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Visible light-driven photocatalytic degradation of organic pollutants by a novel Ag₃VO₄/Ag₂CO₃ p–n heterojunction photocatalyst: Mechanistic insight and degradation pathways

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Abstract

In the field of photocatalysis, the construction of a heterojunction system with efficient charge separation at the interface and charge transfer to increase the photocatalyst performance has gained considerable attention. In this study, the Ag₃VO₄/Ag₂CO₃ p-n heterojunction is first synthesized using a simple co-precipitation method. The composite photocatalyst with a p-n heterojunction has a strong internal electric field, and its strong driving force can effectively solve the problem of low separation and migration efficiency of photogenerated electron-hole pairs. The optimized Ag₃VO₄/Ag₂CO₃ composite can effectively degrade organic pollutants (rhodamine b (RhB), methylene blue (MB), levofloxacin (LVF), and tetracycline). More specifically, the Ag₃VO₄/Ag₂CO₃ photocatalyst with a 1:2 mass ratio (VC-12) can remove 97.8% and 82% of RhB and LVF within 30 and 60 min, respectively. The LVF degradation rate by VC-12 under visible light irradiation is more than 12.8 and 21.51 times higher than those of pure Ag_3VO_4 and Ag_2CO_3 , respectively. The excellent photocatalytic activity of the Ag₃VO₄/Ag₂CO₃ hybrid system is mainly attributed to the internal electric field that forms in the Ag₃VO₄/Ag₂CO₃ p-n heterojunction system, the photogenerated electron hole pairs that separate and facilely migrate, and the specific surface area of VC-12 that is larger than that of the monomer. In addition, the degradation efficiency of VC-12 did not decline significantly after four cycles. In this study, the photocatalytic mechanism for Ag₃VO₄/Ag₂CO₃ photocatalysts is explored in detail based on the energy band analysis results, trapping experiment results, and electron spin resonance spectra.

Finally, the LVF degradation products are analyzed by liquid chromatography-mass spectrometry, and the potential LVF degradation pathway is identified. The experiments performed in this research therefore lead to new motivation for the design and synthesis of highly efficient and widely applicable photocatalysts for environmental purification.

Keywords: Photocatalysis; Ag₃VO₄/Ag₂CO₃; p-n heterojunction; Degradation pathway; Visible light.

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1. Introduction

The rapid development of the world economy and technology has inevitably caused severe environmental pollution [1-3]. For example, antibiotics and printing reagents, which are extensively used, have severely threatened the aquatic environment because of their weak biodegradability and strong toxicity to aquatic organisms and humans [4-7]. Accordingly, to treat organic contaminants in wastewater, various processing techniques, including adsorption [8], microwave catalysis [9], the electro-Fenton process [10], and photocatalysis [11], have been devised. Adsorption technology affords advantages, such as low energy consumption and excellent treatment effects; however, the complex process involved in its preparation hinders its further development [12]. As an advanced oxidation technology, microwave catalysis suffers from a high energy utilization rate [13]. In addition, the technique has insufficient catalytic performance [14]. The electro-Fenton process, as a type of environmental purification technology, exhibits an excellent treatment effect. Although it currently has certain practical applications, its prohibitive cost continues to restrict its widespread application [15]. To resolve the abovementioned problems, the development of low-cost and efficient water treatment technologies is deemed a feasible approach. In this regard, photocatalytic oxidation based on the direct utilization of solar energy for the complete mineralization of refractory organic contaminants in aquatic environments is considered a promising method because it is clean, nontoxic, energy saving, and highly efficient [16-19]. Among the minerals, titanium dioxide (TiO₂) has received considerable attention from

researchers because of its excellent stability and superior ultraviolet (UV) photocatalytic performance [20]. The wide band gap (E_g , ~3.2 eV) of TiO₂, however, makes it difficult to be driven by visible light, thereby hindering the practical use of TiO₂ in water purification [21, 22].

To improve the visible light utilization and carrier mobility of photocatalysts, the development of visible light-driven photocatalysts has become a new goal [23, 24]. Thus far, many new photocatalytic materials have emerged, including metal oxides [25, 26], metal sulfides [27-29], and carbon nitrides [30, 31]. The photocatalytic activity and visible light utilization of these materials have improved significantly over those of TiO₂. In recent years, Ag-based semiconductor materials have been considered predominant candidates for photodegrading organic pollutants because of their moderate band gap. For example, AgX (Cl, Br, and I) [32-34], Ag₃PO₄ [35], Ag₂CO₃ [36], Ag₃VO₄ [19], and Ag₂MoO₄ [37] have exhibited considerable effectiveness in the removal of organic compounds. Konta et al. first reported the use of silver vanadate (Ag₃VO₄) in the field of visible light-driven photocatalysis because of its narrow band gap (E_g , ~2.1 eV) [38]. Furthermore, the Ag 4d and O 2p orbitals of Ag₃VO₄ are hybridized to form a dispersed valence band (VB), and the conduction band (CB) formed by V 3d contributes to charge transfer [39-41]. Nevertheless, the low quantum efficiency and high recombination rate of the electron hole pair limit the generation of active species for the degradation of organics. To ameliorate the abovementioned deficiencies, many Ag₃VO₄-based composite photocatalytic materials have been produced (e.g., Ag₃VO₄/TiO₂ [42], g-C₃N₄/Ag₃VO₄ [43],

Ag₃VO₄/Bi₂O₂CO₃ [44], and Ag₃VO₄/WO₃ [45]). The heterojunction (type II) formed by Ag₃VO₄-based composites enables the spatial separation of photogenerated carriers and effectively suppresses charge recombination. Furthermore, matching different band structures can also expand the light response range.

