WO3/Ag2CO3 Mixed Photocatalyst with Enhanced Photocatalytic Activity for Organic Dye Degradation

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ABSTRACT: The development of an efficient photocatalyst with superior activity under visible light has been regarded as a significant step for pollutant degradation and environmental remediation. Herein, a series of WO3/Ag2CO3 mixed photocatalysts with different proportions were prepared by a simple mixing method and characterized by XRD, SEM, TEM, XPS, and DRS techniques. The photocatalytic performance of the WO3/Ag2CO3 mixed photocatalyst was investigated by the degradation of rhodamine B (RhB). The degradation percentage of RhB by WO3/Ag2CO3 photocatalyst was rapidly increased with the proportion of Ag2CO3 up to 5%. The degradation percentage of RhB by WO3/Ag2CO3−5% reached 99.7% within 8 min. The pseudo-first-order reaction rate constant of WO3/Ag2CO3−5% (0.9591 min−1) was 118- and 14-fold higher than those of WO3 (0.0081 min−1) and Ag2CO3 (0.0663 min−1). The catalytic activities of the mixed photocatalysts are not only higher than those of the WO3 and Ag2CO3 but also higher than that of the WO3/Ag2CO3 composite prepared by the precipitation method. The activity enhancement may be because of the easier separation of photogenerated electron−hole pairs. The photocatalytic mechanism was investigated by free radical capture performance and fluorescence measurement. It was found that light-induced holes (h+) was the major active species and superoxide radicals (·O2−) also played a certain role in photocatalytic degradation of RhB.

1. INTRODUCTION

With rapid industrialization and urban growth, human beings are in an era of wealth and prosperity. However, the consequent energy shortage and environment pollution have been becoming worldwide problems.1–3 Lots of organic dyes in the industrial wastewater discharged by enterprises can lead to a series of problems such as eutrophication and carcinogenesis of water bodies.4–7 Degradation of toxic and harmful organic pollutants with a semiconductor-mediated photocatalyst is of great significance for solving environmental pollution.8–11 Nevertheless, the wide band gap and low quantum efficiency are still the “bottlenecks” for semiconductor photocatalysts to meet the practical application requirements.12 Therefore, it is an urgent need to develop renewable, efficient, and wide light-responsive photocatalysts for pollutant degradation and environmental remediation.13,14

Metal oxide semiconductors such as ZnO,15 TiO2,16 Cu2O,17 SnO2,18 and Fe2O3,19 have been receiving much attention for the photocatalytic degradation of various kinds of pollutants. Tungsten oxide (WO3) has also been widely concerned since 1976 when the first paper on the photocatalysis of WO3 was published.20 As a semiconductor with a band gap of 2.5−2.8 eV,21 WO3 has been widely used in the fields of photochromic,22,23 and photocatalytic applications.24,25 WO3 is one of the most effective and versatile photocatalysts for light corrosion resistance and stable in acidic and oxidizing environments.26 However, due to its relatively low visible light absorption ability and rapid photoelectron−hole pair recombination, the photocatalytic efficiency of WO3 for pollutant degradation is greatly limited.25,27 Silver carbonate (Ag2CO3) is a p-type semiconductor, which has a narrow band gap and easy preparation with good photoactivity under visible light.28 Nevertheless, Ag2CO3 possesses the defect of poor stability and rapid recombination of electron−hole pairs, which makes it not able to meet the need of real application as a photocatalyst.

Doping one semiconductor photocatalyst with other suitable metals, metal oxides, or semiconductor salts can enhance the efficiency of the photocatalyst and also endow the catalyst to be active in the wide light region.34–37 Furthermore, in most cases, the photocatalytic activity of a composite material is better than its simple mixed counterpart.38–41 Yuan and coworkers prepared a Ag2CO3/Ag/WO3 composite photocatalyst by a precipitation−light irradiation method and found that the
photocatalytic activity of the composite was higher than those of the Ag2CO3 and WO3 for the degradation of organic pollutants.\(^{42}\) Gao and coworkers fabricated a polyhedron-like WO3/Ag2CO3 p-n junction photocatalyst with enhanced photocatalytic activity by a deposition–precipitation method.\(^{4}\)

In this work, we report for the first time that the photocatalytic activity of WO3 is highly enhanced by simply mixing with a small amount of Ag2CO3. The proportion of Ag2CO3 on the photocatalytic efficiency of the mixed WO3/Ag2CO3 photocatalyst was systematically investigated by the degradation of RhB under visible light irradiation. The results demonstrated that the photocatalytic efficiency of the mixed WO3/Ag2CO3 photocatalyst was higher than those of both WO3 and Ag2CO3. More interestingly, the photocatalytic activity of the mixed WO3/Ag2CO3 photocatalyst was even higher than that of the WO3 and Ag2CO3 composite prepared by a deposition method. The enhanced photocatalytic activity of mixed WO3/Ag2CO3 might be attributed to the surface synergy between WO3 and Ag2CO3 and WO3 for the degradation of organic pollutants.\(^{42}\) Gao and coworkers fabricated a polyhedron-like WO3/Ag2CO3 p-n junction photocatalyst with enhanced photocatalytic activity by a deposition–precipitation method.\(^{4}\)

