Plasmonic Ag@AgCl-intercalated K$_4$Nb$_6$O$_{17}$ composite for enhanced photocatalytic degradation of Rhodamine B under visible light

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**Abstract**

A novel plasmonic photocatalyst, Ag@AgCl-intercalated layered niobate (denoted K$_4$Nb$_6$O$_{17}$/Ag@AgCl), was synthesized via a microwave-assisted ion-exchange method. The composite materials were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), ultraviolet–visible diffuse reflection spectra (UV–vis), photoluminescence measurements (PL), X-ray fluorescence spectrometer (XRF) and X-ray photoelectron spectroscopy (XPS). The as-prepared plasmonic photocatalyst exhibited an enhanced and stable photocatalytic activity for the degradation of Rhodamine B (RhB) under visible light irradiation. The high activity was attributed to the surface plasmon resonance (SPR) exhibited by Ag nanoparticles on the surface of AgCl. The detection of reactive species by radical scavengers displays that O$_2^-$ and OH$^-$ are the main reactive species for the degradation of RhB under visible light irradiation. The mechanism of separation of the photo-generated electrons and holes at the K$_4$Nb$_6$O$_{17}$/Ag@AgCl composite was discussed.

1. Introduction

Ag@AgX (X = Cl, Br) structures as efficient visible light photocatalysts have recently aroused attention due to the incorporated surface plasmon resonance (SPR) which can greatly increase the utilization of visible light. Plasmonic metallic nanostructures are characterized by their strong interaction with resonant photons through an excitation of surface plasmon resonance. SPR can be described as the resonant photon-induced collective oscillation of conduction electrons, established when the frequency of photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei [5]. Further research into these plasmonic materials revealed that composite photocatalysts composed of plasmonic Ag@AgCl photocatalyst with various semiconductors (such as H$_2$WO$_4$·H$_2$O [6], ZnO [7], TiO$_2$ [8], BiVO$_4$ [9]) can greatly increase the photocatalytic efficiency of the resulting bulk photocatalysts under visible light. However, plasmonic photocatalysts have some obstacles limiting their use in practical applications, such as the short lifetime of the photogenerated electron–hole pair and the low stability or limited visible-light photo response [10].

Layered compounds are another class of photocatalyst, which have potential applications in various fields such as electrocatalysis, photoelectrocatalysis, energy-storage and energy-conversion [11,12]. Among these layered compounds, potassium hexaniobate K$_4$Nb$_6$O$_{17}$ has received much attention due to its distinctive layered structure, which is formed by the connection of octahedral units of NbO$_6$ and oxygen bridging atoms. The layers are negatively charged, with K$^+$ ions existing between the layers to compensate for these charges [13]. Although researchers reported that K$_4$Nb$_6$O$_{17}$, like other layered compounds, exhibited high photocatalytic activity due to its unique layered space, which can suppress the recombination of photo-induced electrons and holes under UV light irradiation [14,15], it cannot exhibit any photocatalytic activity under visible light irradiation, due to its relatively large band gap of 3.1 eV [16]. This restricts its practical use in large-scale application, and therefore, many efforts have been made to improve its photocatalytic performance under visible light by intercalating with narrow-bandgap compounds such as CdS [15,17] or organic molecules [18]. Incorporation of guest semiconductors into the interlayer region is a promising method for fabricating a nanocomposite consisting of host layers with ultrathin particles in the interlayer space, resulting in enhanced photocatalytic activity from the composite semiconductor [19] due to the synergistic roles of quantum and coupling effects between different energy band gaps.

To date, to our knowledge, research on the introduction of plasmonic Ag@AgCl into the layered space of K$_4$Nb$_6$O$_{17}$ has not been
reported. The utilization of a plasmonic and layered compound photocatalyst is thought to be capable of increasing the overall photocatalytic activity observed. Therefore, in this work, we synthesized an Ag@AgCl intercalated K4Nb6O17 composite material for the first time, using a microwave-assisted process. Compared to the conventional methods available, microwave-assisted processes have been shown to be efficient for the synthesis of intercalated layered composites [20]. The photocatalytic activities of the samples were studied through the degradation of RhB under visible light irradiation. Moreover, various scavengers were introduced to the photocatalytic reaction system to explore the roles of different reactive species and the reaction mechanism.