As a typical n-type semiconductor, Ag_3VO_4 participates in a p-n heterojunction that has a stronger internal electric field than a type \Box heterojunction [46]. When a p-type semiconductor and an n-type Ag_3VO_4 are combined to form a p-n heterojunction, a built-in electric field with a strong charge-driven capacity can be formed. This is because of the large flat band potential difference between the two semiconductors, which is beneficial for the rapid separation and transfer of photogenerated carriers [47]. The construction of a Ag_3VO_4 -based p-n heterojunction is therefore an effective means to improve its photocatalytic ability.

As a typical p-type semiconductor, Ag_2CO_3 , which has a moderate band gap (E_g , ~2.3 eV), has been widely reported to exhibit excellent photocatalytic performance. In view of this, Ag_2CO_3 composites (e.g., Ag_2CO_3/TiO_2 [48] and Ag_2CO_3/g -C₃N₄ [49]) are presently undergoing extensive investigation. Certain research works related to Ag_2CO_3 -based p–n heterojunctions have also been reported. With the support of a strong internal electric field, the WO₃/Ag₂CO₃ p–n heterojunction has exhibited superior performance in terms of optical characteristics. The photocatalytic performance of the WO₃/Ag₂CO₃ composite has also significantly improved because of its excellent optical properties [50]. Based on the above research and matching band structure, the construction of the Ag₃VO₄/Ag₂CO₃ p–n heterojunction is

considered promising.

Herein, the Ag₃VO₄/Ag₂CO₃ p-n heterojunction is first synthesized using a simple co-precipitation method. The photocatalysts are characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM). transmission electron microscopy (TEM), X-ray diffraction (XRD), polarized light, and ultraviolet visible diffuse reflectance spectroscopy (UV-Vis DRS). The photocatalytic performance of the as-prepared samples is evaluated by degrading rhodamine b (RhB), methylene blue (MB), levofloxacin hydrochloride (LVF), and tetracycline (TC) under visible light (λ > 420 nm). The stability of Ag₃VO₄/Ag₂CO₃ composites is verified by four stability cycle experiments. Furthermore, the mechanism of Ag₃VO₄/Ag₂CO₃ composites is investigated through quenching experiments and electron spin resonance (ESR). Finally, the LVF reaction intermediate is analyzed by liquid chromatography-mass spectrometry (LC-MS), and the LVF degradation pathway is identified.

2. Experiment

2.1. Materials

Silver nitrate (AgNO₃, \geq 99.8%), sodium bicarbonate (NaHCO₃, \geq 99.5%), sodium sulfate (Na₂SO₄, \geq 99%) 1,4-benzoquinone (BQ, \geq 98%) and isopropanol (IPA, \geq 99.7%) were purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China). Sodium vanadate (Na₃VO₄, \geq 99%) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). All chemicals were analytically pure and did not require further purification. The ultrapure water required for the experiment with a resistivity

of 18.25 MQ·cm.

2.2. Synthesis of Ag₃VO₄/Ag₂CO₃ composites

A one-step coprecipitation method was employed to synthesize Ag_3VO_4/Ag_2CO_3 photocatalysts: 1.5902 g of AgNO₃ was dissolved in 20 mL of deionized water and stirred for 30 min to form solution A; 0.1839 g of Na₃VO₄ and 0.2672 g of NaHCO₃ were dissolved in 20 mL of deionized water and stirred for 30 min to form solution B. Solution B was thereafter gradually dropped into solution A to form a suspension that was rapidly stirred under dark conditions for 10 h. The precipitate was collected by centrifugation, washed several times with deionized water, and oven-dried at 60 °C for 12 h. Composite photocatalysts of Ag_3VO_4/Ag_2CO_3 with different mass ratios were produced by varying the Na₃VO₄–NaHCO₃ weight ratio. The samples were denoted as VC-11, VC-12, and VC-13 to indicate Ag_3VO_4 and Ag_2CO_3 weight ratios of 1:1, 1:2, and 1:3, respectively. Pristine Ag_3VO_4 and Ag_2CO_3 were also prepared using the same method without NaHCO₃ and Na₃VO₄ additions, respectively.

2.3. Characterization

The XRD pattern was obtained using an XRD-6100 advanced diffractometer based on a Cu-Kα beam (Shimadzu, Japan). The morphology of the photocatalytic material was observed using a FEI Nova NanoSEM 230 field emission scanning electron microscope (FEI, USA) and a Tecnai G2 F20/F30 transmission electron microscope (FEI, USA). The surface chemical composition obtained by Thermo ESCALAB 250XI and the electron binding energy of the material were characterized by XPS with Al-Kα radiation (Thermo USA). The UV-vis diffuse reflectance of the

sample (200–800 nm) was recorded using a Hitachi UH4150 spectrophotometer equipped with an integrating sphere. Photoluminescence data were obtained by means of a Hitachi-F2500 fluorescence spectrophotometer (Hitachi, Japan). The specific surface area and pore size distribution were recorded using a Gemini VII 2390 specific surface and pore size distribution analyzer (Micromeritics, USA). The Mott– Schottky curve and photocurrent results were characterized using CHI760E (Chenhua, China), in which a 0.5M Na₂SO₄ solution was used as the electrolyte. The working electrode was fluorine-doped tin oxide coated with photocatalytic material, and the reference and counter electrodes were platinum and saturated Ag/AgCl, respectively. The electron spin resonance (ESR) signal was measured using a JES FA200 electronic resonance spectrometer (JEOL, Japan) at room temperature under visible light ($\lambda >$ 420 nm). The total organic carbon (TOC) was tested by a TOC analyzer (Vario TOC; Elementar, Germany).

