

Research Article

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Synthesis of Ag@AgCl modified anatase/rutile/brookite mixed phase TiO₂ and their photocatalytic property

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Abstract: Pure and Ag@AgCl modified TiO₂ were synthesized by one-step hydrothermal method, which exhibit anatase/rutile/brookite (A/R/B) triphasic structure. The photocatalysts were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope, X-ray photoelectron spectroscopy, photoluminescence, electrochemical impedance spectroscopy, photocurrent response, and diffuse reflectance spectroscopy, and the photocatalytic activity was evaluated by taking 100 mL (10 mg/L) methylene blue (MB) aqueous solution as the target pollutant. The results show that Ag@AgCl modification is beneficial for the separation of photogenerated charges and the absorption in visible region. The degradation degree of MB increases from 75.7% for pure TiO₂ to 97.3% for Ag@AgCl modified TiO₂.

Keywords: TiO₂, triphasic structure, Ag@AgCl modification, photocatalytic activity

1 Introduction

As one of the new green environmental protection technologies, photocatalytic technology can be applied for the degradation of organic pollutants [1–5]. Among many photocatalytic materials, TiO₂ shows the advantages of

low cost, mild reaction conditions, high chemical stability, and no secondary pollution [6–10]. However, due to the shortcomings of TiO₂, such as low sunlight utilization and fast recombination of photogenerated charges, its photocatalytic degradation effect is greatly limited [11–13]. When noble metals and semiconductors are combined, Schottky junctions will be formed on the interfaces, which promote the separation of photogenerated electrons and holes. On the other hand, the surface plasmon resonance (SPR) of noble metal can enhance visible light absorption, advancing the photocatalytic performance [14–17]. Moreover, Ag@AgCl modification can further improve the photocatalytic activity on the basis of Ag modification. Wang *et al.* [18] prepared Ag@AgCl/TiO₂ photocatalyst and found that the recombination of photoinduced electrons and holes is retarded and the absorption in visible region is enhanced through Ag@AgCl modification. Therefore, Ag@AgCl/TiO₂ shows higher photocatalytic activity than pure TiO₂ and Ag/TiO₂.

It is generally believed that TiO₂ with mixed crystal exhibits better photocatalytic performance than single structure owing to the mixed crystal effect. Anatase/rutile TiO₂ is the focus of mixed TiO₂ and has been widely studied. Basis of two-phase mixed crystal, anatase/rutile/brookite triphasic TiO₂ exhibits higher photocatalytic activity than two-phase and monophase TiO₂ [19–21]. It is reported by Mutuma *et al.* [22] that the photocatalytic activity of anatase/rutile/brookite three-phase mixed crystal TiO₂ is higher than that of anatase/rutile two-phase mixed crystal TiO₂.

In our previous work, it has been proved that the anatase/rutile/brookite triphasic TiO₂ shows better activity than two-phase and monophase TiO₂ [20]. In the present work, the advantages of TiO₂ with triphase and Ag@AgCl modification were combined to prepare Ag@AgCl modified anatase/rutile/brookite TiO₂ composite by one-step hydrothermal method. The effect of Ag@AgCl modification on the structure and photocatalytic performance of anatase/rutile/brookite triphasic TiO₂ were investigated.

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2 Experimental

2.1 Synthesis of photocatalyst materials

Polyethylene glycol (analytical reagent, AR), butyl titanate (AR), anhydrous ethanol (AR), hydrochloric acid (AR), silver nitrate (AR), and methylene blue (MB) (AR) were purchased from Chengdu Kelong Chemical Reagent Factory (PR China).

10 mL of butyl titanate was added to 30 mL anhydrous ethanol to obtain solution A. 30 mL of deionized water, 1 mL of hydrochloric acid, and 1 mL of polyethylene glycol were mixed evenly to obtain solution B, which was added to solution A dropwise to obtain a mixture. Then, the mixture was transferred to a hydrothermal reaction kettle for hydrothermal treatment at 190°C for 15 h. The obtained powder was washed several times to neutral, and dried at 80°C in an oven. Finally, after grinding, the pure TiO₂ was prepared, which is marked as ARB.