2. Experimental

2.1. Synthesis of K4Nb6O17

All of the reagents were analytical grade and used without further purification. K4Nb6O17 was prepared by calcination of a 2:1:3 molar mixture of K2CO3 and Nb2O5 at 1000 °C for 2 h according to the procedure described by Cui et al. [21,22]. The product was ground to a fine powder for subsequent use.

2.2. Synthesis of Ag@AgCl intercalated K4Nb6O17

The K4Nb6O17/Ag@AgCl composite was synthesized after obtaining H4Nb6O17 and (C4H9NH3)4Nb6O17 from K4Nb6O17. The H4Nb6O17 and (C4H9NH3)4Nb6O17 were obtained by ion-exchange under the assistance of microwave irradiation according to the procedure described by Cui et al. [21]. Subsequently, the obtained (C4H9NH3)4Nb6O17 sample and 6.0 g silver acetate (C2H3AgO2) were added to 500 ml deionized water. To facilitate ion-exchange, the mixture was reacted under microwave heating at 80 °C for 1.5 h. The suspension was then centrifuged and carefully washed with distilled water and ethanol to remove Ag+ adsorbed on the surface of K4Nb6O17. The dried Ag ion-intercalated K4Nb6O17 powder (designated as K4Nb6O17/Ag+) was added to 0.1 mol/L HCl, and stirred for 1.5 h at 50 °C in the dark, to obtain AgCl intercalated K4Nb6O17. The above mixture was then irradiated with a 250 W metal halide lamp (Philips), equipped with a wavelength cutoff filter for λ > 400 nm, and the irradiation time was 120 min. The resulting sample (K4Nb6O17/Ag@AgCl) was thoroughly washed with distilled water and was centrifuged and dried at 80 °C in an oven for 10 h.

For comparison, Ag@AgCl photocatalysts were prepared by a precipitation method. 0.85 g AgNO3 was dispersed in 50 ml deionized water under magnetic stirring at room temperature, and then 50 ml HCl solution (0.1 mol/L) was added to the above solution drop by drop. After 40 min, the above mixture was then irradiated with a 250 W metal halide lamp (Philips) for 120 min, equipped with wavelength cutoff filters for λ > 400 nm. The resulting sample was thoroughly washed with distilled water and was centrifuged and dried at 80 °C in an oven for 10 h.

2.3. Characterizations

The crystalline phases of the products were determined by powder X-ray diffraction (XRD) using a Rigaku D/Max2500PC diffractometer with CuKα radiation, with an operating voltage of 40 kV and an operating current of 100 mA. Scanning electron microscopy (SEM) images were observed by a Hitachi s-4800 SEM microscope equipped with energy dispersive X-ray detector (EDX, Thermo Noran 7). Transmission electron microscopy (TEM) images were obtained using a JEM-2010 microscope operating at acceleration voltage of 200 kV. UV–vis spectra were recorded with a UV–vis spectrometer (Puxi, UV1901), using BaSO4 as the reflectance standard. The luminescence of the powdered samples was measured on a spectrofluorimeter (Hitachi, F7000). The chemical compositions of the samples were tested by an X-ray fluorescence spectrometer (XRF, Rigaku, ZSX Promius). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra XPS system using monochromated Al Kα radiation to study the surface states of the composites.

2.4. Photocatalytic activity

The photocatalytic activities of K4Nb6O17/Ag@AgCl samples under visible light were evaluated by the photocatalytic degradation of RhB in a Pyrex glass reactor with thermostatic water outside, using a 250 W metal halide lamp (Philips) as light source with a UV filter (λ > 400 nm, transmittance > 90%) at a distance of 10 cm from the beaker. Cooling was provided by an external cooling jacket, and the temperature of the reaction was controlled to 25 ± 2 °C. In a typical photocatalytic activity test, reaction suspensions were prepared by adding 0.25 g of photocatalysts to 250 ml of RhB in aqueous solution. Prior to irradiation, the suspensions were kept in the dark for 30 min to obtain equilibrium absorption between the photocatalysts and the dye. The initial concentration used was 10 ppm. During the irradiation process, 3 ml of the suspension was sampled every 10 min and then centrifuged (10,000 rpm, 6 min) to separate the photocatalyst particles. The supernatant was then removed and analyzed by a UV–vis spectrophotometer. The absorbance of RhB was measured at a wavelength of 554 nm. The degradation efficiency (%) was calculated as follows:

\[
\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100\% \tag{1}
\]

where C0 is the initial concentration of RhB, and C is the concentration of dye after irradiation which varies with the irradiation time.