2.4. Photocatalytic degradation tests

The photocatalytic performance of Ag₃VO₄/Ag₂CO₃ composites at room temperature was determined by measuring the degradation of RhB in an aqueous solution under a 500 W xenon lamp (Changzhou Hongming Technology Co., Ltd., China) equipped with a UV cut-off wavelength filter ($\lambda \ge 420$ nm). Moreover, the illumination intensity on the reaction suspension surface was 90 ± 5 mW/cm². In the test, 50 mg of the photocatalyst was first uniformly dispersed in 100 mL of a 10 mg·L⁻¹ RhB solution and stirred for 1 h in the dark to achieve the adsorption– desorption dynamic equilibrium. Thereafter, during the illumination process, a certain

amount of water sample was extracted through a 0.45 μ m filter membrane at regular intervals. The RhB residual concentration in the obtained solution was recorded by a UV-Vis spectrophotometer (UV-4802S, UNICO Instruments Co., Ltd., China). Furthermore, the degradation performance of MB TC and LVF was investigated using a similar method with an initial concentration of 10 mg·L⁻¹.

3. Results and discussion

3.1. Characterization

The crystal structures of Ag₃VO₄, Ag₂CO₃, and Ag₃VO₄/Ag₂CO₃ composites were analyzed based on the XRD patterns. As shown in Fig. 1, all the XRD peaks of pure Ag₃VO₄ monomer sample fully correspond to the diffraction peak of Ag₃VO₄ monoclinic phase (JCPDS card no. 43-0542), whereas the other impurities have no XRD peaks, proving that the prepared Ag_3VO_4 has a pure monoclinic structure. Furthermore, the XRD diffraction peak of the Ag₂CO₃ monomer sample is consistent with the monoclinic phase of Ag_2CO_3 in the JCPDS card (JCPDS card no. 26-0339). After combining Ag₃VO₄ and Ag₂CO₃, the diffraction peaks of VC-12 samples simultaneously exhibited Ag₃VO₄ and Ag₂CO₃ diffraction peaks, confirming the existence of both Ag₃VO₄ and Ag₂CO₃. Moreover, no characteristic peaks of other impurities were detected, indicating that the synthesized composite is a high purity phase. The crystal size of Ag₃VO₄, Ag₂CO₃, and Ag₃VO₄/Ag₂CO₃ complexes was calculated by Scherrer's equation, $D = K\lambda/\beta\cos\theta$, where D is the crystal size (nm), K is Scherrer's constant (usually set to 0.89), θ is the Bragg diffraction angle (°), and β is the half peak width (rad) of the diffraction angle. According to the main diffraction

peaks, the average crystallite sizes of VC-11, VC-12, and VC-13 of Ag_3VO_4 and Ag_3VO_4 were 7.75, 3.35, 4.59, and 5.41 nm, respectively. The average crystallite sizes of VC-11, VC-12, and VC-13 of Ag_2CO_3 and Ag_2CO_3 were 6.34, 4.87, 5.14, and 6.27 nm, respectively. This indicates that the crystal size of Ag_3VO_4/Ag_2CO_3 composites decreased after Ag_3VO_4 and Ag_2CO_3 were combined.

XPS was used to further explore the surface element compositions of the Ag₃VO₄, Ag₂CO₃, and VC-12 samples. The full survey spectra (Fig. 2(a)) indicate that the composite consists of Ag, V, C, and O. The high resolution XPS spectra of Ag 3d, V 2p, C 1s, and O ls were further analyzed. As shown in Fig. 2(b), the Ag 3d high resolution spectra show characteristic binding energy values of 368.2 and 374.2 eV, which are related to the binding energies of Ag 3d 5/2 and Ag 3d 3/2 [51, 52], respectively. The peaks appearing at 516.7 and 523.7 eV in the high resolution XPS spectra of V (Fig. 2(c)) correspond to V 2p 3/2 and V 2p 1/2, respectively; these are consistent with the characteristic peaks of V⁵⁺ [19]. The C 1s XPS peak of the Ag₂CO₃ monomer and VC-12 composite photocatalyst can be further divided into three peaks, as shown in Fig. 2(e). The binding energies at 284.8 and 286.2 eV for Ag₂CO₃ as well as those at 284.6 and 286.5 eV for VC-12 were attributed to adventitious carbon, whereas those at 288.6 and 288.9 eV were attributed to carbon in CO_3^{2-} [53-55]. More significantly, the binding energies of Ag, V, and C of VC-12 changed slightly (< 0.4 eV) compared to those of Ag_3VO_4 and Ag_2CO_3 . These differences were caused by the interface coupling interaction of VC-12 composite that affects the electron energy distribution of Ag₃VO₄ and Ag₂CO₃ [56]. Fig. 2(d)

illustrates that the oxygen of VC-12 composite is composed of four forms. The peaks at 529.7 and 531.0 eV correspond to the oxygen in the Ag_3VO_4 and Ag_2CO_3 lattices, respectively. The peaks at 531.2 and 532.6 eV were attributed to the water molecule and adsorbed oxygen on the sample surface, respectively [57-59]. The XPS analysis thus further proves the coexistence of Ag_3VO_4 and Ag_2CO_3 .