2. RESULTS AND DISCUSSION

2.1. Characterization. Figure 1 shows the XRD patterns of WO3, Ag2CO3, and WO3/Ag2CO3 mixed samples. The WO3 sample shows a series of diffraction peaks at 2\(\theta\) values of 23.08° (020), 23.52° (020), 24.28° (200), 26.58° (120), 28.60° (112), 33.30° (022), 33.68° (−202), 34.10° (202), 41.86° (222), 47.18° (004), 48.32° (040), 49.76° (140), 50.48° (−114), 53.36° (024), and 55.82° (142), which correspond well with monoclinic phase WO3 (JCPDS No. 43-1035). \(^{43}\) For the Ag2CO3 sample, the diffraction peaks at 2\(\theta\) values of 18.48° (020), 20.38° (110), 32.52° (−101), 33.60° (−130), 36.94° (200), 37.60° (040), 39.54° (031), 41.6° (220), 44.30° (131), 47.08° (230), 51.36° (150), and 56.08° (231) are in good agreement with monoclinic phase Ag2CO3 (JCPDS No. 43-1035).\(^{43,44}\) The XRD characteristic peaks of WO3 in the mixed WO3/Ag2CO3 samples are obvious, while the peaks of Ag2CO3 are very weak. One possible reason may be that the content of Ag2CO3 in the mixed samples is less than that of WO3. Another reason may be due to the low crystallinity of Ag2CO3, which can be seen from the diffraction peaks of the pure Ag2CO3 sample.

![Figure 1. XRD patterns of WO3, Ag2CO3, and mixed WO3/Ag2CO3 with different Ag2CO3 contents.](image)

The composition and element distribution of the mixed WO3/Ag2CO3 samples were examined by energy-dispersive spectroscopy (EDS). The results showed that tungsten (W), oxygen (O), silver (Ag), and carbon (C) were all detected (Figure 4a) but not uniformly distributed, especially for Ag and C elements (Figure 4b–f). The non-uniform distribution of Ag and C elements

![Figure 2. SEM images of (a) Ag2CO3; (b) WO3; (c, d) WO3/Ag2CO3−5%; and (e, f) WO3/Ag2CO3−20%.](image)
might be due to the prepared sample, since the sample was prepared by a simple mixed method and the content of Ag₂CO₃ was just 5%. Therefore, the non-uniform dispersion of Ag₂CO₃ in the mixed sample has a significant impact on the element mapping of Ag and C elements.

X-ray photoelectron spectroscopy (XPS) was employed to examine the chemical composition and surface element states of WO₃/Ag₂CO₃−5%. XPS element detection results showed that Ag, W, O, and C elements were present in the WO₃/Ag₂CO₃−5% (Figure 5a). High-resolution XPS spectra of the Ag, W, O, and C were obtained by using XPS peak 4.1 program fitting according to the Lorentzian−Gaussian model, which facilitated the determination of chemical valence states of different elements. As shown in Figure 5b, the two peaks at about 367.8 and 373.8 in the Ag 3d XPS spectrum can be assigned to the binding energies of Ag 3d₅/₂ and Ag 3d₃/₂, corresponding to the Ag⁺ of Ag₂CO₃.⁴,²⁻,⁴⁷−⁴⁹ The XPS spectrum of W 4f was shown in Figure 5c; the binding energies of W 4f₇/₂ and W 4f₅/₂ of W⁶⁺ can be observed at 35.7 and 37.8 eV,²⁴ respectively. In the O 1s XPS spectrum (Figure 5d), the peak at 530.4 eV belonged to the lattice oxygen in WO₃ and Ag₂CO₃, but the fitting peak at 531.1 eV was related to the C−O in Ag₂CO₃.⁵⁰ In the C 1s spectrum (Figure 5e), the peak at 288.3 eV belongs to the amorphous species,⁴²,⁵¹ whereas the peak at 288.3 eV belongs to the C peak in Ag₂CO₃.⁴²,⁵³

The ultraviolet−visible diffuse reflectance spectra (UV−vis DRS) of WO₃, Ag₂CO₃, and WO₃/Ag₂CO₃−5% were measured on a UV−vis spectrophotometer. All samples exhibit strong absorption in the ultraviolet and part of the visible region (200−470 nm) and weak absorption in the visible region (470−800 nm) (Figure 6a). By using the tangent line method,⁵⁴ the absorption band edge of WO₃ is positioned at 476 nm, and the corresponding band gap (E₉) is 2.605 eV. As for the Ag₂CO₃, the absorption edge is estimated at about 520 nm, and the corresponding E₉ value is 2.385 eV.

The band gaps of WO₃ and Ag₂CO₃ were further calculated according to the Tauc formula:⁵²,⁵₅,⁵₆

\[
\alpha hν = A(hν - E₉)^{n/2}
\]

where α and ν represent the light absorption coefficient and light frequency, while A and E₉ represent a constant and band gap energy, and h is the Plank constant, respectively. The n is an integer, the value of which depends on where the transition is direct (n = 1) or indirect (n = 4).¹²,⁵⁷ Since both WO₃ and Ag₂CO₃ are indirect semiconductors, n = 4 is used to determine the E₉ values by plotting (αhν)^₁/₂ vs hν.¹² After calculating the experimental data based on the tangent line method,⁵⁰ the band gaps of WO₃ and Ag₂CO₃ are 2.61 and 2.36 eV, respectively (Figure 6b). The E₉ values of WO₃ and Ag₂CO₃
that are calculated above are in the range of relevant reports.8,21,61−63

