Application of Ag/AgBr/GdVO₄ composite photocatalyst in wastewater treatment

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ABSTRACT
Ag/AgBr/GdVO₄ composite photocatalysts were designed and synthesized in this paper. The physical and chemical structures, as well as optical properties of the synthesized composite were investigated via XRD, XPS, TEM, and UV–vis. It is found that the composite showed a ternary heterojunction structure of Ag, AgBr and GdVO₄. Meanwhile, it has a high intensity of light current, indicating its high separation efficiency of electron and hole. Photocatalytic oxidation of rhodamine B (RhB) under visible light irradiation was performed to investigate the activity of the Ag/AgBr/GdVO₄ composite. Result indicates that it shows excellent photocatalytic activity. Under visible light irradiation for 12 min, about 80% of RhB (30 μmol/L) was degraded. The degradation rate is estimated to be 0.253 min⁻¹, which is three times higher than that of pure AgBr. The high photoactivity can be ascribed to the synergetic effect of AgBr, GdVO₄, and Ag nanoparticle in separation of electron–hole pairs.

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Introduction
In recent years, the photocatalytic technology as an ideal technology for water pollution control has attracted much attention (Chakrabarti and Dutta, 2004; Su et al., 2004). TiO₂ is the most commonly used photocatalyst due to its excellent photocatalytic activity. However, it can only respond to ultraviolet (UV) light, which greatly limits its large-scale application. This situation induces the research and development of the visible light photocatalytic materials.

Metal vanadate is a new type of photocatalytic material with visible light response capability. Because the electrons on the 3d orbit of V are easily excited by visible light, this new type of photocatalytic material is far greater than TiO₂ in terms of the utilization of light energy. This kind of vanadate photocatalytic materials mainly include Ag₃VO₄ (MousaviAziz and Yangjeh, 2016; Jing et al., 2016), SmVO₄ (He et al., 2009; Li et al., 2013a, 2013b, 2013c, 2013d; Dong et al., 2014a, 2014b), BiVO₄ (Mascaro et al., 2015; Liu et al., 2016; Lin et al., 2016), InVO₄ and so on. Gadolinium vanadate (GdVO₄), as a visible light-responsive semiconductor material with narrow band gap, non-toxic, high refractive index and other excellent properties, is widely used in the field of laser and luminescence manufacture. Additionally, it has been reported that GdVO₄ can be used for photocatalytic decomposition of water and degradation of organic pollutant (Bai et al., 2013), and it is a promising material for visible light photocatalysis. However, the activity of pure GdVO₄ is low, indicating further modification of GdVO₄ is needed to improve its photocatalytic activity. Generally, the modification method can be classified into two types: the first is doping metal ions; for example, Oshikiri (Oshikiri et al., 2014) doped GdVO₄ with Ni through a

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combination of experimentation and theoretical calculation, and realized the improved photocatalytic activity of GdVO₄. Wang (Wang et al., 2009a, 2009b) modified GdVO₄ with Bi. The synthesized Bi-GdVO₄ photocatalyst realized the stable and complete water decomposition into hydrogen and oxygen under UV. At the same time, it also proved that the adjustment of the gap width through the formation of solid solution was an effective method for the synthesis of photocatalysts with high activity. Another one to improve the photocatalytic activity of GdVO₄ is semiconductor coupling. For example, He (He et al., 2010) coupled GdVO₄ with V₂O₅ to generate an effective photocatalyst. The acetone degradation rate of the composite catalyst reached 99.2% under visible light. He (He et al., 2013) prepared g-C₃N₄/GdVO₄ composite photocatalyst and applied it in rhodamine B (RhB) degradation. It is found that the degradation rate of the composite catalyst was 3.4 and 31 times higher than that of g-C₃N₄ and GdVO₄, respectively. However, generally speaking, there are still not many researches of the GdVO₄-based photocatalyst at present and its photocatalytic activity cannot satisfy the demand of practical application. Therefore, it is still desirable to develop GdVO₄-based composite photocatalysts with high photocatalytic activity.