The morphologies of Ag₃VO₄, Ag₂CO₃, and VC-12 were characterized by SEM and TEM. Fig. 3(a) shows that the prepared Ag₃VO₄ consists of nanoparticles with an average particle diameter of 0.5–3 μ m. Fig. 3(b) shows that pure Ag₂CO₃ is mainly rod-shaped with an average size of $1 \times 3 \mu m$. For the VC-12 samples, it is evident that Ag₃VO₄ nanoparticles and rod-shaped Ag₂CO₃ particles closely adhere to each other (Fig. 3(c)); Ag₂CO₃ nanorods are indicated by red circles. Fig. 3(d) illustrates the element mapping of the VC-12 composite photocatalyst, indicating that VC-12 contains four elements: silver, vanadium, carbon, and oxygen. Moreover, in the rod-like region of the sample, the vanadium content is significantly lower and the carbon content is higher than those in the peripheral region. These results are further confirmed by the TEM images. It is evident that Ag₃VO₄ consists of nanoparticles (Fig. 4(a)) and that Ag_2CO_3 has a cubic rod-like morphology (Fig. 4(b)). Fig. 4(c) clearly reveals that Ag₃VO₄ nanoparticles are tightly bound to rod-shaped Ag₂CO₃ particles. Fig. 4(d) shows the high resolution TEM image of VC-12. The (220) and (031) crystal planes of Ag₃VO₄ and Ag₂CO₃ are 0.207 and 0.264 nm, respectively. Consistent with the XRD results, the distance between the two lattices also proves the coexistence of Ag₃VO₄ and Ag₂CO₃. These results therefore consistently demonstrate

that the Ag_3VO_4/Ag_2CO_3 composite was successfully synthesized through one step precipitation.

To determine the specific surface area and pore size distribution of the prepared samples, the nitrogen adsorption-desorption isotherm was measured. As shown in Fig. 5, Ag₃VO₄, Ag₂CO₃, and VC-12 display the characteristics of a type \Box isotherm with an H3 hysteresis loop, consistent with a mesoporous structure [60, 61]. The calculated specific surface area and pore size obtained by the Brunauer-Emmet-Teller model and Barrett-Joyner-Halenda method are summarized in Table 1. It was found that the specific surface area of VC-12 composite sample is $3.28 \text{ m}^2 \cdot \text{g}^{-1}$, which is significantly larger than those of Ag₃VO₄ (0.68 m²·g⁻¹) and Ag₂CO₃ (0.38 m²·g⁻¹). The increase in the specific surface area can be attributed to the decrease in particle size and the increase in Ag₃VO₄ dispersion during the co-precipitation process. Further, the average pore diameters of Ag₃VO₄, Ag₂CO₃, and VC-12 are 4.60, 19.99, and 11.22 nm, respectively. It is well known that a large specific surface area can provide more reactive sites on the surface exposed to organic molecules [62]. The larger specific surface area of VC-12 therefore contributes to the improvement of its photocatalytic activity.

Light absorption capacity is an important indicator of photocatalyst performance. As shown in Fig. 6(a), the optical absorption properties of Ag_3VO_4 , Ag_2CO_3 , and VC-12 were characterized by UV-vis DRS. The absorption edge of single phase Ag_3VO_4 was observed at 540 nm, and that of Ag_2CO_3 was observed at 430 nm. Based on comparison, it was found that the light absorption intensity of VC-12 heterojunction over the entire visible light region increased because of the formation of p–n heterojunction [46]. This allows the compound to absorb more solar energy, thereby improving the photocatalytic activity. Generally, the band gap (E_g) of a semiconductor photocatalyst can be calculated according to the following Kubelk– Munk formula:

$$\alpha h v = A(h v - E_a)^{n/2} \tag{1}$$

where α , h, v, E_g, and A are the absorption coefficient, Planck constant, light frequency, band gap, and constant, respectively. The value of n is determined by the optical transition form of the photocatalytic semiconductor (n = 1 for the direct transition semiconductor; n = 4 for the indirect transition semiconductor). Typical direct and indirect bandgap semiconductors are Ag₃VO₄ and Ag₂CO₃, respectively [63, 64]. The n values of Ag₃VO₄ and Ag₂CO₃ are 1 and 4, respectively. The semiconductor band gap can be obtained by plotting the linear portions of (α hv)² or (α hv)^{1/2} and hv. As shown in Fig. 6(b), the band gaps of Ag₃VO₄ and Ag₂CO₃ are 2.05 and 2.32 eV, respectively.