Ag@AgCl modified TiO₂ marked as Ag@AgCl-ARB can be obtained by adding certain amount of AgNO₃ in solution B, and keeping the other steps same as the preparation procedure of ARB. The molar ratio of Ag/Ti is 2%.

2.2 Characterization

The crystal structure and phase information were studied by X-ray diffraction (XRD) using a DX-2700 X-ray diffractometer with Cu K α radiation as the X-ray source, the scan range 2θ was 20–70° and scan speed was 0.06°/s (Dandong Haoyuan Instrument Co. Ltd, Dandong, China). The morphology was observed by a JEM-F200 transmission electron microscope (TEM and HRTEM) and a Hitachi SU8220 scanning electron microscope (SEM) (FEI Company, Hillsboro, OR, USA). The composition and valence of elements were analyzed by an XSAM800 multifunctional surface analysis system (X-ray photoelectron spectroscopy, XPS) (Thermo Scientific K-Alpha, Kratos Ltd, Manchester, UK). The photoluminescence (PL) spectra were measured using an F-4600 fluorescence spectrum analyzer with an Xe lamp at an excitation wavelength of 320 nm (Shimadzu Group Company, Kyoto, Japan). The photocurrent response (PC) and electrochemical impedance spectroscopy (EIS) were measured by a DH-7000 electrochemical workstation (Beijing Jinyang Wanda Technology Co., Ltd, Beijing, China). The optical absorption was analyzed by a UV-3600

ultraviolet-visible spectrophotometer (Shimadzu Group Company, Kyoto, Japan).

2.3 Photocatalytic activity test

The photocatalytic activity of samples was evaluated by measuring the decomposition of MB. 100 mL of 10 mg/L MB aqueous solution and 0.05 g sample powder were mixed together and stirred in dark for 30 min to achieve adsorption–desorption equilibrium. Then, the irradiation was carried out using a 250 W Xe lamp as the light source. After centrifugal separation, the solution was taken every 15 min and the absorbance at 664 nm was measured. The degradation degree was calculated by formula $(A_0 - A_t)/A_0 \times 100\%$.

On the basis of the MB degradation system, 2 mL (0.1 mol/L) of *p*-benzoquinone (BQ, $\cdot\text{O}_2^-$ trapping agent), isopropanol (IPA, $\cdot\text{OH}$ trapping agent), and ammonium oxalate (AO, h^+ trapping agent) were added to investigate the active species.

3 Results and discussion

3.1 Phase composition

Figure 1 presents the XRD patterns of samples. The diffraction peaks of ARB at 25.4, 38.0, and 48.0° are indexed

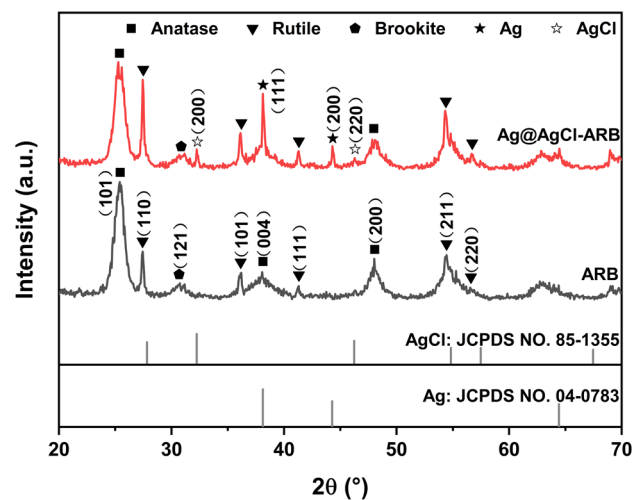


Figure 1: XRD patterns of the samples.

to the (101), (004), and (200) planes of anatase. The diffraction peaks at 27.4, 36.2, 41.3, 54.4, and 56.6° are indexed to the (110), (101), (111), (211), and (220) planes of rutile. In addition, the diffraction peak corresponding to the (121) planes of brookite appears at 31.1°, implying that the prepared ARB is composed of three phases, namely, anatase, rutile, and brookite [23]. As for Ag@AgCl-ARB, besides the anatase, rutile, and brookite phase, new diffraction peaks at 38.1 and 44.4° are indexed to the (111) and (200) planes of metallic Ag [24], and peaks at 32.3 and 46.3° correspond to the (200) and (220) planes of AgCl, respectively [19].