The potential values of the valence band (VB) and conduction band (CB) of the semiconductor can be theoretically calculated by using the electronegativity of Mulliken and the band gap of the semiconductor.

$$E_{VB} = X - E_e + 0.5E_g$$

$$E_{CB} = E_{VB} - E_g$$

In the above formula, $E_{VB}$ and $E_{CB}$ represent the edge potentials of VB top and CB bottom. $X$ is the geometric mean value of Mulliken electronegativity of the constituent atoms in the semiconductor. According to relevant literature reports, the $X$ values for WO$_3$ and Ag$_2$CO$_3$ are 6.59$^{54}$ and 6.02 eV$^{52,65,66}$ respectively. $E_e$, usually 4.5 eV, is the free electron energy on the hydrogen scale.64,67 As a result, the $E_{VB}$ of WO$_3$ and Ag$_2$CO$_3$ are calculated as 3.40 and 2.70 eV vs NHE$^{52,63}$ respectively. Meanwhile, the $E_{CB}$ of WO$_3$ and Ag$_2$CO$_3$ are 0.79 eV and 0.34 eV vs NHE. These results agreed well with the reported values.48,68,69

Figure 5. High-resolution XPS spectra of WO$_3$/Ag$_2$CO$_3$−5%: (a) full spectrum; (b) Ag 3d; (c) W 4f; (d) O 1s; (e) C 1s.
2.2. Photocatalytic Performance. The photocatalytic activity of the mixed WO3/Ag2CO3 was explored by the degradation of RhB under visible light irradiation (λ > 400 nm). The original solution of RhB showed a strong absorption peak at 554 nm (Figure 7). When WO3/Ag2CO3−5% was used for the photodegradation of RhB, the absorption band of RhB solution obviously blue-shifted at 4 min, and the absorbance value at 554 nm decreased rapidly and almost approached zero after 6 min of visible light irradiation (Figure 7a). According to the previous publications, the photodegradation of RhB by WO3/Ag2CO3−5% was accompanied by the decomposition of N-deethylation and conjugated chromophores. It also indicated that WO3/Ag2CO3−5% has high photocatalytic activity toward RhB degradation. For comparison, pure Ag2CO3 and WO3 were also used as photocatalysts to degrade RhB. The peak intensity of RhB at 554 nm decreased at a slow rate in the presence of Ag2CO3, and only about 50% was degraded within 8 min under visible light illumination (Figure 7b). When WO3 was used as a catalyst, RhB was almost not degraded within 8 min (Figure S1). To better observe the photocatalytic degradation effect of RhB by WO3, we conducted a prolonged photocatalytic reaction (120 min) on RhB degradation. The RhB dye was slowly degraded under long time light irradiation (Figure 7c) in the presence of WO3, as indicated by the absorbance decrease at 554 nm. In order to show the degradation effects of WO3, Ag2CO3, and WO3/Ag2CO3−5%.

Figure 6. UV−vis DRS spectra WO3, Ag2CO3, and WO3/Ag2CO3−5% (a) and (αhv)1/2 vs energy (hv) plots for calculating the band gap of WO3 and Ag2CO3 (b).

Figure 7. UV−vis spectra of RhB solution under visible light irradiation (λ > 400 nm) with (a) WO3/Ag2CO3−5%, (b) Ag2CO3, and (c) WO3 photocatalysts. (d) Kinetics plots.
Ag$_2$CO$_3$−5% on RhB more intuitively, the kinetic diagrams were analyzed by plotting $C/C_0$ vs illumination time ($t$). It can be clearly observed from Figure 7d that the degradation effect of WO$_3$/Ag$_2$CO$_3$−5% toward RhB is obviously higher than those of WO$_3$ and Ag$_2$CO$_3$. The above results indicated that the photocatalytic activity of WO$_3$ was greatly improved by mixing with Ag$_2$CO$_3$.

In order to more comprehensively uncover the effect of Ag$_2$CO$_3$ content on the photocatalytic performance of the WO$_3$/Ag$_2$CO$_3$ mixed photocatalyst, a series of mixed WO$_3$/Ag$_2$CO$_3$ samples with different Ag$_2$CO$_3$ proportions were prepared and their photocatalytic degradation properties were investigated. As shown in Figure 8a,b, RhB was hardly photodegraded in the absence of a catalyst, which indicated that the photodegradation of RhB could be ignored without a catalyst. The WO$_3$ showed very poor photocatalytic activity for the degradation of RhB. The combination of WO$_3$ with Ag$_2$CO$_3$ greatly improved the photocatalytic activity of WO$_3$ for RhB degradation. The photocatalytic activity of mixed WO$_3$/Ag$_2$CO$_3$ increased significantly at first and then remained unchanged with the increase of Ag$_2$CO$_3$, which indicated that there is a synergistic effect between WO$_3$ and Ag$_2$CO$_3$. Interestingly, the photocatalytic performance of the WO$_3$/Ag$_2$CO$_3$ mixed photocatalyst was similar when the content of Ag$_2$CO$_3$ accounts for 5−20% of the total mass of WO$_3$/Ag$_2$CO$_3$, which may be related to the fact that the short rod-shaped Ag$_2$CO$_3$ has covered the bulk WO$_3$ surface and the synergistic effect has reached the maximum. RhB was almost completely degraded with a degradation rate of 99.7% within about 6 min in the presence of WO$_3$/Ag$_2$CO$_3$−5%, which further confirmed that WO$_3$/Ag$_2$CO$_3$ was a highly efficient photocatalyst for the degradation of RhB.

