Facile synthesis of Ag$_3$VO$_4$/$\beta$-AgVO$_3$ nanowires with efficient visible-light photocatalytic activity

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Ag$_3$VO$_4$/β-AgVO$_3$ nanocomposites were successfully fabricated by chemical precipitation and hydrothermal method. The composites displayed excellent photocatalytic activity in comparison with those of pure β-AgVO$_3$ and Ag$_3$VO$_4$, which may be primarily ascribed to the matched energy structures. The sample with a molar ratio of 30% Ag$_3$VO$_4$ to β-AgVO$_3$ showed the highest photocatalytic activity for RhB degradation, which was almost 9 and 2.4 times higher than those of pure β-AgVO$_3$ and Ag$_3$VO$_4$, respectively. In addition, the trapping experiments also confirmed that holes and hydroxyl radicals are the active species for RhB degradation, and the possible mechanism for enhanced photocatalytic activity was proposed.

1 Introduction

Heterogeneous photocatalysis has gained widespread attention from researchers because it is one of the most green and effective methods to solve the energy shortage and environmental problems. Over the past several decades, more and more photocatalysts have been developed, including TiO$_2$, ZnO, TAO$_2$, and CuO. However, most of them had a high rate of charge carrier recombination and no response in the visible light range. It is very important to effectively utilize solar energy to overcome the above two limitations. Heterostructured photocatalysts, an effective media, have been developed to avoid the recombination of photoinduced electron–hole and increase the charge carrier separation efficiency because of the interface electric field. Hence, many different composites have been prepared and reported, such as Ag/AgX,$^{17}$ Ag/AgX/GO,$^{18}$ RGO/Bi$_{1.64}$M$_{3.63}$O$_{5.55}$, AgX/Ag$_3$PO$_4$,$^{21}$ InVO$_4$/BiVO$_4$ (ref. 22–26) and BiPO$_4$/Ag$_3$PO$_4$.($^{27}$

The monoclinic scheelite Ag$_3$VO$_4$ with a band energy of 2.3 eV has received much attention due to its good photocatalytic activity under visible light irradiation. Although the pure Ag$_3$VO$_4$ exhibits high photocatalytic performance, its photocatalytic activity is limited because of its low quantum yield and the poor absorption in the visible light region. Therefore, a suitable material coupled with Ag$_3$VO$_4$ is of great importance to solve its limited application in photocatalysis.

In this study, we reported novel Ag$_3$VO$_4$/β-AgVO$_3$ composites through a chemical precipitation approach. We chose one-dimensional β-AgVO$_3$ nanowires as the substrate materials because they have lots of advantages such as visible light responding and supporting materials. A facile chemical precipitation can efficiently suppress the aggregation of Ag$_3$VO$_4$ and boost the contact between Ag$_3$VO$_4$ and β-AgVO$_3$. The Ag$_3$VO$_4$/β-AgVO$_3$ hybrid materials were used for the photo-degradation of RhB under visible light and exhibited much higher photocatalytic activity than single Ag$_3$VO$_4$ and β-AgVO$_3$. Moreover, a possible photocatalytic mechanism and the stability of the Ag$_3$VO$_4$/β-AgVO$_3$ heterojunction were also investigated.

2 Experimental

2.1 Preparation of β-AgVO$_3$ nanowires

All reagents for synthesis and analysis were analytical grade and used without further purification. β-AgVO$_3$ nanowires were synthesized by the previously reported hydrothermal method. $^{39}$ 1 mmol NH$_4$VO$_3$ (Tianjin bo reagent co., LTD, Certified China) was dissolved in 60 mL deionized water (Harbin zhong
jia chemical reagent co., LTD, Certified China) with magnetic stirring for 5 min to obtain a transparent solution under room temperature. Then, 1 mmol AgNO₃ (Shanghai shi yi chemical reagent co., LTD, Certified China) was slowly added into the above solution and stirred for another 3 min. The pH value of the solution was adjusted to 8–8.2 by using NH₃·H₂O (25–28%) and then the mixture was homogeneously transferred into five 20 mL Teflon-lined stainless vessel and heated at 180 °C for 12 h. The β-AgVO₃ nanowires were collected by centrifugation, washed with deionized water three times, dried at 60 °C for 10 h.