3.2 Morphology

Figure 2 depicts the SEM images of ARB and Ag@AgCl-ARB. Both the samples are irregular in shape and ranging in size from ten to tens of nanometers. ARB and Ag@AgCl-ARB present almost the same morphology, implying that Ag@AgCl modification has no distinct influence on the morphology. Figure 2(c) and (h) are the element mappings of Ag@AgCl-ARB. The Ag@AgCl-ARB is mainly composed of Ti, O, Ag, and Cl, distributed uniformly in the sample, which demonstrates that Ag and Cl elements are present in Ag@AgCl-ARB.

Figure 3 shows TEM and HRTEM images of the samples. From Figure 3(a), it can be observed that the single particle is roughly granular, and the size is between 10–20 nm. The crystal plane spacings marked in Figure 3(c) 0.35, 0.32, and 0.29 nm can be attributed to the (101) plane of anatase, the (110) plane of rutile, and the (121) plane of brookite [20,25,26], respectively, indicating that ARB consists of anatase, rutile, and brookite phase, which is in accordance with the XRD results. Figure 3(d) shows the HRTEM images of Ag@AgCl-ARB, the crystal lattice fringes 0.35, 0.32, and 0.29 nm correspond to the crystal plane of anatase (101), rutile (110), and brookite (121), respectively.

3.3 Element composition

Figure 4(a) shows the full XPS spectra of ARB and Ag@AgCl-ARB. The Ag@AgCl-ARB is mainly composed of Ti, O, Ag, and Cl. No other impurity peaks were detected in ARB and Ag@AgCl-ARB, indicating the high purity of samples. Figure 4(b) shows the high resolution spectra of Ti 2p. Two peaks at 458.4 and 464.1 eV in the

spectrum of ARB are indexed to Ti 2p_{3/2} and Ti 2p_{1/2}, verifying that the Ti element exists in 4+ valence state [27,28]. In Figure 4(c), the O 1s peaks of ARB are located at 529.6 and 530.3 eV, corresponding to lattice oxygen (O²⁻) and surface hydroxyl group (OH⁻), respectively [28]. After Ag@AgCl modification, the binding energies of Ti 2p and O 1s shift to lower position, which can be ascribed to the interaction between Ag, Cl elements, and Ti, O elements [29,30]. The peaks at Ag 3d_{5/2} 366.7 and Ag 3d_{3/2} 372.8 eV are attributed to metals Ag⁰ and Ag⁺ in Figure 4(d) [31,32]. As demonstrated in Figure 4(e), the characteristic peaks of Cl 2p_{3/2} and Cl 2p_{1/2} of Cl element are located at 197.5 and 199.0 eV, respectively, which indicate that Cl element is in -1 valence state [31].

3.4 Photogenerated charges separation analysis

Figure 5(a) shows the PL spectra of samples. Since the PL peaks are responsible for the recombination between photogenerated electrons and holes, the stronger the PL peak intensity, the higher the recombination of photogenerated charge [33]. Compared with ARB, although the PL peak positions of Ag@AgCl modified ARB does not change, the peak intensity is significantly lower than that of ARB, implying that Ag@AgCl modification retards the recombination effectively.