To further illustrate the photocatalytic ability of the mixed catalysts toward RhB, we performed the diagram of ln($C/C_0$) versus irradiation time (Figure 8c) based on the equation of ln($C/C_0$) = $-kt$ (k denotes the pseudo-first order rate constant), assuming that the photodegradation of RhB obeys pseudo-first order kinetics ($dC/dt = kC$). The calculated pseudo-first order rate constants from Figure 8c are compared and displayed in Figure 8d. It was found that the rate constant of WO$_3$/Ag$_2$CO$_3$−5% (0.9591 min$^{-1}$) was 118-fold higher than that of WO$_3$ (0.0081 min$^{-1}$) and 14-fold higher than that of Ag$_2$CO$_3$ (0.0663 min$^{-1}$). It can be also seen from Figure 8d that the rate constant of WO$_3$/Ag$_2$CO$_3$−5% was the highest among all samples, showing that WO$_3$/Ag$_2$CO$_3$−5% possesses the best photocatalytic performance toward RhB degradation.

It has been often reported that the photocatalytic activity of a composite photocatalyst was usually better than its simply mixed...
In order to compare the photocatalytic activity of our mixed WO$_3$/Ag$_2$CO$_3$ photocatalyst with that of the WO$_3$/Ag$_2$CO$_3$ composite, we also prepared WO$_3$/Ag$_2$CO$_3$ composite photocatalysts by a deposition–precipitation method and performed photocatalytic degradation experiment. All the WO$_3$/Ag$_2$CO$_3$ composite photocatalysts prepared in this work displayed improved photocatalytic activity compared to pure WO$_3$ and Ag$_2$CO$_3$ (Figure S2), which is in accordance with general observations that the catalytic activity of a composite photocatalyst is often higher than its constituent photocatalyst. However, the photocatalytic activity of the composite photocatalysts was lower than that of its mixed counterparts in this study (Figure 9), which is contrary to general reports.

The result is very interesting, although the reason for this discrepancy is unclear at present, and we will perform further studies to reveal the mechanism in the future. To understand the photocatalytic degradation process of RhB catalyzed by the WO$_3$/Ag$_2$CO$_3$ mixed photocatalyst, the intermediate products of RhB degradation in the presence of WO$_3$/Ag$_2$CO$_3$−5% were further explored by MS analysis (Figure 10a,b). Before light irradiation, the sample mainly showed a peak at an $m/z$ of 443.2 that belongs to the original RhB (Figure 10a). Eight different $m/z$ peaks (475.3, 443.2, 415.2, 387.2, 362.3, 359.3, 318.3, and 274.3) were detected after degradation with irradiation (Figure 10b). Based on the measured $m/z$ results and previously reported works, the corresponding mass spectra and chemical structures of the possible intermediate products are listed in Table S1. A possible degradation process of RhB is illustrated in Figure 10c. There are four ethyl groups and one carboxyl group in the RhB molecule. It can be clearly observed that N-deethylation is the primary step in the degradation process of RhB, and a large number of N-deethylation intermediates can be found in the intermediates. Upon light irradiation, the N-deethylation intermediates were generated, and the mass peaks at $m/z$ values of 415.2, 387.2, and 359.3 were identified as N,N,N′-tri-ethylated rhodamine, N,N′-diethylated rhodamine, and N-ethylated rhodamine molecules. The active radicals in the aqueous solution generated by WO$_3$/Ag$_2$CO$_3$−5% attack the N-deethylation intermediates, thus producing several primary oxidation products. When the four ethyl groups in the RhB molecule are degraded, decarboxylating and ring opening may be occurred gradually under the attacking of the active radicals in the solution, resulting in the formation of intermediates with a smaller molecular weight, and the solution becomes colorless gradually. Finally, the substances with a smaller molecular weight were decomposed into H$_2$O and CO$_2$. Besides deethylation, hydroxylation may also be involved in the photodegradation of RhB, since two possible hydroxylated intermediates with $m/z$ values of 475.3 and 349.2 were observed in the mass spectroscopy (Figure 10b and Table S1). It was also noted that the peak at the $m/z$ of 443.2 disappeared after 6 min of light irradiation (Figure S3), indicating the complete structure destruction of the original RhB molecule, in line with the UV–visible spectral change.

The stability of a photocatalyst is considered as a very important factor in practical applications. In this study, the stability of the photocatalyst was evaluated with the photocatalytic degradation of RhB by using WO$_3$/Ag$_2$CO$_3$−5%. The photocatalytic activity of WO$_3$/Ag$_2$CO$_3$−5% on RhB degradation was significantly reduced after the first cycle, and the photocatalytic degradation efficiency was as low as 20% (Figure S4a), which indicated that the stability of WO$_3$/Ag$_2$CO$_3$−5% was poor. Therefore, how to improve the stability of the prepared WO$_3$/Ag$_2$CO$_3$−5% has become the goal of further research.