Silver bromide (AgBr) as a photosensitive material is widely used in films. Huang (Huang et al., 2015) found that although AgBr has the shortcoming of being light sensitive, it is a kind of highly efficient photocatalyst. Additionally, the compounding of AgBr with other semiconductors can effectively improve the stability of AgBr under light. This is because the photo-generated electron on the conduction band of AgBr can migrate to the coupled semiconductor due to the difference of band potential. This process decreases the electron concentration on AgBr and thus retards the decomposition of AgBr. At the same time, it can also improve the lifetime of the charge carriers and subsequently enhance the photocatalytic activity of the composite semiconductor. Therefore, AgBr is also considered an effective cocatalyst. Till now, AgBr has been used for the modification of SmVO₄ (Li et al., 2013a, 2013b, 2013c, 2013d), g-C₃N₄ (Xu et al., 2013), AgPO₄ (Maryam and Aziz, 2016; Meng et al., 2016), TiO₂ (Yoshihiro et al., 2016; Liu et al., 2015; Wang et al., 2015), Go (Bai et al., 2016a, 2016b), Fe₂O₃ (Tsuz et al., 2016), AgₓO (Cao et al., 2015), WO₃ (Cao et al., 2011a, 2011b), etc., and it was found that the addition of AgBr additive had significantly improved the catalytic properties of the pure phase catalyst.

Bai (Bai et al., 2015, 2016a, 2016b) reported that the loading of Pd nanoparticles on carriers such as C₃N₄, TiO₂, and rGO can effectively induce the transfer of the photoexcited electron onto the metal, thus improve the separation efficiency of the electron and holes and in turn increase the performance of the photocatalytic hydrogen production. Considering the light sensitivity of the AgBr additive, Ag nanoparticles would easily be formed and construct Ag/AgBr composite. These Ag particles can work like the Pd or Pt nanoparticles to improve the separation efficiency of photo-generated electrons and holes, and further enhance the photocatalytic performance. Therefore, a new type of Ag/AgBr/GdVO₄ composite photocatalyst was designed and prepared in this paper. The ternary heterojunction structure of the Ag, AgBr, and GdVO₄ components greatly improves the photocatalytic performance of the GdVO₄. Based on the reactive species trapping experiment, the possible reaction mechanism is also discussed.

1. Experimental

1.1. Preparation of catalysts

Pure GdVO₄ was prepared via hydrothermal method. The detailed process is performed as follows. 0.667 g of Gd₂O₃ was dissolved in dilute HNO₃ solution to obtained solution A. 0.430 g of NH₄VO₃ was dissolved in water to get solution B. After solution A and solution B were mixed, the pH value was adjusted to 7 with NH₃ solution. Then, the mixture was transferred in a Teflon-lined stainless-steel autoclave and heated at 140°C for 12 hr. After the autoclave was cooled to room temperature, the resulting products were separated by centrifugation, followed by washing with deionized water and absolute ethanol for several times and calcined at 500°C for 4 hr.

AgBr was prepared via deposition method. 0.904 g of AgNO₃ was dissolved in dilute NH₃ solution to obtain [Ag(NH₃)₂]⁺ solution. Then, NaBr solution with the same amount of NaBr as AgNO₃ was slowly added to generate a yellow precipitate. After the suspension was stirred for 4 hr at room temperature, the precipitate was separated and washed with water for three times. AgBr powders were obtained after the deposition was dried at 60°C for 24 hr.