According to a simplified Langmuir–Hinshelwood (L–H) kinetic model [23,24], the photocatalytic RhB degradation can be expressed by the following first order kinetic equation [25]:

\[
-ln \left( \frac{C}{C_0} \right) = k_{app} t \tag{2}
\]

where C0 and C are the concentrations of dye in solution at times 0 and t, respectively, and k is the apparent first-order rate constant (min⁻¹).

3. Results and discussion

3.1. Catalysts characterization

The XRD spectra of the as-prepared samples are given in Fig. 1. Based on Fig. 1, the XRD peaks of potassium niobate (curve a) can be readily indexed to a pure phase of orthorhombic K4Nb6O17, according to JCPDS (21–1295). The main peak appeared at 10.64°, corresponding to the 0 4 0 crystal plane, which indicated that the d value was 0.83 nm. The width of the layered space was calculated to be 0.27 nm by subtracting the layered thicknesses of the Nb6O17 [26] from the d040 value. In contrast, for the prepared H4Nb6O17 (shown in curve b), the main peak of the 0 4 0 crystal face was observed at 11.06°, indicating that the width of the layered space of H4Nb6O17 was 0.245 nm, which was narrower than that of K4Nb6O17. The change can be explained by the replacement of K+ (radius-0.133 nm) by H+ (radius-0.332 nm). Because the radius of H+ is smaller than that of K+, the width of the space decreased. In addition, the results showed evidence of the successful entrance of H+ into the interlayer of K4Nb6O17. As shown in the spectra observed for (C4H9NH3)4Nb6O17 (curve c), the main peak of the 0 4 0 crystal face shifted to 10.29°, indicating that
the width of the layered space of $\left(C_{4}H_{9}NH_{3}\right)_{4}Nb_{6}O_{17}$ was 0.30 nm, which was wider than that of $K_{4}Nb_{6}O_{17}$. 0.03 nm. Compared to the spectra obtained for $K_{4}Nb_{6}O_{17}$ and $H_{2}Nb_{6}O_{17}$, the intensity of the diffraction peaks observed for $\left(C_{4}H_{9}NH_{3}\right)_{4}Nb_{6}O_{17}$ became negligible except for the main peak of 0 40, which may have been due to effect of N-butylamine. XRD spectra for $K_{4}Nb_{6}O_{17}/AgCl$ and $K_{4}Nb_{6}O_{17}/Ag@AgCl$ are also given in Fig. 1, and from these, it was observed that the 0 40 crystal face was shifted to 8.55° and 9.15°, respectively, these changes indicated an increase of the layer space. The 0 40 peak of $K_{4}Nb_{6}O_{17}/Ag@AgCl$ at 9.15° was larger than that of $K_{4}Nb_{6}O_{17}/AgCl$, which may have been due to the photo-reduction of AgCl. Under irradiation, part of AgCl was reduced to Ag0 nanoparticles (NPs) which were uniformly dispersed on the surface of AgCl. Therefore, the layered space of $K_{4}Nb_{6}O_{17}/Ag@AgCl$ was narrower than that of $K_{4}Nb_{6}O_{17}/AgCl$. These results confirmed that AgCl and Ag@AgCl were successfully intercalated into the interlayer space of $K_{4}Nb_{6}O_{17}$.

The XRD patterns of $K_{4}Nb_{6}O_{17}/AgCl$ and $K_{4}Nb_{6}O_{17}/Ag@AgCl$ shown in Fig. 1 were found to be comprised mainly of AgCl phase, which was characterized by the peaks located at 2θ values of 27.8°, 32.2°, 48.3°, 54.8°, 57.4°, 67.4° and 76.7°, corresponding well to cubic phase AgCl according to JCPDS (31-1238). However, the diffraction peaks attributed to metallic Ag could not be easily observed in the reduced composite, which may have been due to the amount and the size of Ag NPs incorporated, which were too small to be detected in the partially reduced Ag@AgCl photocatalysts, similar to the result reported by Ma et al. [27] as observed for Ag–AgCl/WO3.