Since the photocatalytic degradation rates of WO$_3$/Ag$_2$CO$_3$−5% and WO$_3$/Ag$_2$CO$_3$−20% are similar within 8 min, the cyclic photocatalytic degradation of RhB by WO$_3$/Ag$_2$CO$_3$−20% was also studied. The photocatalytic stability of WO$_3$/Ag$_2$CO$_3$−20% was also not good (Figure S4b). However, we found that the cyclability of WO$_3$/Ag$_2$CO$_3$−20% was better than that of WO$_3$/Ag$_2$CO$_3$−5%. Based on the above observation, we put forward the idea that the stability may be related to the percentage of Ag$_2$CO$_3$ in the mixed WO$_3$/Ag$_2$CO$_3$. When the percentage of Ag$_2$CO$_3$ in the mixed WO$_3$/Ag$_2$CO$_3$ is higher, the loss percentage of Ag$_2$CO$_3$ is relatively small during the photocatalytic reaction process. Therefore, we speculated that improving the stability of Ag$_2$CO$_3$ may be the key factor to maintaining the photocatalytic activity of the WO$_3$/Ag$_2$CO$_3$ photocatalyst.

XRD and XPS measurements were conducted for the WO$_3$/Ag$_2$CO$_3$−5% after photodegrading RhB. There are two XRD peaks at 2θ = 38.1 and 44.2° that appeared after use (Figure S5), which can be assigned to the (111) and (200) facets of the cubic phase of metallic Ag (JCPDS No. 65-2871). The Ag 3d XPS spectrum of WO$_3$/Ag$_2$CO$_3$−5% after use is shown in Figure S6. The two peaks at about 368 and 374 eV can be deconvoluted into two groups, one group at binding energies of 367.7 and 373.7 eV can be assigned to the Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ of Ag$^0$ of the Ag$_2$CO$_3$ mixture, and the peak location is the same as the Ag 3d XPS of WO$_3$/Ag$_2$CO$_3$−5% before use, whereas the other group at 368.2 and 374.3 eV can be attributed to metallic silver (Ag$^0$) according to previous reports. These results suggested that part of Ag$^0$ in Ag$_2$CO$_3$ were reduced to metallic Ag under light illumination in the photocatalytic reaction.

It has been reported previously that the addition of AgNO$_3$ in the photocatalytic reaction system can inhibit the photocorrosion of Ag$_2$CO$_3$. Therefore, the addition of AgNO$_3$ may also inhibit the photoactivation of WO$_3$/Ag$_2$CO$_3$ mixed photocatalyst. With this idea in mind, we performed the photocatalytic reaction in the presence AgNO$_3$. Figure 11a shows the effect of AgNO$_3$ concentration on the photocatalytic activity of WO$_3$/Ag$_2$CO$_3$−5%. The photocatalytic activity of the WO$_3$/Ag$_2$CO$_3$−5% was almost not affected when the
concentration of AgNO₃ was 0.002 or 0.0035 M, while the catalytic activity was slightly decreased with the increase of AgNO₃ up to 0.005 M. Therefore, 0.002 M AgNO₃ was used as the stabilizer in the further study considering both catalytic efficiency and economic benefit.

Figure 11b shows the cycle experiment of photocatalytic degradation of RhB by WO₃/Ag₂CO₃−5% with 0.002 M AgNO₃ as stabilizer. After five cycles repeated use, about 85% degradation efficiency was maintained, indicating the strong inhibition ability of AgNO₃ to the photoinactivation of WO₃/Ag₂CO₃−5%. These results demonstrated that AgNO₃ can be used as a stabilizer for improving the stability of the mixed WO₃/Ag₂CO₃ photocatalyst.

As we all know, Ag₂CO₃ is a slightly soluble substance with a solubility product constant \( K_{sp} \) of \( 8.46 \times 10^{-12.81} \). According to the relationship of solubility and \( K_{sp} \), the solubility of Ag₂CO₃ is calculated to be \( 1.284 \times 10^{-4} \) mol·L⁻¹ and the solubility of Ag⁺ can reach \( 2.57 \times 10^{-4} \) mol·L⁻¹ (see the Supporting Information for calculation). The Ag⁺ dissolved in the solution is easily reduced to Ag, promoting the dissolution of Ag₂CO₃, thus reducing the stability of the Ag₂CO₃ photocatalyst. Based on the movement principle of the precipitation–dissolution equilibrium, the solubility of Ag₂CO₃ will be decreased with the increase of Ag⁺ concentration. Therefore, the addition of AgNO₃ into the photocatalytic reaction system can inevitably increase the stability of Ag₂CO₃. In addition, it is also well known that Ag₂CO₃ is a light-sensitive compound; the Ag⁺ ions on the surface of Ag₂CO₃ particles is easily decomposed to metallic Ag under light conditions, resulting in the decrease of the photocatalytic stability of Ag₂CO₃. Thus, the addition of AgNO₃ to the photocatalytic reaction system can also prevent Ag₂CO₃ from photodecomposition under light irradiation. To sum up, the main function of AgNO₃ on the inhibition of Ag₂CO₃ photoinactivation lies not only in reducing the solubility of Ag₂CO₃ in water but also in inhibiting the photodecomposition of Ag₂CO₃ under light irradiation.