2.2 Synthesis of Ag₃VO₄/β-AgVO₃ composites

Ag₃VO₄/β-AgVO₃ composites were prepared by a chemical precipitation method. 0.1034 g as-prepared β-AgVO₃ nanowires and 0.1010 g AgNO₃ (Shanghai shi yi chemical reagent co., LTD, Certified China) dispersed in 40 mL deionized water with magnetic stirring for 5 min. Subsequently, 20 mL of a certain amount of Na₃VO₄·12H₂O (Beijing chemical reagent co., LTD, Certified China) aqueous solution was dropped into the above solution and stirred for 3 h. The obtained yellow precipitate was washed with distilled water three times and dried in oven at 60 °C for 6 h. Ag₃VO₄/β-AgVO₃ composites with different molar ratios of Ag₃VO₄ were obtained: 5%, 10%, 20%, 30%, 40% and the samples prepared were denoted as 5% Ag₃VO₄/β-AgVO₃, 10% Ag₃VO₄/β-AgVO₃, 20% Ag₃VO₄/β-AgVO₃, 30% Ag₃VO₄/β-AgVO₃ and 40% Ag₃VO₄/β-AgVO₃, respectively.

2.3 Characterization of Ag₃VO₄/β-AgVO₃ composites

The crystalline structures of the samples were recorded on a Rigaku D/MAX-rA XRD (Japan) with Cu Kα radiation (λ = 0.15405 nm) in the range of 20–70° (2θ). The images of the micro-morphology were determined by scanning electron microscopy (SEM, Hitachi, SU8010) and Transmission electron microscopy (TEM, Tecnai, G2F30). The surface analysis was studied by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB250Xi) with a Mg Kα source. The binding energies were calibrated with the C 1s peak of surface adventitious carbon at 284.8 eV. The Ultraviolet-visible Diffuse Reflectance Spectra (UV-vis DRS) were obtained in the range of 255–800 nm using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO₄ was used as the reflectance standard material. The BET surface area was measured by N₂ adsorption using a surface analysis instrument (Beishide, 3H-2000PSI, China). The photoluminescence spectra (PL) of the catalysts were recorded using a FluoroMax-4 photoluminescence instrument (HORIBA JobinYvon) with a 350 nm excitation wavelength.

2.4 Evaluation of photocatalytic performance

The photocatalytic properties of the Ag₃VO₄/β-AgVO₃ composite samples were evaluated by the degradation of rhodamine B (RhB) dye under visible light irradiation. A 300 W Xe lamp was employed as visible light (λ > 400 nm) source and NaNO₂ solution was poured between the lamp and the photocatalyst to filter out UV light (λ < 400 nm). The vertical distance between the light source and the surface of the solution was about 12 cm. 0.0500 g photocatalyst was dispersed into the 70 mL of RhB (10 mg L⁻¹) in a quartz reactor. Prior to the light illumination, the suspension was stirred in the dark for 30 min to achieve the adsorption–desorption equilibrium on the surface of photocatalyst. At defined time (10 min), about 3 mL of the reaction solution was withdrawn and centrifuged (11 000 rpm, 1 min) to remove the photocatalyst particles. The residual amount of RhB in the solution was recorded by measuring its characteristic optical absorption at 554 nm using UV-vis spectrophotometer.

3 Results and discussion

The typical XRD patterns for the pure β-AgVO₃, Ag₃VO₄ and Ag₃VO₄/β-AgVO₃ composites are shown in Fig. 1. The pure β-AgVO₃ patterns match well with the JCPDS (29-1154) standard data, which suggests that the prepared β-AgVO₃ has a monoclinic structure. The diffraction peaks of Ag₃VO₄ can be indexed as the JCPDS (43-0542) standard data. It was clearly found that all the Ag₃VO₄/β-AgVO₃ composites exhibit a cooccurrence of both β-AgVO₃ and Ag₃VO₄ phases. Furthermore, with the Ag₃VO₄ amounts increasing, the diffraction peak intensity of Ag₃VO₄ becomes stronger gradually. Meanwhile, the diffraction peak positions of β-AgVO₃ do not shift, indicating that the introduction of Ag₃VO₄ does not influence the crystal structure of β-AgVO₃.