The SEM images of the (a) $K_{4}Nb_{6}O_{17}$, (b) $K_{4}Nb_{6}O_{17}/Ag@AgCl$ and (c) the EDX for $K_{4}Nb_{6}O_{17}/Ag@AgCl$ are shown in Fig. 2. The layered structure of pure $K_{4}Nb_{6}O_{17}$ is observable in Fig. 2a. Upon introduction of Ag@AgCl, the morphology of the layered structure of the $K_{4}Nb_{6}O_{17}$ was not affected after the microwave assisted intercalation. However, the layered space of the $K_{4}Nb_{6}O_{17}$ was found to be much wider than that of pure $K_{4}Nb_{6}O_{17}$ upon the Ag@AgCl intercalation. In addition, it can be seen from Fig. 2b that Ag@AgCl particles with individual sizes about 100 nm existed in the interlamellar region of $K_{4}Nb_{6}O_{17}$. The typical EDX spectrum obtained from $K_{4}Nb_{6}O_{17}/Ag@AgCl$ is given in Fig. 2c. In the spectrum, peaks associated with Ag, Cl, K, Nb and O were observed. The K, Nb, and O peaks resulted from $K_{4}Nb_{6}O_{17}$, while the Ag and Cl peaks were from AgCl respectively. The EDX results confirmed that the obtained product was composed of $K_{4}Nb_{6}O_{17}$ layered material intercalated with Ag@AgCl.

To further investigate the morphology and structural information, TEM was performed on the samples, and a representative image is shown in Fig. 2d for $K_{4}Nb_{6}O_{17}/Ag@AgCl$. From the TEM imaging, it was observed that the Ag NPs with a diameter of about 10 nm were uniformly dispersed in the layered nanomaterial. Based on the quantum effect and small size effect, the photo-induced electron was transformed to the surface of Ag nanoparticle rapidly and results in an efficient separation of electron–hole pairs. These nanoparticles were thought to give rise to the high photocatalytic activity observed under visible light irradiation.

The elemental content of the as-prepared samples was determined by XRF analysis and are given in Table 1. The K/Nb molar ratio of $K_{4}Nb_{6}O_{17}$ was found to be much higher than that of $K_{4}Nb_{6}O_{17}/AgCl$ and $K_{4}Nb_{6}O_{17}/Ag@AgCl$. This may have indicated that most of the K+ was replaced by H+, while a small amount of K+ still existed in the layered compound, which is in agreement with the expected result [21]. The K+/Nb molar ratio of $K_{4}Nb_{6}O_{17}$ was 77.49:100, which was slightly higher than its stoichiometric ratio of 4:6, due to the excess K2CO3 provided via the high temperature solid phase reaction. Furthermore, the Ag/Cl molar ratio of $K_{4}Nb_{6}O_{17}/Ag@AgCl$ was higher than that of $K_{4}Nb_{6}O_{17}/AgCl$, indicating that Ag NPs were formed on the surface of the AgCl under visible light irradiation, which could broaden the region of visible light absorption in the composite material due to the SPR of Ag NPs, ultimately resulting in an enhanced photodegradation of RhB under visible light irradiation.

The UV–vis absorption spectra of the samples are shown in Fig. 3A. As shown in Fig. 3A, the strong absorption of $K_{4}Nb_{6}O_{17}$ below 400 nm, corresponding to a band gap of approximately 3.1 eV, indicated that the layered material could not absorb visible light. AgCl was reported to have an indirect band gap of 3.25 eV [28], and also could not absorb visible light. Curve b shows the absorption spectrum of $K_{4}Nb_{6}O_{17}/AgCl$, and, compared to curve a, a stronger absorption in visible light region was observed, which may have been attributable to a small amount of silver NPs formed under weak environmental irradiation present during the preparation of the material [28]. Fig. 3A (curve c) shows the UV–vis absorption spectrum of $K_{4}Nb_{6}O_{17}/Ag@AgCl$. The $K_{4}Nb_{6}O_{17}/Ag@AgCl$ exhibited a broader and stronger absorption than that of $K_{4}Nb_{6}O_{17}/AgCl$ in the visible light region. Because of the SPR absorption of $K_{4}Nb_{6}O_{17}/Ag@AgCl$, the absorption peak was slightly red-shifted and became stronger than curve b when AgCl was partly reduced to silver NPs in the interlayer space of potassium niobate. It also indicated that the Ag@AgCl was successfully intercalated into the interlayer space of $K_{4}Nb_{6}O_{17}$. From the spectrum of pure Ag@AgCl (curve d), a showed strong visible light absorption ranging from 400 nm to 700 nm was observed. The broadness of the peak could be explained by the surface plasmon resonance (SPR) effect of Ag NPs, which were produced by the photo-reduction of AgCl [27] and depended not only on the nature of the metal, but also on the size and shape of metallic nanostructures [30,31]. Under irradiation, the shapes and diameters of Ag NPs varied over a large range. As a result, the frequency of the plasmon oscillations covered a wide range to absorb visible light.