2.3. Photocatalytic Mechanism. The interface charge separation efficiency of photogenerated electrons (e⁻) and holes

Figure 10. Mass spectra of RhB (a) before irradiation and (b) after irradiation for 2 min; (c) schematic diagram of possible intermediates for the photocatalytic degradation of RhB by WO₃/Ag₂CO₃−5%.
(h⁺) has been reported as an important factor in determining photocatalytic performance. The transfer rate of the interface charge in the photocatalyst was studied by the electrochemical impedance spectroscopy (EIS) technique. Figure 12a shows the Nyquist plots of EIS for WO₃, WO₃/Ag₂CO₃−1.5%, and WO₃/Ag₂CO₃−5% mixed samples. It can be clearly observed that the arc radius of the electrode modified with WO₃/Ag₂CO₃−5% is smaller than that of WO₃/Ag₂CO₃−1.5%,
and much smaller than pure WO₃. These results indicated that the charge transfer resistance is smaller and the photogenerated electron−hole pair separation and interface charge transfer are more effective in WO₃/Ag₂CO₃−5%. Then, photoelectrochemical properties were studied by measuring the transient photocurrent in a three-electrode cell. As shown in Figure 12b, under light illumination (λ > 400 nm), the photocurrent intensity of WO₃/Ag₂CO₃−5% is about 1.7 and 5 times as high as that of WO₃/Ag₂CO₃−1.5% and pure WO₃, respectively. This result indicated that the separation rate of photogenerated electron−hole pairs was increased after the combination of WO₃ with Ag₂CO₃, and the WO₃/Ag₂CO₃−5% showed the highest separation efficiency of photocharges. The changes of the size of the arc radius and the photocurrent intensity are consistent with that of photocatalytic activity. Based on the above experimental results, it can be concluded that the enhanced photocatalytic activity of WO₃/Ag₂CO₃−5% is attributed to the higher separation efficiency of photoinduced charges and the lower charge transfer resistance.

The active species of the photocatalytic process were detected by a trapping experiment. In this study, 1,4-benzoquinone (BQ)⁴² and isopropanol (IPA)⁴¹ were used as scavenging agents for superoxide radical (·O₂⁻) and hydroxyl radical (·OH), respectively. Ammonium oxalate (AO),⁴⁷ triethanolamine (TEOA),⁴ and disodium ethylenediaminetetraacetate (EDTA-2Na)⁴⁴,⁶¹ were used for scavenging of hole (h⁺). It can be seen that the degradation efficiency of RhB was significantly reduced no matter adding AO, TEOA, or EDTA-2Na (Figure 13a,b), which showed that h⁺ was the main active species in the reaction process. The degradation rate decreased to a certain degree with the addition of BQ, indicating that ·O₂⁻ has a certain effect for RhB degradation. When IPA was added as the scavenger of ·OH, the degradation efficiency of RhB was only slightly decreased, indicating the minor effect of ·OH in the photodegradation of RhB.

The role of ·OH in the photocatalytic process were further explored with fluorescence technology by detecting ·OH in the solution in the presence of WO₃/Ag₂CO₃−5%. Terephthalic acid (TA) can react with ·OH to generate hydroxyl terephthalic acid (TA-OH), which can display a fluorescence peak at about 425 nm under the excitation wavelength of 315 nm.⁴⁷,⁸³ For comparison, ·OH generated by nano-TiO₂ under UV−visible light was also conducted as a positive control. It can be seen clearly that the fluorescence absorption peak at 425 nm increased with time under light illumination in the presence of TiO₂ (Figure 14a), indicating the formation of TA-OH.⁵³ However, no obvious fluorescence spectral change was observed when WO₃/Ag₂CO₃−5% was used as a photocatalyst under visible light irradiation, which indicated that TA-OH was not produced in this process (Figure 14b). These results demonstrated that ·OH was scarcely produced in the presence of WO₃/Ag₂CO₃−5% during the catalytic reaction.

On the basis of the above experimental results and the energy band calculation, a probable catalytic mechanism for RhB photodegradation by mixed WO₃/Ag₂CO₃ was proposed (Figure 15). According previous literature studies, WO₃ is an n-type semiconductor and Ag₂CO₃ is a p-type semiconductor, and the Fermi level of WO₃ is higher than that of Ag₂CO₃.⁴ After WO₃ and Ag₂CO₃ contacted and compactly

![Figure 14. Fluorescence spectra of 0.5 mM alkaline terephthalic acid solution (λ_ex = 315 nm) in the presence of (a) TiO₂ under UV−visible light irradiation and (b) WO₃/Ag₂CO₃−5% under visible light irradiation (λ > 400 nm).](https://doi.org/10.1021/acsomega.1c03694)