To measure the migration and recombination rates of photogenerated electron-hole pairs, photoluminescence (PL) spectroscopy was employed. It is generally assumed that a weak PL intensity represents a low carrier recombination rate [65]. Fig. 7 shows the PL spectra of Ag_3VO_4 , Ag_2CO_3 , VC-11, VC-12, and VC-13 at an excitation wavelength of 420 nm. The pure-phase Ag_2CO_3 and Ag_3VO_4 have high PL intensities, indicating that photogenerated carriers easily recombine and release intense fluorescence. The PL strength of VC-1X (X=1, 2, 3) composites,

however, is considerably reduced, proving that the p–n heterojunction contributes to the swift separation and migration of electron-hole pairs of composite materials.

To further investigate the behavior of photogenerated carriers of prepared materials, the transient photocurrent intensities of Ag₃VO₄, Ag₂CO₃, and VC-12 were recorded under visible light ($\lambda \ge 420$ nm) irradiation in a 0.5 M Na2SO4 electrolyte solution. As shown in Fig. 8(a), the Ag₃VO₄ and Ag₂CO₃ monomers exhibited low photocurrent strengths because of higher carrier recombination rates. In contrast, the VC-12 sample exhibited a strong photocurrent intensity, indicating that the p-n heterojunction can effectively promote the migration of photoexcited electron-hole pairs. The electrochemical impedance of the three samples is shown in Fig. 8(b). The radius of the Nyquist curve of VC-12 is significantly smaller than those of Ag₃VO₄ and Ag₂CO₃. Moreover, the equivalent circuit diagram corresponding to the Nyquist diagram is composed of three parts: solution resistance (R1), charge transfer resistance (R2), and double layer capacitor (CPE1). It should be noted that the solution resistance (R1) is 17.43–18.96 Ω ; the resistance values of Ag₂CO₃ (R2), Ag₃VO₄ (R2), and VC-12 (R2) are 2494, 758.6, and 448.3 Ω , respectively. These results indicate that the formation of a p-n heterojunction between Ag₃VO₄ and Ag₂CO₃ can aid in the separation and migration of photogenerated electron-hole pairs. The VC-12 sample therefore has a smaller charge transfer resistance, indicating a stronger charge transport performance [66].

The Mott–Schottky test was employed to characterize the semiconductor type and flat band potential (E_{fb}) of the prepared material. As shown in Fig. 8(c and d),

Ag₃VO₄ and Ag₂CO₃ were evaluated as n-type and p-type semiconductors based on the slope of the tangent to the Mott-Schottky curve, respectively. The p-n heterojunction formation was verified by measuring the Mott-Schottky curve of the Ag₃VO₄/Ag₂CO₃ sample. As shown in Fig. 8(e), the characteristic feature of the p-n heterojunction was explicitly observed from the Mott-Schottky curve of the VC-12 composite in which an inverted 'V-shaped' curve was observed [67]. This indicates that two different electronic actions (n-type and p-type) are exhibited by the electrode. The E_{fb} values of Ag_3VO_4 and Ag_2CO_3 are measured to be -0.16 and 1.59 eV (vs. Ag/AgCl) from the Mott-Schottky curve, respectively. Moreover, the E_{fb} (vs. Ag/AgCl) of Ag₃VO₄ and Ag₂CO₃ can be converted to E_{fb} (vs. NHE) by the formula E_{fb} (vs. NHE) = E_{fb} (vs. Ag/AgCl) + 0.197 [68]. The E_{fb} (vs. NHE) values of Ag₃VO₄ and Ag₂CO₃ are 0.037 and 1.787 eV, respectively. Generally, the conduction band (CB) of the n-type semiconductor is 0.1 eV lower than E_{fb} , and the valence band (VB) of the p-type semiconductor is 0.1 eV higher than E_{fb} [69]. The CB and VB of Ag₃VO₄ and Ag₂CO₃ were 0.063 and 1.887 eV, respectively. The band gaps of Ag₃VO₄ and Ag₂CO₃ were 2.05 and 2.32 eV, respectively. The corresponding VB and CB were obtained by [70]

$$E_{VB} = E_{CB} + E_q \tag{2}$$

where E_g is the band gap, E_{VB} is the valence band edge potential, and E_{CB} is the conduction band edge potential. The VB and CB of Ag_3VO_4 and Ag_2CO_3 were calculated to be 1.987 and -0.433 eV, respectively.