![Fig. 1. XRD spectra of (a) $K_{4}Nb_{6}O_{17}$, (b) $H_{2}Nb_{6}O_{17}$, (c) $\left(C_{4}H_{9}NH_{3}\right)_{4}Nb_{6}O_{17}$, (d) $K_{4}Nb_{6}O_{17}/AgCl$, and (e) $K_{4}Nb_{6}O_{17}/Ag@AgCl$.](image)
The excited electron life was further studied by photoluminescence (PL) spectrum. The recombination of electron–hole pair emits photons resulting in photoluminescence. A lower photoluminescence intensity means a lower electron–hole recombination rate, and hence a longer life of photogenerated carriers [32]. Fig. 3B gives the fluorescence spectra of the prepared samples using an ultraviolet light with 250 nm wavelength as an excitation source. As shown, the pure K₄Nb₆O₁₇ showed a strong peak ranging from 325 nm to 425 nm while no obvious emission spectrum was detected from pure Ag@AgCl (curve c). From the emission spectrum of K₄Nb₆O₁₇/Ag@AgCl, it was found that the emission intensity declined drastically upon intercalation of Ag@AgCl due to the matching band potentials between the Ag@AgCl and K₄Nb₆O₁₇ [33]. In addition, this decline may have also been partially due to the in situ generation of Ag₆ NPs on the surface of AgCl. The Ag₆ NPs may have been adopted as electron traps to facilitate the separation of photogenerated electrons and holes efficiently [32,34], therefore the electron–hole recombination rate was decreased. According to Fig. 3A and B, it was inferred that a combined band structure was formed between Ag@AgCl and K₄Nb₆O₁₇, which acted to promote the efficient separation of the photogenerated electrons and holes.

The surface chemical states of K₄Nb₆O₁₇/Ag@AgCl were investigated by X-ray photoelectron spectroscopy (XPS), and the results are given in Fig. 4. From the silver spectra shown in Fig. 4A, two bands of silver were observed at binding energies at 372.7 eV and 366.5 eV and were ascribed to Ag 3d3/2 and Ag 3d5/2, and these bands showed a lower binding energy in comparison with the Ag 3d3/2 and Ag 3d5/2 in AgCl [3], which may be partially due to the interaction among the Ag, AgCl and K₄Nb₆O₁₇. The Ag 3d3/2 peak was deconvoluted into two different peaks at 372.6 eV and 373.4 eV, and the peak of Ag 3d5/2 was deconvoluted into 364.7 eV and 366.5 eV, respectively. The peaks at 372.6 eV and 364.7 eV could be attributed to monovalent Ag (AgCl), while the peaks at 373.4 eV and 366.5 eV could be attributed to the metallic Ag, respectively, conforming that Ag⁺ ions were successfully reduced to metallic Ag via irradiation. From the high resolution XPS spectra of O 1s for Ag@AgCl intercalated K₄Nb₆O₁₇, a broad peak was observed, which was subsequently deconvoluted into two peaks at 531.7 eV and 530.2 eV, respectively. The main peak was attributed to the oxygen lattice (Nb-O) in K₄Nb₆O₁₇, and the other could be ascribed to the hydroxyl oxygen. Furthermore the binding energy of O 1s for the K₄Nb₆O₁₇/Ag@AgCl was slightly higher than that of pure K₄Nb₆O₁₇. This may have been due to the reduced surrounding electron density of oxygen atoms due to the introduction of largely electronegative Cl element into the layered K₄Nb₆O₁₇, which resulted in a decrease in the shielding effect for the oxygen atom, causing the binding energy to be increased. These results from XPS test confirmed that the Ag@AgCl was incorporated into the K₄Nb₆O₁₇ structure.