![Figure 15. Diagrams of the energy band (a) and photoexcited electron−hole separation (b) for RhB degradation in the presence of the WO₃/Ag₂CO₃ photocatalyst under visible light irradiation (λ > 400 nm).](http://pubs.acs.org/journal/acsodf)
coupled with each other, electrons would diffuse from WO$_3$ with a high Fermi level to Ag$_2$CO$_3$ with a low Fermi level, and consequently, positive charge centers were formed at the interface region of WO$_3$ and negative charge centers at the interface of Ag$_2$CO$_3$. The built-in electric field formed in the interface of WO$_3$ and Ag$_2$CO$_3$ can prevent the continuous diffusion of electrons from WO$_3$ to Ag$_2$CO$_3$ and finally a thermal equilibrium state between WO$_3$ and Ag$_2$CO$_3$ can be established. Simultaneously, the Fermi level of WO$_3$ (n-type semiconductor) moved down with the Fermi level of Ag$_2$CO$_3$ (p-type semiconductor) moving up (Figure 15a). As a result, the CB band of Ag$_2$CO$_3$ might be more negative than the potential of O$_2$/O$_2^-$ (−0.33 V), and the VB of Ag$_2$CO$_3$ more negative than the potential of H$_2$O/OH (±2.38 V). As is shown in Figure 15b, both WO$_3$ and Ag$_2$CO$_3$ can be photoexcited upon visible light (λ > 400 nm) irradiation to generate electrons and holes (eqs 4 and 5) since the band gap of WO$_3$ and Ag$_2$CO$_3$ are 2.61 and 2.36 eV, respectively (Figure 15a). The photoinduced holes in the CB band of Ag$_2$CO$_3$ could be captured by dissolved O$_2$ generating O$_2^-$ to oxidized RhB (eqs 10 and 11), while the photoinduced electrons in the VB of Ag$_2$CO$_3$ could not oxidized H$_2$O to OH since the VB energy of Ag$_2$CO$_3$ was lower than the potential of H$_2$O/OH.

In addition, it is also possible that RhB itself could be photoexcited under visible light irradiation and stimulated to an excited state (RhB$^*$.). Then, the electrons in the lowest unoccupied molecular orbital (LUMO) of RhB are injected to the CB of Ag$_2$CO$_3$ or captured by O$_2$, generating superoxide radicals O$_2^-$ (eqs 8 and 9). In addition, the photoexcited electrons in the CB of WO$_3$ may partially move to the highest occupied molecular orbital (HOMO) of RhB so that stabilize the photogenerated holes in the VB of WO$_3$.

$$\text{WO}_3 + h\nu \rightarrow h^+ (\text{WO}_3) + e^- (\text{WO}_3)$$

$$\text{Ag}_2\text{CO}_3 + h\nu \rightarrow h^+ (\text{Ag}_2\text{CO}_3) + e^- (\text{Ag}_2\text{CO}_3)$$

$$h^+ (\text{WO}_3) + \text{RhB} \rightarrow \text{products + WO}_3$$

$$h^+ (\text{WO}_3) + \text{Ag}_2\text{CO}_3 \rightarrow h^+ (\text{Ag}_2\text{CO}_3) + \text{WO}_3$$

$$h^+ (\text{WO}_3) + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{H}^+ + \text{WO}_3$$

$$\text{OH} + \text{RhB} \rightarrow \text{products}$$

$$\text{O}_2 + e^- (\text{Ag}_2\text{CO}_3) \rightarrow \cdot\text{O}_2^- + \text{Ag}_2\text{CO}_3$$

$$\text{RhB} + \cdot\text{O}_2^- \rightarrow \text{products}$$

3. CONCLUSIONS

A series of mixed WO$_3$/Ag$_2$CO$_3$ with different mass ratios were successfully prepared by a simple mechanical mixing method. In the presence of a proper proportion of mixed WO$_3$/Ag$_2$CO$_3$, RhB was completely degraded within 8 min under visible light irradiation (λ > 400 nm), which was better than both WO$_3$ and Ag$_2$CO$_3$. When the mass percentage of Ag$_2$CO$_3$ ranged from 5 to 20% of WO$_3$/Ag$_2$CO$_3$, the degradation rate of RhB was more than 99.5% within 8 min, which can be attributed to the following: (1) massive WO$_3$ provides a large number of active sites for Ag$_2$CO$_3$; (2) type II double transfer mechanism greatly promotes the separation of the electron hole pairs. The degradation rate of RhB by mixed WO$_3$/Ag$_2$CO$_3$ can still maintain 85.6% after five cycles with the addition of 0.002 M AgNO$_3$ as a stabilizer. The results of the free radical capture indicated that the main active substances were $\cdot\text{O}_2^-$ and $h^+$, while $\cdot\text{OH}$ was almost not produced in the degradation of RhB. The present work may provide a strategy to prepare efficient visible light photocatalysts.

4. EXPERIMENTAL SECTION

4.1. Materials. Tungsten trioxide (WO$_3$) was purchased from Adamas Reagent Co., Ltd.; silver nitrate (AgNO$_3$) and rhodamine B (RhB) were obtained from Chengdu Kelong Chemical Reagent Factory; and sodium bicarbonate (NaHCO$_3$) was purchased from Tianjin Komiu Chemical Reagent Co., Ltd. Other chemical reagents were of analytic grade and used without further purification.

4.2. Preparation of Ag$_2$CO$_3$. First, NaHCO$_3$ solution was prepared by dissolving 0.42 g NaHCO$_3$ in 50 mL deionized water. Then, the NaHCO$_3$ solution was dropwise added into 50 mL of 0.1 M AgNO$_3$ under magnetic stirring. After stirring in the dark for 30 min, the Ag$_2$CO$_3$ precipitate was collected by centrifugation and repeatedly washed three times with deionized water before drying in an oven at 60 °C for 6 h.