3.2 Photocatalytic activity and stability analysis

The photocatalytic oxidation performance of the Ag₃VO₄/Ag₂CO₃ composites was investigated by degrading two types of pollutants, specifically dyes (RhB and methylene MB) and antibiotics (levofloxacin hydrochloride (LVF) and tetracycline (TC)), under visible light (λ > 420 nm). As shown in Fig. 9(a), when the reaction system reaches the adsorption-desorption equilibrium after a 1-h dark reaction, the RhB degradation efficiency is represented by C/C_0 , where C corresponds to the RhB concentration at time t and C₀ corresponds to the concentration of RhB at the adsorption-desorption equilibrium. The adsorption and desorption equilibrium diagrams are shown in Fig. S1. The RhB removal rates by pure Ag₃VO₄ and Ag₂CO₃ were 76.8% and 71.7% within 30 min, respectively. Compared with the monomer materials, the Ag₃VO₄/Ag₂CO₃ composites with mass ratios of 1:1, 1:2, and 1:3 (VC-11, VC-12, and VC-13, respectively) had significantly improved RhB degradation rates within 30 min. It is clear that as the Ag₂CO₃ proportion increased, the degradation efficiency first increased and thereafter decreased. Initially, as the proportion of Ag₂CO₃ increased, the contact between the two photocatalysts became more sufficient, and the charge transport distance was quite short [71]. Therefore, the photocatalytic effect of Ag₃VO₄/Ag₂CO₃ composites improved. With the overloading of Ag₂CO₃, the heterojunction structure was partially destroyed, resulting in a decrease in the photocatalytic effect [72]. Among the composites, VC-11 and VC-13 exhibited RhB removal rates of 94.6% and 92.3%, respectively; VC-12 had the highest RhB degradation rate (97.8%) after 30 min of visible light irradiation. Fig. 9(b) shows the degradation rate of LVF on the photocatalytic material with different components. It is clearly observed that 39.1% and 8.2% of LVF were degraded within 60 min in the presence of pristine Ag₃VO₄ and Ag₂CO₃, respectively. The degradation effect of composites with different proportions on the LVF, however, is consistent with their effect on RhB. Substantial photocatalytic activity in LVF degradation was exhibited by VC-11, VC-12, and VC-13; within 60 min, LVF was naturally degraded by 77.1%, 82%, and 78.9%, respectively.

It is well known that the degradation of RhB and LVF follows the Langmuir– Hinshelwood first-order kinetic model [66, 73]. The simulated first-order kinetic formula is $\ln(C_0/C) = kt$, where C_0 represents the RhB and LVF concentrations at the adsorption–desorption equilibrium, C represents the RhB and LVF concentrations at time t, k is the reaction rate constant, and t is time. As shown in Fig. 9(d and f), the first-order kinetic fit curves of $\ln(C_0/C)$ vs. time are plotted to show that the reaction rate constants (k) of Ag₃VO₄ and Ag₂CO₃ monomers are (0.0482 and 0.0085 min⁻¹) and (0.0359 and 0.0015 min⁻¹), respectively. It should be noted that the heterojunction formed between Ag₃VO₄ and Ag₂CO₃ promotes the effective separation and migration of photogenerated electron-hole pairs. The reaction rate constants (k) of VC-12 sample to RhB and LVF are 0.1398 and 0.0264 min⁻¹, which are 2.9 and 12.8 times that of pure Ag₃VO₄ and 3.9 and 21.5 times that of Ag₂CO₃ monomers, respectively.

To investigate the universality of VC-12 for the degradation of organic pollutants, two other pollutants (i.e., MB and TC) were selected as test objects in this experiment.

Fig. 9(h) shows that under visible light irradiation ($\lambda > 420$ nm), the degradation rates of MB and TC by VC-12 composites were 99.2%, 81.9%, and 75.1%. These are considerably higher than the degradation efficiencies of Ag₃VO₄ and Ag₂CO₃ monomers. These results indicate that the Ag₃VO₄/Ag₂CO₃ composite photocatalyst has excellent versatility in degrading organic pollutants.

From a practical perspective, photocatalytic materials with good stability are essential. Accordingly, cyclic degradation studies on RhB and LVF were performed by collecting the samples after the photocatalytic degradation reaction. As shown in Fig. 10(a), the RhB and LVF degradation rates within 30 and 60 min were 90.3% and 72.8% after four cycles, respectively. This indicates that there is no significant photocatalytic activity attenuation in used samples after four cycles compared to fresh samples. Compared with those of the VC-12 composites, the photocorrosion effects of Ag_3VO_4 and Ag_2CO_3 were extremely evident. As shown in Fig. S2(a), the removal rates of RhB and LFV by Ag₃VO₄ after four cycles decreased to 12.1 and 6.3%, respectively. Fig. S2(b) illustrates that the removal rates of RhB and LFV by Ag₂CO₃ decreased to 4.8 and 1.9%, respectively. This shows that the stability of VC-12 composites was considerably improved compared to that of the monomers. Moreover, the XRD patterns of the composites before and after the cycle were analyzed to further evaluate the stability of materials. In Fig. 10(b), the XRD pattern of the composite material shows a diffraction peak corresponding to the (111) plane of metallic silver at 38.1° after four cycles. This indicates that the Ag₃VO₄/Ag₂CO₃ composite material exhibits a certain stability after repeated use. Furthermore, Fig.

10(c) depicts the high resolution XPS spectra of Ag 3d for used and fresh VC-12 composites. The peaks at 374.4 and 368.4 eV can be ascribed to Ag^+ , and the emergence of two peaks at 374.9 and 369 eV are assigned to Ag^0 [74, 75]. The foregoing results are highly consistent with the XRD analysis. It was observed that although the Ag₃VO₄/Ag₂CO₃ material has a weak photocorrosion, it continues to exhibit good photocatalytic performance and stability after repeated use. This can be attributed to the surface plasmon resonance caused by the generation of elemental silver [76].