Ag/AgBr/GdVO₄ composite was also prepared via hydrothermal method. Typically, Gd(NO₃)₃ solution and NH₄VO₃ solution with the same atomic ratio of Gd and V were mixed slowly to get suspension A. [Ag(NH₃)₂]⁺ solution and NaBr solution with the same atomic ratio of Ag and Br were mixed to get suspension B. Then, the two suspensions were mixed together and transferred in a Teflon-lined stainless-steel autoclave. After the autoclave was heated at 140°C for 12 hr, the precipitate was separated, washed with water, and finally calcined at 500°C for 2 hr. All Ag/AgBr/GdVO₄ composites with different AgBr weight contents were prepared via the same way. In order to make clarity, the Ag/AgBr/GdVO₄ composite with the AgBr weight contents of 30 wt.%, 40 wt.%, 50 wt.%, 60 wt.%, and 70 wt.% were denoted to 30ABGd, 40ABGd, 50ABGd, 60ABGd, and 70ABGd, respectively. Ag/GdVO₄ catalyst as a reference sample was also synthesized via impregnation method. The content of Ag was controlled to be 5 wt.% based on the XPS result of 40ABGd. The preparation method refers to the literature (Li et al., 2013a, 2013b, 2013c, 2013d) with AgNO₃ as Ag sources.

1.2. Characterization of catalysts

The specific surface areas were measured on Autosorb-1 (Quantachrome Instruments) by the Brunauer–Emmett–Teller (BET) method. Powder X-ray diffraction (XRD) was obtained on a Philips PW3040/60 X-ray diffractometer with Cu Kα radiation (40 kV/40 mA). Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 Field emission scanning electron microscope. Transmission electron microscopy (TEM) analysis was conducted on a JEM-2010F electron...
microscope at an accelerating voltage of 200 kV. UV–visible (UV–vis) absorbance spectra were obtained by a UV–visible spectrophotometer (PerkinElmer Lambda900) equipped with an integrating sphere. BaSO₄ was used as a reflectance standard in a UV–visible diffuse reflectance experiment. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Quantum 2000 Scanning ESCA Microprobe instrument using AlKα. The C 1s signal was set to a position of 284.6 eV. The photocurrent (PC) responses measurements were performed by using a CHI 660B electrochemical workstation with a standard three-electrode cell at room temperature.

1.3. Photocatalytic test

The photocatalytic activities of Ag/AgBr/GdVO₄ heterojunction were evaluated by the degradation of RhB in aqueous solution under visible light irradiation of a 350 W xenon lamp with a UV cut and an infrared spectroscopy (IR) cut filters (800 nm > λ > 420 nm). In each experiment, 100 mg of catalyst was suspended in an aqueous solution (100 mL) of RhB. The initial concentration of RhB was 30 μmol/L. Prior to irradiation, the suspension was agitated for an hour to ensure the establishment of adsorption–desorption equilibrium. At given irradiation time intervals, samples were withdrawn and centrifuged to remove photocatalyst for analysis. The concentration of aqueous RhB was determined by measuring the maximum absorbance at 554 nm using a UV–vis spectrophotometer. The procedures of the scavenging experiments of reactive oxygen species were similar to the photodegradation experiment.

2. Results and discussion

2.1. Characterization results of catalysts

The crystal phase structure of the catalyst prepared was analyzed using XRD, and the results are shown in Fig. 1. The GdVO₄ has rather strong diffraction peaks. The Joint Committee on Powder Diffraction Standards (JCPDS, 17-0260) at 24.47, 32.83 and 48.95°, indicating that it is of the tetragonal structure. The strong diffraction peaks of AgBr are observed at 26.63, 30.86, 44.33, 55.06, 64.44, and 73.29°, respectively, which accords well with the standard card (PDF# 06-0438) and indicates its face centered cubic structure. In the XRD patterns of Ag/AgBr/GdVO₄ composite catalysts, the characteristic diffraction peaks of GdVO₄ and AgBr are observed simultaneously. However, the diffraction peak of the metal Ag is not detected, which may be ascribed to the low content or well dispersion of the formed Ag nanoparticles with the increase of the AgBr content. The characteristic diffraction peak of AgBr in the composite catalyst gradually increases, while the peaks of GdVO₄ gradually decrease.