4.3. Preparation of the Mixed WO$_3$/Ag$_2$CO$_3$ Photocatalyst. Briefly, a certain amount of WO$_3$ and Ag$_2$CO$_3$ was weighed in a 5 mL centrifuge tube and stirred evenly to prepare a series of mixed catalysts with different mass ratios, in which the mass of Ag$_2$CO$_3$ accounted for 1, 1.25, 1.5, 2, 2.5, 5, 7.5, 10, and 20% of the total mass. The mixed WO$_3$/Ag$_2$CO$_3$ were labeled as WO$_3$/Ag$_2$CO$_3$–x% (% is the mass percentage of Ag$_2$CO$_3$ in the mixture).

4.4. Preparation of WO$_3$/Ag$_2$CO$_3$ Composite Photocatalyst. The WO$_3$/Ag$_2$CO$_3$ composite was prepared by a precipitation method. Briefly, 0.621 g WO$_3$ was dispersed in 20 mL deionized water by ultrasonication for 30 min, and then 0.1 M AgNO$_3$ (5 mL) solution was added to the above dispersion under magnetic stirring. After stirring for 30 min, 0.1 M NaHCO$_3$ (5 mL) was added dropwise into the above solution and further stirred for 2 h. Finally, the WO$_3$/Ag$_2$CO$_3$ composite was collected by centrifugation, washed with deionized water, and dried in an oven at 60 °C for 6 h. This sample was labeled as WO$_3$/Ag$_2$CO$_3$–p–100%. Other WO$_3$/Ag$_2$CO$_3$ composites with different Ag$_2$CO$_3$ content were prepared with the same synthetic steps by varying the proportion of Ag$_2$CO$_3$ to WO$_3$. The composites were labeled as WO$_3$/Ag$_2$CO$_3$–p–x% (% is the mass percentage of Ag$_2$CO$_3$ in the composite).

4.5. Characterizations. The phase information, morphol-
out within a certain irradiation interval. Before the absorption measurement, the mixed WO$_3$/Ag$_2$CO$_3$ catalyst was removed by using a membrane filter (0.45 μm), and then the absorbance values for the RhB solution was measured with a UV−vis spectrophotometer (Agilent Technologies, Cary 8454) or a visible spectrophotometer (723 N, Shanghai Jingke Scientific Instrument Co., Ltd., China). The detection wavelength was selected at 554 nm, the maximum absorption wavelength of RhB in the visible region.

The photocatalytic degradation intermediates of RhB were analyzed by a mass spectroscope (Agilent Technologies 6120 Quadrupole).

4.7. Photoelectrochemical Measurement. Photoelectrochemical impedance spectroscopy (EIS) and photocurrent were measured by using a typical three-electrode system in a CHI 760E electrochemical workstation. In the measurement process, Pt wire and Ag/AgCl were used as the counter electrode and the reference electrode, respectively, and the photocatalyst was covered on the ITO conductive glass as the working electrode. In addition, 0.2 M Na$_2$SO$_4$ was used as the electrolyte. EIS was measured at a potential of 1.5 V with a frequency of 0.1−10$^5$ Hz and an amplitude of 5 mV. The photocurrent was measured under a bias voltage of 0.5 V, and a 300 W xenon lamp with an ultraviolet light cut-off filter (λ > 400 nm) was used as the light source.

4.8. Active Species Identification. The active species trapping experiment was basically the same as that of the degradation experiment except that specific scavenging agents were added. A total of 10 mM ammonium oxalate (AO), 5 mM ethylenediaminetetraacetic acid disodium (EDTA-2Na), and 1 mM triethanolamine (TEOA) were used as scavengers for the photoinduced holes (h$^+$). A total of 10 mM isopropanol (IPA) and 0.2 mM benzoquinone (BQ) were selected as scavenging agents for the hydroxyl radical (·OH) and superoxide anion radical (·O$_2^−$).

Under the excitation wavelength of 315 nm, terephthalic acid (TA) was used as the fluorescent probe, and the content of ·OH was determined on a G9800A Carry eclipse fluorescence spectrophotometer. In addition, the RhB solution was replaced by basic terephthalic acid, and the fluorescence experiment was performed with the replaced solution. The concentration of the terephthalic acid was 0.5 mM in 1.5 mM NaOH; the sampling time after the reaction was the same as the photocatalytic degradation experiment; and the fluorescence spectrum was measured after filtering with a filter (0.45 μm).

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03694.

Calculation of the solubility of Ag$_2$CO$_3$; chemical structure of the intermediate products of RhB degradation; UV−vis spectral changes of RhB solution under visible light irradiation (λ > 400 nm) with pure WO$_3$ data of photocatalytic degradation of RhB with WO$_3$/Ag$_2$CO$_3$ composite photocatalysts prepared by the deposition−precipitation method; mass spectra of RhB degradation products by the WO$_3$/Ag$_2$CO$_3$−5% mixed photocatalyst; photochemical stability study of WO$_3$/Ag$_2$CO$_3$ mixed samples; XRD comparison of the WO$_3$/Ag$_2$CO$_3$−5% mixed sample before and after photocatalysis; Ag 3d XPS spectrum of the WO$_3$/Ag$_2$CO$_3$−5% mixed sample after photocatalysis; and the adsorption of RhB dye onto the photocatalysts (PDF)

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#### Notes

The authors declare no competing financial interest.

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