Figure 5(b) shows the EIS Nyquist plots of ARB and Ag@AgCl-ARB. According to Nyquist theorem, the arc radius of Ag@AgCl-ARB is smaller than ARB, which indicates that Ag@AgCl-ARB possesses lower charge movement resistance [34–36]. Figure 5(c) shows the PC curves of samples. Generally, the higher the photocurrent, the stronger the photoinduced electrons and holes separation ability [35,37]. Both ARB and Ag@AgCl-ARB produce photocurrent under light irradiation. Nevertheless, Ag@AgCl-ARB shows higher photocurrent density, implying that Ag@AgCl modification is beneficial to the separation of photoinduced charges. The electrochemical test results are consistent with PL spectra.

3.5 Optical absorption analysis

Figure 6 presents the UV-visible absorption spectra and band gap of the samples. It can be found in Figure 6(a) that the absorption edges of ARB and Ag@AgCl-ARB are basically the same, both showing absorption edges at

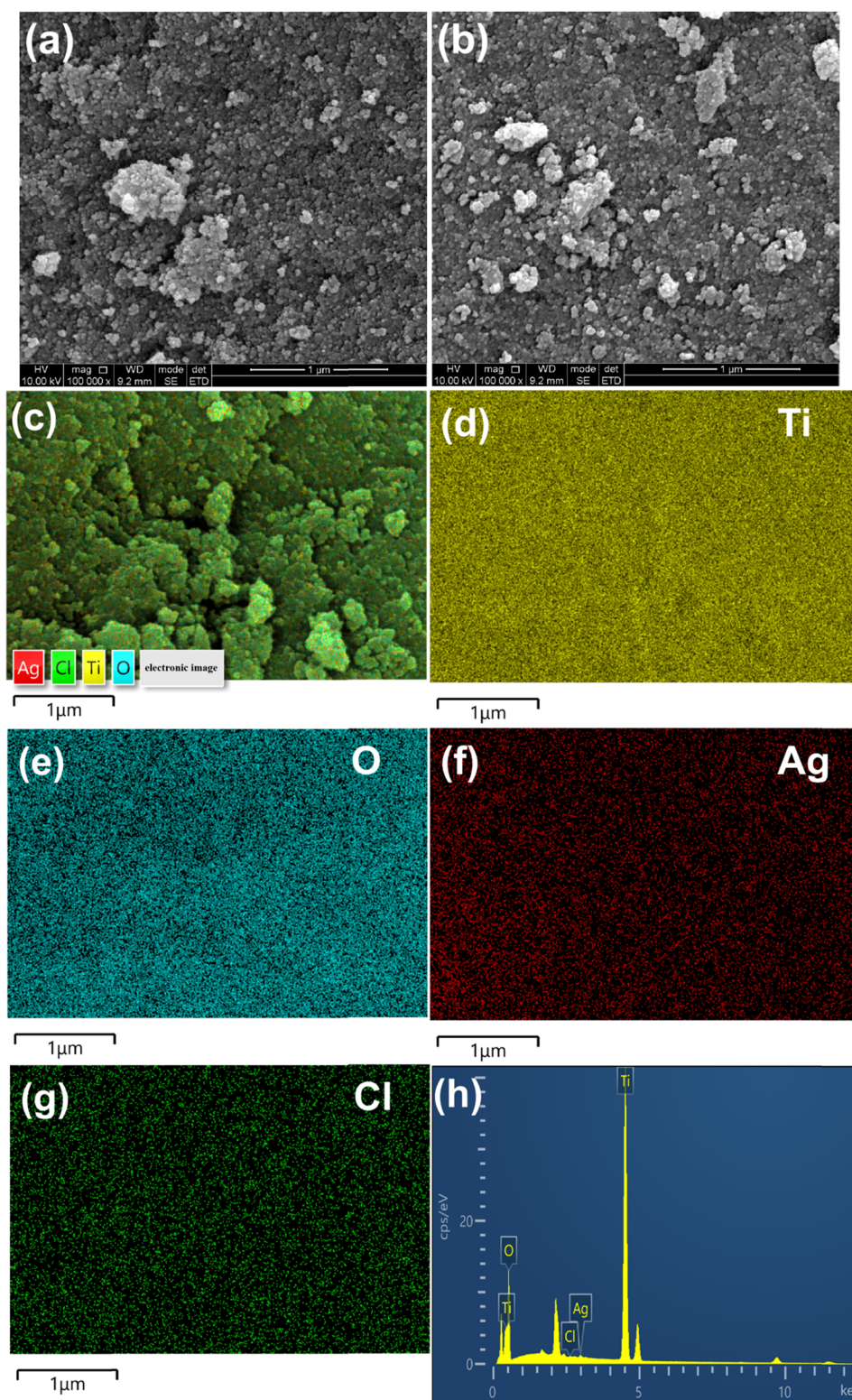


Figure 2: SEM images of ARB (a), Ag@AgCl-ARB (b), element mappings (c–g), and EDS analysis of Ag@AgCl-ARB (h).

400 nm approximately. Figure 6(b) shows the $(\alpha h\nu)^{1/2}$ – $h\nu$ curves of the samples. The band gap width of the semiconductor can be estimated by Tauc-plot [38–40]. The

gap width of Ag@AgCl-ARB (2.84 eV) is smaller than that of ARB (2.93 eV). In the visible region, Ag@AgCl-ARB shows higher absorption than that of ARB, indicating

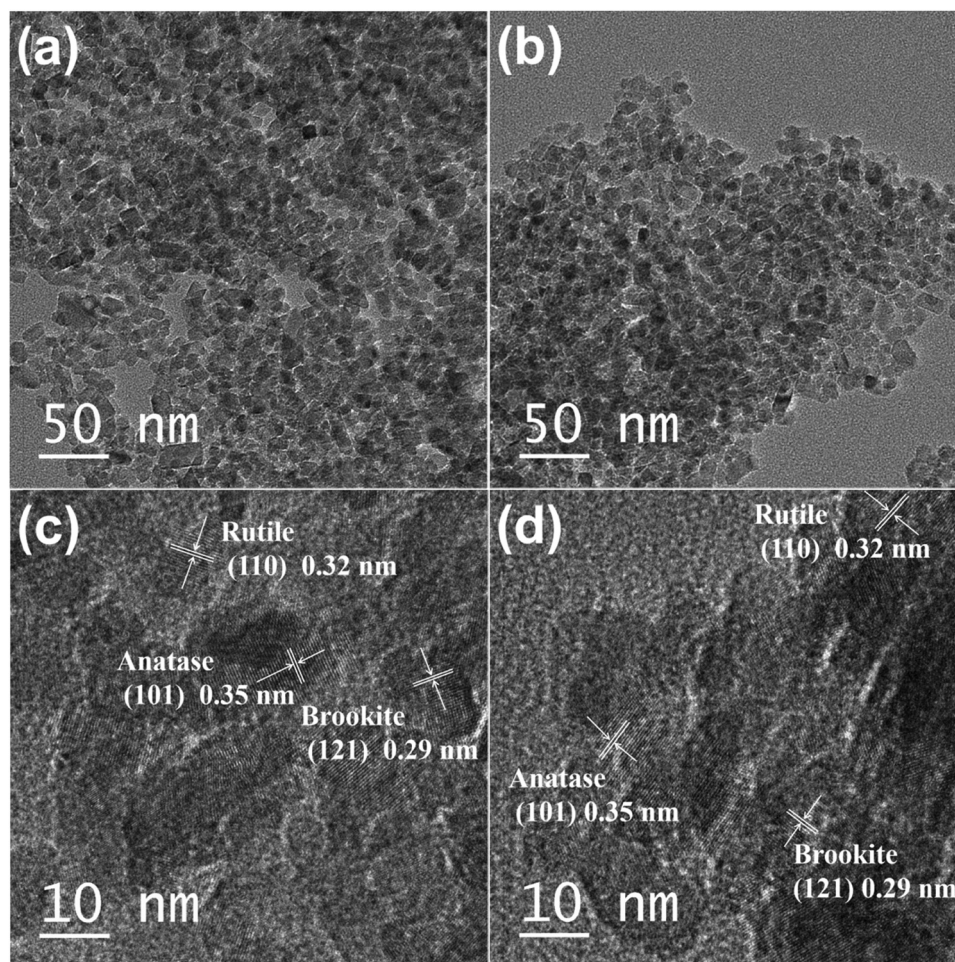


Figure 3: TEM images of ARB (a), Ag@AgCl-ARB (b), HRTEM images of ARB (c), and Ag@AgCl-ARB (d).

that the plasma resonance effect caused by Ag particles is beneficial to increasing the absorption of visible light [41].