The surface chemical composition and chemical state of the Ag/AgBr/GdVO₄ catalyst were characterized through XPS. Fig. 2a shows the high resolution X-ray photoelectron spectroscopy of Gd 4d, Ag 3d, and Br 3d, respectively. It can be observed that the binding energy of the individual components. The binding energy (BE) of V 2p3/2 and V 2p1/2 is 517.0 and 515.0 eV, respectively, which can be attributed to V⁵⁺. The XPS peak of the O 1s lies at 530.0 eV, which can be attributed to the lattice oxygen of the GdVO₄. The BE of Gd 4d5/2 and 4d3/2 is respectively 141.5 eV and 147.3 eV, which can be ascribed to the Br⁻ in AgBr. Fig. 2e is the high resolution XPS spectrum of Ag 3d5/2. It can be seen that the Ag 3d5/2 peak of 40ABGd is much weaker than that of AgBr, which is related to the low concentration of AgBr in 40ABGd. Compared with AgBr, the Ag 3d5/2 peak of 40ABGd does not shift. However, two kinds of silver species are observed simultaneously. The peak with the BE of 367.4 eV could be attributed to Ag⁺, and the peak with the BE of 368.1 eV is metal silver. This phenomenon is related to the instability of AgBr. Clearly, the XPS analysis proves that the ternary composite catalyst system of Ag, AgBr and GdVO₄ is successfully prepared.

Fig. 3 is the TEM image of 40ABGd. It can be seen from the figure that the composite catalyst has two different particles. The ones with darker color and larger size are the AgBr particles, while those relatively lighter in overall color and smaller in size are the GdVO₄ particles. Fig. 3b is the high resolution image of 40ABGd which shows the microstructure of the composite catalyst. Three different lattice fringes are observed. The 0.205 nm lattice fringe corresponds to the (002) crystal surface of Ag, the 0.267 nm lattice fringe corresponds to the (200) surface of AgBr, and the 0.361 nm lattice fringe can be ascribed to the (200) surface of GdVO₄. Obviously, the AgBr/GdVO₄ system is transformed into the Ag/AgBr/GdVO₄ system under the illumination of light, which is consistent with the results of the XPS.

Fig. 4 is the UV–vis diffuse reflectance spectra of AgBr, GdVO₄ and Ag/AgBr/GdVO₄ composite photocatalyst. In order to make the spectrum clarity, only 30 wt.% Ag/AgBr/GdVO₄, 40 wt.% Ag/AgBr/GdVO₄, and 50 wt.% Ag/AgBr/GdVO₄ are chosen. From the figure, it can be seen that both AgBr and
Fig. 2 – XPS spectra of AgBr and 40 wt.% Ag/AgBr/G + dVO₄. (a) Survey spectra; (b) V 2p and O 1s; (c) Gd 4d; (d) Br 3d; (e) Ag 3d.
XPS: X-ray photoelectron spectroscopy.

Fig. 3 – TEM (a) and HR-TEM (b) images of 40 wt.% Ag/AgBr/GdVO₄ composite. TEM: transmission electron microscopy, HR-TEM: high resolution transmission electron microscopy.
GdVO₄ are able to absorb UV light and visible light. According to the Kubelka-Munk equation, the band gap energy of GdVO₄ and AgBr (Wang et al., 2009a, 2009b) is estimated to be 2.21 eV and 2.38 eV, respectively. The UV–vis spectrum of Ag/AgBr/GdVO₄ composite catalyst can be regarded as the superposition of the absorption of AgBr and GdVO₄. With the increase of the AgBr content, the optical absorption performance is slightly enhanced. But in general, the difference between optical absorption performances of Ag/AgBr/GdVO₄ composite catalysts is minor.

