC–MS analysis. Meanwhile, the photochemical experiment was also expanded to the other organic compounds phenol and aniline (Fig. 10). Phenol and aniline completely disappeared within 6h and 8h of irradiation, respectively. Correspondingly, 73% and 58% of TOC content was removed. The results further confirmed that NiO/Ag$_3$VO$_4$ is a visible-induced photocatalyst because the both compounds have no absorption in the visible region, in which the self-photosensitization process was avoided.

Fig. 11a shows the TEM image of the Ni 2.0 wt%/Ag$_3$VO$_4$ photocatalyst. Nearly spherical NiO particles (104 nm) were clearly observed as islands on the surface of Ag$_3$VO$_4$. The composition of the Ni 2.0 wt%/Ag$_3$VO$_4$ was analyzed with energy-dispersive X-ray (EDX) as shown in Fig. 11b. Ag, V, O, and Ni lines were observed. The concentration of Ni was about 6.58 wt%, which was more than the dosages of Ni ~2.0 wt%. The result demonstrated that most NiO was localized on the surface of the Ag$_3$VO$_4$. The ESR spin-trap technique (with DMPO) was used to detect the nature of the reactive oxygen species generated on the surface of catalysts under visible irradiation (Fig. 12). The six characteristic peaks of the DMPO-O$_2$ adducts were observed only in NiO/Ag$_3$VO$_4$ methanol dispersion under visible-light irradiation (curve a). No such signals were detected in the dark and visible-light-irradiated Ag$_3$VO$_4$ system under otherwise identical conditions (curves b and c). The evidence that O$_2$ are produced on the surface of visible illuminated NiO/Ag$_3$VO$_4$ provide a solid indication that the catalyst can be efficiently excited by visible-light to create electron–hole pairs and that the charge separation is maintained long enough to react with adsorbed oxygen/H$_2$O and to produce active oxygen radicals. No O$_2$ was formed in the visible-light-illuminated Ag$_3$VO$_4$ methanol suspension, indicating that the recombination rate of the photogenerated electron–hole pairs from the Ag$_3$VO$_4$ excited by visible-light was higher than that one of their separation. The results confirmed that the NiO/Ag$_3$VO$_4$ system behaves as a short-circuited microphotoelectrochemical cell. The surface of NiO is the cathode, and the surface of Ag$_3$VO$_4$ is the anode. The NiO on the external surface of Ag$_3$VO$_4$ trapped photogenerated electrons, facilitating the electron–hole

![Fig. 9](image_url) The reaction constant $k$ as a function of Ni content in NiO/Ag$_3$VO$_4$ (0.1 g photocatalyst added into 60 ml of 50 ppm ARB solution). The insert shows absorption changes of ARB solution under photocatalytic process (0.1 g Ni 2.0 wt%/Ag$_3$VO$_4$ added into 60 ml of 50 ppm ARB solution).
Fig. 10. Changes in concentration and the removal of TOC during the course of photocatalytic degradation of different contaminant (20 mg l$^{-1}$, 60 ml) in the presence of Ni 2 wt%/$\text{Ag}_3\text{VO}_4$ (0.1 g) under visible-light irradiation ($\lambda > 420$ nm): (A) phenol, and (B) aniline.

Fig. 11. (a) TEM image and (b) EDX analysis of the Ni 2 wt%/$\text{Ag}_3\text{VO}_4$ photocatalyst.
separation leading to $O_2^{\cdot-}$ formation. The $O_2^{\cdot-}$ is the main active species in the decoloration of ARB and the decomposition of phenol and aniline.

4. Conclusion

Ag$_3$VO$_4$ prepared in the excess vanadium at 160 °C for 48 h by hydrothermal method exhibited highest visible-light-driven activity. The excess vanadium in the preparation increased the crystallinity of Ag$_3$VO$_4$ and suppressed the formation of grain boundaries, while the appropriate formation of Ag$^+$ 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$_3$VO$_4$ was increased by 11 times when a NiO was loaded. It is contributed to conduct a short-circuited microphotocatalytic cell between NiO and Ag$_3$VO$_4$, facilitating the excited electron transfer and hence suppress efficiently the recombination of photogenerated electron–hole.

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References