3.3 Photocatalytic mechanism analysis

Reactive substances (e.g., $\cdot O_2^-$, $\cdot OH$, and h^+) are generally considered to be key factors in the photocatalytic degradation of organic pollutants. In this study, 1,4-benzoquinone(BQ), triethanolamine (TEOA), and isopropanol (IPA) were used as capture agents for $\cdot O_2^-$, h^+ , and $\cdot OH$, respectively [77-79]. The main active species in the degradation of RhB and LVF by VC-12 composites were analyzed. As shown in Fig. 11(a), when TEOA was included in the photocatalytic degradation experiments of RhB and LVF, the degradation rate considerably decreased. This indicates that the direct oxidation of holes is an important step in the degradation process of dyes and antibiotics via the as-prepared photocatalytic materials. Furthermore, the addition of BQ has a relatively considerable effect on the degradation rates of RhB and LVF, indicating that $\cdot O_2^-$ is also the main oxidizing substance in the degradation process. The addition of IPA to the reaction system, however, weakly inhibited the degradation of RhB and LVF. In the degradation process by the VC-12 composite photocatalyst, h^+ and $\cdot O_2^-$ were the main active substances, and $\cdot OH$ only performed a certain subordinate function.

To further ensure that active substances ($\cdot O_2^-$ and $\cdot OH$) were produced during the aforementioned degradation process, $\cdot O_2^-$ and $\cdot OH$ capture experiments were performed with the ESR spin capture technique under visible light irradiation. Fig. 11(b) shows the four signal peaks of VC-12 DMPO $-\cdot O_2^-$ adduct in methanol; no signal peaks were produced in the dark. The signal peak intensity, however, increased during a (5–10) min period under illuminated conditions. It was confirmed that $\cdot O_2^-$ free radicals were generated in VC-12 under illumination. As shown in Fig. 11(c), no signal characteristic peak of DMPO $-\cdot OH$ was detected under dark conditions. As the illumination time was extended to 10 min, the signal peak gradually increased, suggesting the appearance of $\cdot OH$ in the reaction system.

Based on the experimental results above, the reaction mechanism of VC-12 was determined through analysis, as shown in Scheme 1. When n-type Ag_3VO_4 and p-type Ag_2CO_3 come into contact, a p–n heterojunction is formed. The Fermi level difference of the two semiconductors is large; hence, the electrons of n-type Ag_3VO_4 in the p–n interface region tend to diffuse to the interface of p-type Ag_2CO_3 [80]. The foregoing factors lead to band bending; the Fermi level also reaches equilibrium, and a built-in electric field at the p–n interface is formed [81]. Under visible light irradiation, the electrons in the valence bands of Ag_3VO_4 and Ag_2CO_3 transit to the conduction band, resulting in electron-hole pairs. Depending on the effect of the internal electric field, the electrons on the conduction band of Ag_2CO_3 transfer to that of Ag_3VO_4 . Moreover,

they react with dissolved oxygen in the aqueous solution to form $\cdot O_2^-$, which directly oxidizes organic contaminants or reacts with H⁺ adsorbed on the surface of VC-12 to form \cdot OH. The holes in the VB of Ag₃VO₄ and Ag₂CO₃ can also be involved in the degradation process of organic pollutants. The mechanism for the degradation of organic pollutants by VC-12 photocatalyst is thus described as follows.

$$Ag_{3}VO_{4} + h\nu \rightarrow Ag_{3}VO_{4}(h^{+}/e^{-})$$
 (3)

$$Ag_{2}CO_{3} + h\nu \rightarrow Ag_{2}CO_{3}(h^{+}/e^{-})$$

$$e^{-}(Ag_{2}CO_{3}) \rightarrow e^{-}(Ag_{3}VO_{4})$$

$$h^{+}(Ag_{3}VO_{4}) \rightarrow h^{+}(Ag_{2}CO_{3})$$

$$e^{-}(Ag_{3}VO_{4}) + O_{2} \rightarrow O_{2}^{-}$$

$$(4)$$

$$(5)$$

$$(6)$$

$$(7)$$

$$\cdot O_2^-(Ag_3VO_4) - + H^+ \to \cdot OH \tag{8}$$

 $h^+(Ag_2 CO_3) + OH/O_2^-(Ag_3 VO_4) + pollutants \rightarrow degraded products$ (9)

3.4 Possible degradation path of LVF

Numerous researches on the degradation pathway of RhB have been reported; accordingly, these are not be discussed here [82-84]. The degradation of LVF was therefore chosen to illustrate the photocatalytic process of VC-12. To further analyze the possible degradation pathway of LVF, LC–MS detection was employed to identify the intermediate structure that may exist in the degradation process of LVF by VC-12; the specific MS spectrum is shown in Fig. S3. As shown in Fig. S3(a), the $[M + H]^+$ ion peak shown at m/z = 362.15 was attributed to LVF molecules, indicating that the molecular structure of the LVF is not destroyed in the absence of illumination. The degradation of LVF mainly includes demethylation, decarboxylation, defluorination,

and piperazine ring and quinoline ring destruction. The first possible pathway is the replacement of F by OH groups because the attack of hydroxyl radicals forms P1 [85]. Thereafter, the carboxyl group is completely oxidized, and the piperazine ring undergoes oxidative ring-opening to form P4. The superoxide radical attacks the N atom in the piperazinyl part to form P7 on successive attacks. Another possible pathway is that the piperazine ring is demethylated by the attack of non-selective hydroxyl and superoxide radicals to form P2 and P3, thereby leading to the generation of P5 and P6, respectively [86]. Subsequently, P5 and P6 piperazine rings are removed, and the quinoline ring is decarboxylated to form P8 and P9 [87]; P10 is formed by oxidizing the OH groups and F atoms of P7, P8, and P9. The quinoline ring and morpholine ring of P10 are further oxidized and finally completely mineralized. The possible LVF degradation path is shown in Fig. 12.