2.2. Photocatalytic activity of Ag/AgBr/GdVO₄

The photocatalytic activity of the Ag/AgBr/GdVO₄ catalyst was evaluated by the photocatalytic degradation of RhB. Fig. 5 shows the activity of the Ag/AgBr/GdVO₄ catalyst in the degradation of 30 mg/L RhB solution and the corresponding first-order kinetics plot. It can be seen that the degradation rate of RhB is negligible when no catalyst was added. With the presence of GdVO₄, the degradation rate of RhB is still very low, whereas AgBr shows much higher photocatalytic efficiency than that of GdVO₄. The degradation rate reaches 0.079 min⁻¹. Compared with AgBr, the activity of Ag/AgBr/GdVO₄ composite catalyst is even higher, and this activity is related to the concentration of AgBr. With the increase of the concentration of AgBr, the photocatalytic activity of the corresponding catalyst increases first and then decreases. The sample with the AgBr content of 40% shows the highest photocatalytic activity. The degradation rate reaches 0.253 min⁻¹, which is three times higher than that of AgBr. In addition, during the reaction process, the color of the catalyst is found to change from light yellow to black under the light. This phenomenon could be attributed to the formation of Ag nanoparticles under the light, which is consistent with the results of XPS and TEM. It is widely accepted that metal Ag can act as electron trap to improve the separation efficiency of electron–hole pairs. Hence, in order to reveal the role of metal Ag, Ag/GdVO₄ composite was prepared and investigated. The result shown in Fig. 5a indicates that metal Ag does improve the photocatalytic activity of GdVO₄. However, the photocatalytic activity is still far lower than that of Ag/AgBr/GdVO₄ composites, suggesting that the excellent photocatalytic activity of the Ag/AgBr/GdVO₄ results from the synergetic effect of the three consisting phases.

Fig. 6 shows the cycling runs of the 40ABGd composite in RhB degradation under visible light. At the end of each reaction, the catalyst was recycled via centrifugation, then washed and dried for the next cycle. From the figure it can be seen that the activity of the Ag/AgBr/GdVO₄ catalyst is not significantly reduced after five repetitions, indicating that the composite catalyst is rather stable. Taking into account the high activity and stability of the Ag/AgBr/GdVO₄ catalyst, it may have broad application prospects in the purification of water treatment.

The catalytic testing results show that AgBr and GdVO₄ had been successfully compounded into a new efficient photocatalyst. For this kind of composite photocatalyst, many successful precedents have been reported, such as AgBr/SmVO₄, AgI/SmVO₄, AgBr/Ag₃VO₄ and so on. The specific surface area of a photocatalyst is usually correlated to the photocatalytic activity. Therefore, BET analysis was performed to investigate the specific surface of the synthesized Ag/AgBr/GdVO₄ composite. Result indicates that pure GdVO₄ presents the largest specific surface area of 94 m²/g, while pure AgBr has the smallest value of 1.2 m²/g. The coupling of AgBr with GdVO₄ greatly decreases the BET surface area, and the BET value of Ag/AgBr/GdVO₄ decreases with the increase of AgBr content. For the samples of 30ABGd, 40ABGd, 50ABGd, 60ABGd and 70ABGd, the BET values are 34, 21, 23, 18, and 10 m²/g, respectively. The loading of Ag nanoparticles does not significantly affect the specific surface area of GdVO₄. The BET surface area of Ag/GdVO₄ is equal to 78 m²/g. Based on the results of BET analysis and photocatalytic test (Fig. 5), it can be concluded that the RhB adsorption of sample is not closely correlated with the BET surface area, which can be ascribed to the fact that the RhB adsorption process is affected by many factors, not just the surface area. Meanwhile, the inconsistency between the photocatalytic activity and the surface area is also observed. The sample with the largest BET surface area does not exhibit the best photocatalytic performance. Hence, the BET surface area is not the key factor influencing the photocatalytic process. The high catalytic activity of the Ag/AgBr/GdVO₄ composite should be ascribed to the enhanced separation efficiency of photo-induced charge.