3.6 Photocatalytic activity

Figure 7(a) presents the degradation degree curves of MB. The self-degradation of MB without photocatalyst is 8%, which is relatively low in the degradation process. Therefore, the degradation of MB is mainly derived from the presence of photocatalysts under irradiation. After illumination for 60 min, the degradation degree of MB by ARB is 75.7%, and it is 97.3% for Ag@AgCl-ARB, indicating that the photocatalytic efficiency is significantly improved for Ag@AgCl modification. For comparison, Ag-ARB (Ag/Ti = 2%) was prepared, which shows a degradation degree of 86.5%. It is proved that Ag

modification improves the photocatalytic activity of TiO_2 , but the effect is inferior to Ag@AgCl modification.

The kinetics fitting results are shown in Figure 7(b). It can be found that the time t shows a linear relationship with $-\ln(C/C_0)$, which suggests that the reaction of photocatalytic degradation of MB conforms to the first-order reaction [42]. The higher the reaction rate constant, the higher the photocatalytic activity. The first-order reaction rate constants of ARB, Ag-ARB, and Ag@AgCl-ARB are 0.022, 0.032, and 0.055 min^{-1} , respectively. Ag@AgCl-ARB shows the highest k value, which is in line with the photocatalytic degradation results.

To study the reusability of Ag@AgCl-ARB photocatalyst, the cycling experiment of degradation MB was carried out. The experimental results are shown in Figure 8. As the number of cycles increases, the degradation degree of MB decreases slightly. After 5 cycles, the degradation degree of Ag@AgCl-ARB composite decreases from 97.3 to 85.2%.