3.2. Photocatalytic activity under visible light irradiation

The photocatalytic performance of as-prepared samples in terms of photodegradation of RhB molecules under visible light irradiation was investigated, and the results are shown in Fig. 5A. From the observed degradation, the K₄Nb₆O₁₇/Ag@AgCl photocatalyst was found to exhibit excellent photocatalytic activity under visible light irradiation, and almost 94% of RhB was degraded.
after irradiation for 2 h. In contrast the concentration of RhB dye remained unchanged for 2 h under visible light irradiation in the absence of photocatalyst and in the dark controls, respectively. This was suggestive of a purely photocatalytic reaction mechanism. The pure K4Nb6O17 exhibited no photocatalytic activity due to its wide band gap of 3.1 eV. For comparison, the photocatalytic activity of K4Nb6O17/AgCl and an equivalent amount of Ag@AgCl (calculated based on the equivalent Ag@AgCl content in K4Nb6O17/Ag@AgCl) were also studied under the same conditions. The results demonstrated that K4Nb6O17/AgCl catalyst showed limited photocatalytic activity during the initial stages of the photodegradation of RhB, because AgCl did not produce the photoelectrons and holes due to its large band gap of 3.25 eV. However, after 40 min reaction, the photocatalytic activity of K4Nb6O17/AgCl was rapidly enhanced. This was thought to be attributable to the generation of Ag NPs on the surface of AgCl during visible light irradiation, which broadened the visible light response of the composite. The Ag@AgCl catalyst had a much slower degradation rate than that of K4Nb6O17/Ag@AgCl. The typical evolution of the absorption spectra of RhB under visible light irradiation was also studied, and the results are shown in Fig. 6B. The characteristic absorption peaks of RhB at 554 nm were found to diminish with increasing time up to 120 min, indicating complete degradation of RhB occurred over the course of the reaction. The results presented in Fig. 5 suggested that the Ag@AgCl intercalated K4Nb6O17 exhibited high photocatalytic activity when irradiated under visible light due to the existence of Ag@AgCl and the associated SPR effect.

The stability of the K4Nb6O17/Ag@AgCl was investigated through the cyclic degradation of RhB under visible light irradiation as shown in Fig. 6. It can be seen from Fig. 6A that the high photocatalytic performance of K4Nb6O17/Ag@AgCl was effectively maintained after 5 cyclic experiments. A 9.3% decrease in the photodegradation of RhB between the first run and the fifth run (94.0–85.3%, respectively), indicated that K4Nb6O17/Ag@AgCl had high stability under visible light. The slight decrease of the activity during the repeated runs was thought to be due to the loss of the catalyst during the photocatalytic trials as suggested by other researchers [35].

The XRD pattern of the samples used for consecutive photodegradation experiments (Fig. 6B) indicated that the crystal structures of K4Nb6O17/Ag@AgCl did not obviously change, though the single AgCl component is usually unstable under light irradiation. As shown in Fig. 6B, for the used K4Nb6O17/Ag@AgCl, the peak at 38.13°, assigned to AgCl corresponding to 111 crystal plane became stronger in the diffraction pattern. The presence of this peak could result in an inhibition of the further decomposition of AgCl under visible light irradiation and an acceleration of charge transfer. All the above results indicate that the reported K4Nb6O17/Ag@AgCl is an active and stable visible-light-driven plasmonic catalyst, which may serve as a promising candidate for practical use in the degradation of hazardous pollutants in water.
4. Proposed mechanism

4.1. Roles of reactive species

To further evaluate the role of reactive species, a series of quenchers were used to scavenge the relevant reactive species. Isopropanol was added to the reaction system as an -OH scavenger [9], benzoquinone [36] was adopted to quench $O_2^{-}$, and NaHCO$_3$ was introduced as the scavenger for the adsorbed -OH radical and holes [37]. As shown in Fig. 7, the catalytic activity was slightly enhanced with the addition of NaHCO$_3$ to the reaction. This was attributed to the promoted scavenging of holes and the improved separation of photogenerated electrons and holes [38]. This result implies that the absorbed -OH radicals and holes are not the dominant reactive species in the photocatalytic oxidation process. In addition, the $k_{app}$ of RhB decreased from 0.018 min$^{-1}$ to 0.004 min$^{-1}$ and 0.006 min$^{-1}$, respectively, with the addition of benzoquinone and isopropanol. This results demonstrate that $O_2^{-}$ and -OH radicals were produced and acted as reactive species in the RhB photocatalytic degradation under visible light irradiation.