Fig. 2(a) shows the UV-vis diffuse reflectance spectra of pure β-AgVO₃, Ag₃VO₄ and Ag₃VO₄/β-AgVO₃ composite photocatalysts in order to investigate the optical absorption properties. As depicted from Fig. 2(a), β-AgVO₃ and Ag₃VO₄ display excellent optical absorption in visible light. Their absorption edges were approximately 640 nm and 615 nm respectively. From the formula: αhv = A(hν – E_g)ⁿ/², where α is the absorption coefficient, hν is the energy, A is a constant, and E_g is the band gap. The value of n depends on whether the transition is direct (n = 1) or indirect (n = 4) discrete photon in a semiconductor. As shown in Fig. 2(b), we can get the band gap E_g of pure β-AgVO₃ and Ag₃VO₄ to be 2.20 eV and 2.37 eV, respectively. Moreover, the potential of conduction band of Ag₃VO₄ and β-AgVO₃ was calculated to be 0.1 eV and 0.44 eV, respectively.
AgVO₃ could be calculated by the following Mulliken electronegativity theory:

$$E_{CB} = \chi - E^* - 0.5E_g$$

where $\chi$ is the absolute electronegativity of the semiconductor, $E^*$ is the energy of free electrons (4.5 eV), and $E_g$ is the band gap energy of semiconductor. The $\chi$ values of Ag₃VO₄ and $\beta$-AgVO₃ are 5.64 and 5.88, respectively. So the $E_{CB}$ values of Ag₃VO₄ and $\beta$-AgVO₃ were calculated to be −0.045 and 0.28 eV, respectively. Based on the equation $E_{VB} = E_{CB} + E_g$, the corresponding $E_{VB}$ values were also predicted to be 2.325 and 2.48 eV, respectively. The results indicate that the composite could successfully fabricate the matched energy structures between Ag₃VO₄ and $\beta$-AgVO₃.

The microstructures of pure $\beta$-AgVO₃, Ag₃VO₄ and Ag₃VO₄/$\beta$-AgVO₃ composite photocatalysts were measured by SEM. As shown in Fig. 3(a), pure $\beta$-AgVO₃ displays a number of nanowires with about 100 nm in width and more than 20 μm in length and its surface is very smooth. As depicted in Fig. 3(b)–(f), the composites of Ag₃VO₄/$\beta$-AgVO₃ do not influence the shape of $\beta$-AgVO₃ and the size of Ag₃VO₄ particles becomes larger with the Ag₃VO₄ content increasing, which is in agreement with the enhanced intensity of Ag₃VO₄ XRD patterns.

The morphology of 30% Ag₃VO₄/$\beta$-AgVO₃ composite is further illustrated by TEM and HRTEM. Fig. 4(a)–(c) show that some Ag₃VO₄ nanoparticles appeared on the smooth surface of $\beta$-AgVO₃ nanowires. HRTEM in Fig. 4(d) is the location of the circle in Fig. 4(c). By measuring the lattice fringes, the interplanar spacing is 0.317 nm and 0.243 nm, which are corresponding to the (−301) plane of $\beta$-AgVO₃ and the (202) plane of Ag₃VO₄.

XPS analysis was carried out to further clarify the surface chemical composition and bonding environment of 30%
Ag₃VO₄/β-AgVO₃ composite and the results are displayed in Fig. 5. The binding energy at 248.8 eV of C 1s is calibrated. The Fig. 5(a) and (b) demonstrates the predominant presence of silver and vanadium. The two peaks at 367.5 and 373.5 eV can be corresponding to the Ag 3d₅/₂ and Ag 3d₃/₂ of Ag⁺ both in Ag₃VO₄ and β-AgVO₃. The V 2p peaks of 30% Ag₃VO₄/β-AgVO₃ at 516.9 and 524.2 eV can be assigned to V 2p₃/₂ and V 2p₅/₂ of V⁵⁺ both in Ag₃VO₄ and β-AgVO₃.