Fig. 4 – UV–vis spectra of Ag/AgBr/GdVO₄ composite photocatalyst (a) and the band gaps of AgBr and GdVO₄.
carrier which relies on the energy band potential of the component semiconductors. This explanation is believed to be also suitable to the Ag/AgBr/GdVO₄ composite catalyst. According to reported literature, the potential of the conduction band bottom and the valence band top of AgBr is determined to be −1.05 and 1.33 V respectively. As for GdVO₄, the valence band top is at 2.06 V. Via the equation of \( E_g = E_{VB} - E_{CB} \), the conduction band bottom of GdVO₄ is estimated to be −0.15 V. Obviously, AgBr and GdVO₄ have proper band structure and band potentials, indicating that they are suitable to form a heterojunction structure which is beneficial for the separation of the photo-induced charge carriers. As shown in Fig. 7, under the irradiation of visible light, both AgBr and GdVO₄ are capable of generating photo-induced electrons and holes. Driven by the potential difference, the photo-induced electrons on the conduction band of AgBr could migrate onto the conduction band of GdVO₄, while the holes on the valence band of GdVO₄ could transfer to the valence band of AgBr. This directional migration of electrons and holes retards the recombination of the current carriers, thereby prolonging the life of the charge carriers and eventually leading to the high catalytic activity of the composite catalyst. Besides, the Ag nanoparticles generated by decomposition of AgBr under light are also helpful for the separation of the current carriers in the system. Based on reported literatures (Zhou et al., 2012; Li et al., 2013a, 2013b, 2013c, 2013d; Wang et al., 2011; Lin and Lee, 2010), these Ag nanoparticles can form a Schottky barrier with AgBr, which can function as electron trap to accept the electron on the conduction band of AgBr. It could both promote the separation of the electron–hole pair and also delay the reaction of Ag⁺ with the photo-induced electrons, thus improving the stability of the photocatalyst.

In order to confirm this mechanism, that is, the photocatalytic activity of the composite catalyst is enhanced due to the improvement in the separation efficiency of electron–hole pairs, the photocurrents of GdVO₄ and 40ABGd under visible light irradiation are investigated. Photocurrent technology is commonly used to reveal the interfacial migration electrons of composite photocatalyst. In general, the higher the
photocurrent intensity, the higher the current carrier separation efficiency is. As shown in Fig. 8, as the source of the visible light is turned on and off, the photocurrent in GdVO₄ and 40ABGd responds quickly. The intensity of the photocurrent of GdVO₄ is significantly weaker than that of 40ABGd, indicating that the prepared composite photocatalyst had stronger electron–hole separation efficiency, which is consistent with the mechanism proposed in Fig. 7.

Moreover, the active species of the AgBr/GdVO₄ catalyst in the process of photocatalytic reaction were also investigated. By adding different capture agents, the different effect of the corresponding active species in the reaction process can be observed. In general, the more obvious the reactivity declines, the more important the active species is in the photocatalytic process. Fig. 9 shows the photocatalytic activity of 40ABGd with the addition of different capture agents. Among these, isopropanol (IPA) is the capture agent of OH; ammonium oxalate (AO) the capture agent of h⁺ and parabenzoquinone (BQ) of O₂. It can be observed that the activity of the 40ABGd catalyst is almost unaffected by the addition of IPA and AO, which indicates that OH or h⁺ is not the active species of the reaction. After the addition of BQ, the activity of the catalyst decreases by a certain extent, suggesting that O₂ is the active species of the degradation of RhB. However, it should be noted that BQ does not completely inhibit the photocatalytic reaction, which indicates that there is another important active species in the reaction. Due to the accumulation of holes on the valence band of AgBr, the Br⁻ can be oxidized into Br². Hence, Br² may also be the active species in the degradation of RhB, which explains why h⁺ shows minor influence on the activity (Li et al., 2013a, 2013b, 2013c, 2013d; Cao et al., 2011a, 2011b; Lan et al., 2013).

3. Conclusions

A new Ag/AgBr/GdVO₄ composite photocatalyst was prepared by hydrothermal method. The synthesized composite exhibited excellent activity in photodegradation of RhB under visible light irradiation. The sample with the weight ratio of AgBr to GdVO₄ of 40% showed the best activity. Under visible light irradiation for 12 min, 80% of RhB (30 μmol/L) was degraded, which is about three times of AgBr. The high photocatalytic activity was ascribed to the formed heterojunction structure between AgBr and GdVO₄, which can retard the recombination of charge carriers so as to improve the separation efficiency of electrons and holes. Besides, the Ag nanoparticles generated via decomposition of AgBr under light were also helpful for improving the separation efficiency of the charge carriers in the composite system.

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