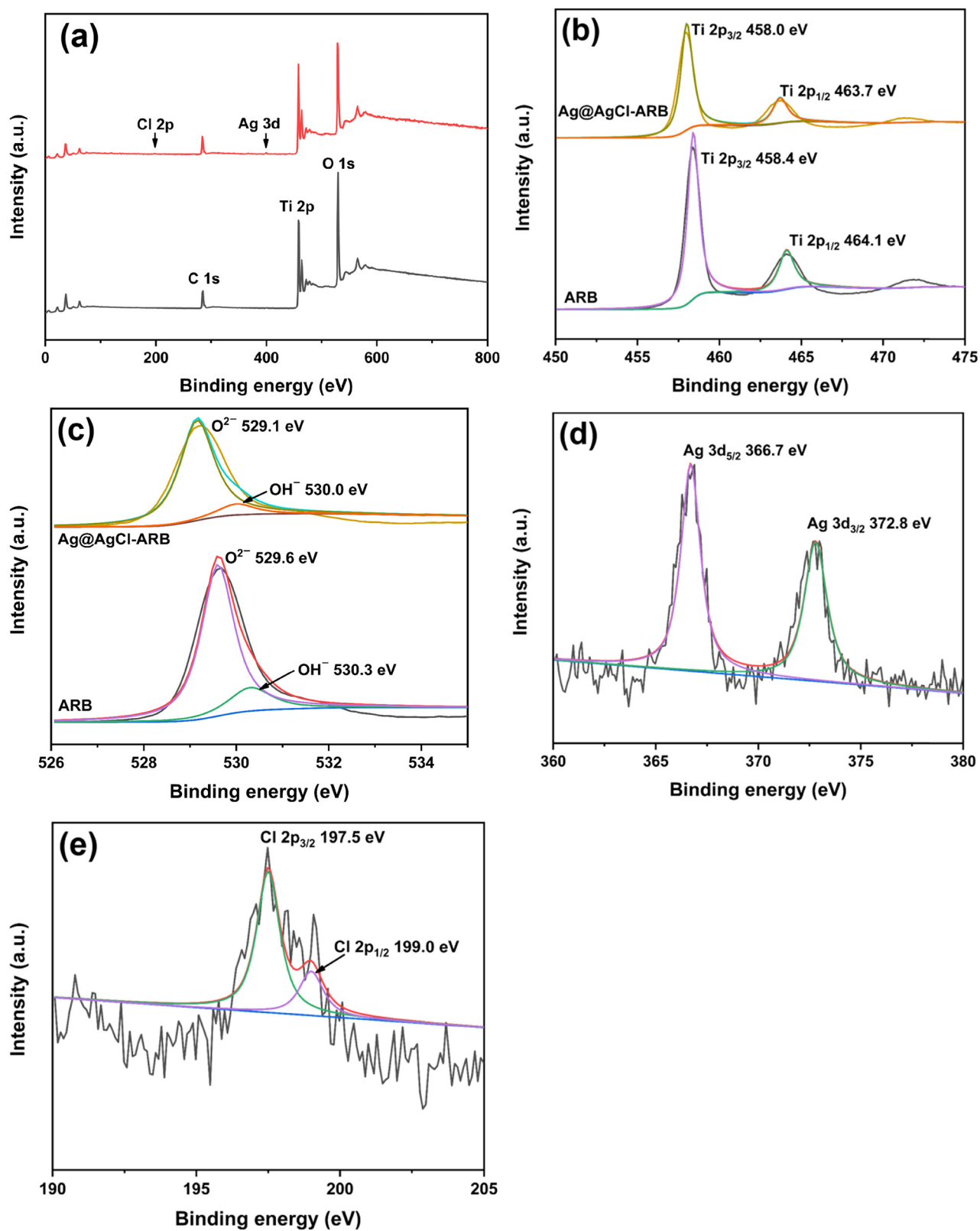


Figure 4: XPS survey of ARB and Ag@AgCl-ARB (a), high resolution spectra of Ti 2p (b), O 1s (c), Ag 3d (d), and Cl 2p (e).