The photocatalytic performance of pure β-AgVO₃, Ag₃VO₄ and Ag₃VO₄/AgVO₃ composites was evaluated by photocatalytic degradation of RhB under visible light illumination. Fig. 6 displays the experimental results. It can be seen that after 60 min of visible light irradiation the degradation efficiency of pure β-AgVO₃ and Ag₃VO₄ were 23% and 57% respectively. Obviously, all the composites have more effective photocatalytic performance than the pure samples, which can be attributed to the presence of Ag₃VO₄ on the surface of β-AgVO₃, accelerating the separation of photoinduced electrons and holes. The best photocatalytic performance comes from 30% Ag₃VO₄/β-AgVO₃ composite, which is 9 times and 2.4 times than pure β-AgVO₃ and Ag₃VO₄. However, with the content of Ag₃VO₄ enhanced to 40%, the decomposition efficiency of RhB declines, suggesting that the excessive Ag₃VO₄ particles deposited on the surface of β-AgVO₃ might intervene the photocatalytic activity sites.

Fig. 7 exhibits the obvious changes of RhB solution in UV-visible absorption spectra of 30% Ag₃VO₄/β-AgVO₃ composite at different times. It can be clearly observed that the absorbance maximum peak of RhB shifts from 554 nm to 504 nm, which is in good accordance with the previous reports of the degradation of RhB over TiO₂ (ref. 44) and Ag₂O/Ag₃VO₄/Ag₄V₂O₇.⁴⁴ The color of RhB solution changes from pink to almost colourless after 60 min illumination, which indicates the cleavage of conjugated chromophore structure of RhB.

As depicted from Fig. 8, the experimental results were fitted to pseudo-first-order and all Ag₃VO₄/β-AgVO₃ composites exhibit higher photocatalytic performance than single Ag₃VO₄ and β-AgVO₃ nanowires. The apparent rate constant k was shown in inset. It can be seen that the composite with mole ratios of 30% Ag₃VO₄/β-AgVO₃ shows the highest value of apparent rate constant k, which was 9 and 2.4 times higher than pure β-AgVO₃ and Ag₃VO₄. This indicates that the composite
with 30% molar ratio is the most suitable for β-AgVO₃ and Ag₃VO₄, which could boost the separation of charge carriers and enhance the photocatalytic performance.

Furthermore, as is shown in Fig. 9, 30% Ag₃VO₄/β-AgVO₃ composite has weak adsorption and desorption. The surface areas of β-AgVO₃ and 30% Ag₃VO₄/β-AgVO₃ composite were 3.096 and 4.610 m² g⁻¹, respectively. It was worthwhile to note that the surface area of 30% Ag₃VO₄/β-AgVO₃ composite becomes larger with the Ag₃VO₄ nanoparticles deposited on the β-AgVO₃ nanoribbons, which can provide more active sites and enhance photocatalytic activity.

The stability of photocatalysts is an important factor for the further application. As is shown in Fig. 10, the photocatalytic activity of the 30% Ag₃VO₄/β-AgVO₃ composite still reached 67%, even though it had been used 3 times.

Additionally, to further reveal the photocatalytic mechanism, the trapping experiments were performed, as shown in Fig. 11. Under visible illumination the photodegradation of RhB is slightly inhibited by adding the IPA (hydroxyl radical scavenger) and ammonium oxalate (hole scavenger), which indicates that hydroxyl radical and hole are the main species that can degenerate RhB.