4.2. Proposed mechanism

The possible reaction mechanism of the photocatalytic process by the K$_4$Nb$_6$O$_{17}$/Ag@AgCl catalyst is proposed in Fig. 8. As shown in Fig. 8, a possible mechanism of photocatalytic action of the K$_4$Nb$_6$O$_{17}$/Ag@AgCl was proposed as follows: under visible light irradiation, a visible light photon could be absorbed by a silver nanoparticle, causing the conduction electron in the Ag NP to oscillate coherently with the oscillating electric field, generating a hole and an electron in the Ag NP such that the electron was transferred to the surface of Ag NP [3,39] and then inject into the CB of K$_4$Nb$_6$O$_{17}$ through the Schottky barrier formed at the Ag/K$_4$Nb$_6$O$_{17}$ interface [40], and the electric field in the space charge layer could promote transport of excited electrons at the Ag surface (i.e. at the Ag/K$_4$Nb$_6$O$_{17}$ interface) to the K$_4$Nb$_6$O$_{17}$ bulk. Therefore, such electrons transfer from Ag to K$_4$Nb$_6$O$_{17}$ should be possible, and similar processes were also proposed in Ag–AgCl–TiO$_2$ [41] and Ag/AgCl/TiO$_2$ [42] systems. Besides, the photo-generated electrons transfer from Ag to CB of K$_4$Nb$_6$O$_{17}$ can also be explained by
An irradiation.
The followings are catalytic species of K4Nb6O17 [46,42], which are likely terminated by Cl− ions, and therefore negatively charged [44]. So, the hole was transferred to the surface of AgCl [3,44], leading to the formation of ClO atoms from the oxidation of Cl− ions. The ClO atoms are powerful reactive radial species that can attack organic pollutants adsorbed on the surface of the photocatalyst and simultaneously be reduced to Cl−. The reduced Cl− can subsequently combine with Ag+ to regenerate AgCl again [35,45]. The holes located on the surface of AgCl will also combine with H2O molecules adsorbed on the surface of the catalyst to produce -OH radicals. The presence of these -OH radicals was confirmed in this study via quenching experiments, and these species were thought to induce the degradation of RhB in the reaction. The detailed reactions are described by Eqs. (3)–(11) as follows [46,42]:

\[
\begin{align*}
\text{AgNPs} + \text{hv(Visible light)} & \rightarrow \text{AgNPs}^+ \\
\text{AgNPs}^+ + \text{K4Nb6O17} & \rightarrow \text{AgNPs}^+(h^+) + \text{K4Nb6O17}(e^-) \\
e^- + \text{O}_2 & \rightarrow \text{O}_2^- \\
\text{h}^+ + \text{OH}^- & \rightarrow \cdot\text{OH} \\
\text{h}^+ + \text{AgCl} & \rightarrow \text{Ag}^+ + \text{Cl}^- \\
\text{O}_2^- + \text{RhB} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\cdot\text{OH} + \text{RhB} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{Cl}^0 + \text{RhB} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- \\
\text{Ag}^+ + \text{Cl}^- & \rightarrow \text{AgCl}
\end{align*}
\]

As a result of these discussed mechanisms, the photogenerated electron–hole pairs were separated efficiently, the activity was kept at a high level and, more importantly, the stability of K4Nb6O17/Ag@AgCl was ensured.

5. Conclusions

Ag@AgCl intercalated K4Nb6O17 photocatalysts were successfully synthesized by an ion-exchange method using a microwave-assisted synthesis. The as-prepared photocatalysts exhibited higher photocatalytic activity than that of K4Nb6O17/AgCl and an equivalent amount of Ag@AgCl for the degradation of RhB under visible light irradiation. The prepared photocatalyst showed good stability upon reuse for up to five cycles, and this was thought to be due to the surface plasmon resonance of silver NPs formed on the surface of AgCl and the effect of intercalation, as considered in the proposed mechanism. Due to its excellent activity and stability, as-prepared K4Nb6O17/Ag@AgCl is a promising visible light photocatalyst for the photodegradation of organic pollutants in wastewater.

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