4. Conclusions

In summary, Ag_3VO_4/Ag_2CO_3 p–n heterojunctions were prepared using a simple co-precipitation method. Among the as-prepared composites, the Ag_3VO_4/Ag_2CO_3 composite with a ratio of 1:2 exhibited the best degradation performance and excellent stability. The synthesized VC-12 p–n heterojunction system exhibited excellent degradation efficiency and remarkable mineralization ability (λ >420 nm). These exceptional photocatalytic properties were attributed to the following synergistic effects: (a) The formation of p–n heterojunctions effectively promoted the separation and migration efficiency of photoexcited electron-hole pairs. (b) Compared with the monomer, the larger specific surface area of the composite photocatalysts provided a larger reaction area. Moreover, a possible LVF degradation pathway was proposed by analyzing the degradation intermediates. This explains the improvement of TOC removal with the oxidation of piperazine ring and quinoline ring. The composites of Ag_3VO_4/Ag_2CO_3 therefore have excellent application prospects in the field of environmental functional materials.

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Table.1. BET Specific surface area, pore volume and pore size of Ag₃VO₄, Ag₂CO₃

and	VC-	12
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Photocatalyst	$S_{BET} (m^2 g^{-1})$	Pore diameter (nm)	Pore volume (cm ³ g ⁻¹)
Ag ₃ VO ₄	0.6841	4.6022	0.000308
Ag ₂ CO ₃	0.3751	19.9410	0.000355
VC-12	3.2773	11.2244	0.501917



Fig.1. XRD patterns of the prepared Ag₃VO₄, Ag₂CO₃, VC-11, VC-12 and VC-13

materials.

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Fig.2. XPS survey spectrum (a) of Ag_3VO_4 , Ag_2CO_3 and VC-12 and high-resolution XPS spectra; (b) Ag 3d of Ag_3VO_4 , Ag_2CO_3 and VC-12; (c) V 2p of Ag_3VO_4 and VC-12; (d) O1s of Ag_3VO_4 , Ag_2CO_3 and VC-12; (e) C 1s of Ag_2CO_3 and VC-12



Fig.3. SEM images of samples Ag_3VO_4 (a), Ag_2CO_3 (b), VC-12 (c). Corresponding elemental maps of VC-12 (d).

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Fig.4. (a-c) TEM images of Ag_2CO_3 , Ag_3VO_4 and VC-12, respectively; (d) HRTEM image of VC-12.



Fig.5. Isothermal adsorption-desorption curves of Nitrogen (a), (b) Barrett–Joyner– Halenda pore size distribution of Ag₃VO₄, Ag₂CO₃ and VC-12

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Fig.6. (a) UV-visible diffuse reflectance absorption spectra of Ag_3VO_4 , Ag_2CO_3 and VC-12, (b) Plots of $(\alpha hv)^2$ or $(\alpha hv)^{1/2}$ vs hv of Ag_3VO_4 and Ag_2CO_3 monomers.

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Fig.7. Photoluminescence (PL) spectra of Ag₃VO₄, Ag₂CO₃, VC-11, VC-12 and

VC-13.

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Fig.8. (a) The transient photocurrent intensities of Ag_3VO_4 , Ag_2CO_3 and VC-12; (b) EIS Nyquist plots of pure Ag_3VO_4 , Ag_2CO_3 and VC-12 under visible light irradiation; Mott-Schottky (MS) plots of pure Ag_3VO_4 (c), Ag_2CO_3 (d) and VC-12 (e).



Fig.9. (a) The photocatalytic performance of Ag₃VO₄, Ag₂CO₃, VC-11, VC-12 and VC-13 for RhB degradation under visible light (λ > 420 nm); (b)The photocatalytic performance of Ag₃VO₄, Ag₂CO₃, VC-11, VC-12 and VC-13 for LVF degradation under visible light (λ > 420 nm); (c) TOC removal performance; the pseudo-first-order

reaction kinetics for (d) RhB and (e) LVF degradation; apparent degradation rate constants for (f) RhB and (g) LVF degradation; (h) the photocatalytic performance of VC-12 for MB and TC degradation under visible light irradiation .



Fig.10. (a) Degradation rate of VC-12 for four consecutive cycles of LFV and RhB;(b) XRD pattern of VC-12 before and after the cycle; (c) Ag 3d high-resolution XPS spectra of VC-12 before and after the cycle



Fig.11. (a) Trapping experiment of the active species for the degradation of RhB and LFV by VC-12 under visible light irradiation ($\lambda > 420$ nm); DMPO spin-trapping ESR spectra with the VC-12 sample in methanol dispersion (b) and in aqueous dispersion (c) under visible light irradiation.



Scheme 1. Possible photocatalytic organic pollutants degradation mechanism under visible light irradiation over VC-12 p-n junction composites.

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Fig.12. Possible degradation pathway of levofloxacin over VC-12 under visible light $(\lambda > 420 \text{ nm}).$

Highlights

- Ag₃VO₄/Ag₂CO₃ p-n heterojunction was prepared by a one-step co-precipitation method.
- Photocatalytic activity and stability of VC-12 was significantly enhanced.
- The detailed LVF photocatalytic degradation intermediate pathway is proposed.
- •The internal electric field of the composite facilitates the separation of carriers.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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