In order to investigate the process of charge carriers trapping, migration and separation efficiency, the PL spectra of β-AgVO₃, Ag₃VO₄, and 30% Ag₃VO₄/β-AgVO₃ samples under the excitation wavelength of 350 nm, as shown in Fig. 12. It was generally acknowledged that the lower PL intensity indicates that the higher separation capacity of charge carriers, which results in higher photocatalytic activity. It was observed that the main emission peak of β-AgVO₃, Ag₃VO₄, and Ag₃VO₄/β-AgVO₃ composites all center at about 595 nm. Compared with pure β-AgVO₃ and Ag₃VO₄ samples, the lower PL peak intensity of 30% Ag₃VO₄/β-AgVO₃ composites implies that the interface between Ag₃VO₄ and β-AgVO₃ can migrates the photogenerate electrons and holes more effectively.
possible mechanism of migration of carriers in the Ag₃VO₄/AgVO₃ composite heterostructures was discussed. Both Ag₃VO₄ and AgVO₃ can be excited under visible light illumination according to the UV-vis diffuse reflectance spectra (eqn (1a) and (1b)). The electrons on the conduction band of Ag₃VO₄ can transfer into the conduction band of Ag₃VO₄ and the holes on the valence band of Ag₃VO₄ can transfer into the valence band of Ag₃VO₄, because the conduction band of Ag₃VO₄ is negative than β-AgVO₃ and the valence band of Ag₃VO₄ is positive than β-AgVO₃. So, photoinduced electrons and holes can separate effectively, which is crucial for enhancing photocatalytic activities.

In fact, the pathway of RhB degradation over Ag₃VO₄/β-AgVO₃ composite under visible light is rather complex. Based on the above experimental results and photocatalytic degradation reports, the possible reactions are summarized by eqn (1)–(4).

\[
\begin{align*}
\text{Ag}_3\text{VO}_4 + h\nu &\rightarrow \text{Ag}_3\text{VO}_4 (e_{\text{CB}}^- + h_{\text{VB}}^+) \quad (1a) \\
\beta\text{-AgVO}_3 + h\nu &\rightarrow \beta\text{-AgVO}_3 (e_{\text{CB}}^- + h_{\text{VB}}^+) \quad (1b) \\
\text{Ag}^+ (\text{in } \beta\text{-AgVO}_3) + e_{\text{CB}}^- &\rightarrow \text{Ag}^{0} \quad (2a) \\
\text{Ag} + h\nu &\rightarrow \text{Ag} (\text{SPR}) \quad (2b) \\
4h_{\text{VB}}^+ + 2\text{H}_2\text{O} &\rightarrow 4\text{H}^+ + \text{O}_2 \quad (3a) \\
4h_{\text{VB}}^+ + 2\text{OH}^- &\rightarrow 2\text{H}^+ + \text{O}_2 \quad (3b) \\
h_{\text{VB}}^+ + \text{H}_2\text{O} &\rightarrow \cdot\text{OH} + \cdot\text{H}^+ \quad (3c) \\
\text{RhB}_{\text{ads}} + h\nu &\rightarrow \text{RhB}_{\text{ads}}^* \quad (4a) \\
\text{RhB}_{\text{ads}}^* + e_{\text{CB}}^- &\rightarrow \text{RhB}_{\text{ads}} \quad (4b) \\
\text{RhB}_{\text{ads}}^* + \cdot\text{OH} &\rightarrow \text{N-ethyl rhodamine} \rightarrow \text{CO}_2 + \text{H}_2\text{O}^{**} \quad (4c)
\end{align*}
\]

Scheme 1 Photocatalytic mechanism of 30% Ag₃VO₄/β-AgVO₃ toward the degradation of RhB.

In summary, we have successfully synthesized Ag₃VO₄/β-AgVO₃ heterojunctions via chemical precipitation and hydrothermal method. They show much better photocatalytic activity than pure Ag₃VO₄ and β-AgVO₃ toward RhB degradation under visible light and the 30% Ag₃VO₄/β-AgVO₃ composite exhibits the highest. It is found that the photocatalytic activity increased with the Ag₃VO₄ amount increasing, which can be ascribed to the matched energy structure in the Ag₃VO₄/β-AgVO₃ heterojunction that can efficiently enhanced separation of photoinduced carriers. The holes and hydroxyl radicals play significant roles in the photocatalytic degradation of RhB under visible light.

4 Conclusions
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Notes and references