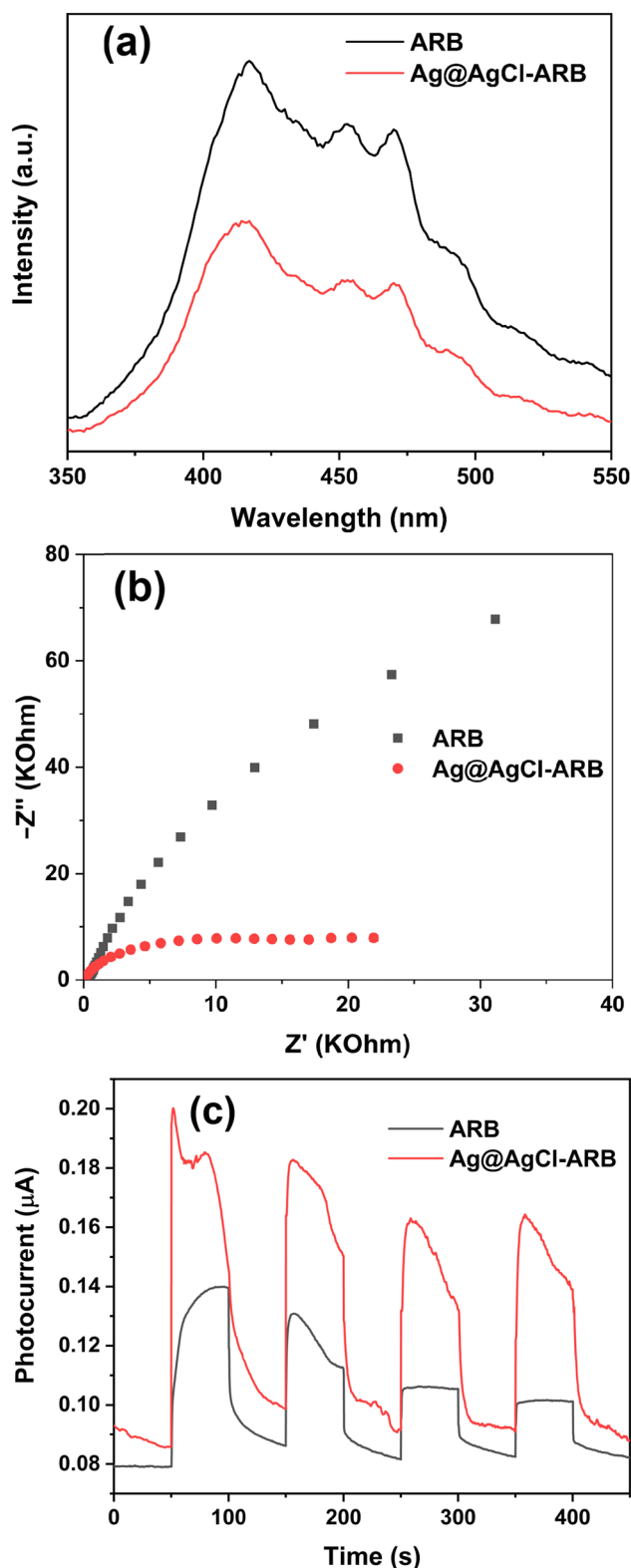


Figure 5: PL spectra (a), EIS (b), and PC curves (c) of ARB and Ag@AgCl-ARB.

The XRD pattern of Ag@AgCl-ARB composite photocatalyst after five cycles is shown in Figure 9. Compared with the initial sample, it is found that the diffraction peak intensity of AgCl (200) crystal plane at 32.3° decreases after cycle experiment, implying that part of AgCl is decomposed during the photocatalytic experiment [43]. The positions of other peaks are unchanged; however, the peak intensity decreases slightly, which may be caused by a small amount of undegraded MB molecules covering the surface of Ag@AgCl-ARB [44,45]. Meanwhile, it also causes the decline in photocatalytic activity, which is consistent with the cycling experimental results.

Inductively coupled plasma optical emission spectrometer was used to investigate the silver ion leached out from the photocatalyst in the supernatant after reaction. It is measured to be 0.0660 ± 0.0003 mg/L in the solution, indicating that a small amount of Ag ion was leached into the solution.

3.7 Photodegradation mechanism

Figure 10 shows the results of active group capture experiment of Ag@AgCl-ARB. After adding BQ, IPA, and AO in MB degradation system, the order of photocatalytic degradation degrees of MB in the samples are BQ (30.8%) < IPA (76.5%) < AO (84.2%) < no Scavenger (97.3%), which suggests that $\cdot O_2^-$ is the main active species, while $\cdot OH$ and h^+ are the secondary active species.

The formation of $\cdot O_2^-$ was further verified by the nitro blue tetrazole (NBT) experiment. Figure 11(a) shows the absorbance curves of Ag@AgCl-ARB. With the increase in illumination time, the absorbance of NBT decreases gradually, which verifies the formation of $\cdot O_2^-$ species [46–48]. Figure 11(b) shows the NBT absorbance curves of ARB and Ag@AgCl-ARB after 30 min irradiation. The NBT absorbance of Ag@AgCl-ARB is lower than that of ARB, indicating that more $\cdot O_2^-$ species are generated in Ag@AgCl-ARB photocatalyst compared to ARB, which is consistent with the PL spectra.

The band potential can be estimated through the electronegativity equation of $E_{CB} = X - E_0 - E_g/2$ and $E_{VB} = E_g + E_{CB}$, where E_{VB} is the valence band potential, E_{CB} is the conduction band potential, E_0 is the free electron energy on the hydrogen scale ($E_0 = 4.5$ eV), E_g is the bandgap energy of the photocatalytic material, and X is the absolute electronegativity of the semiconductor [49–51]. Based on the DRS result (the band gap of

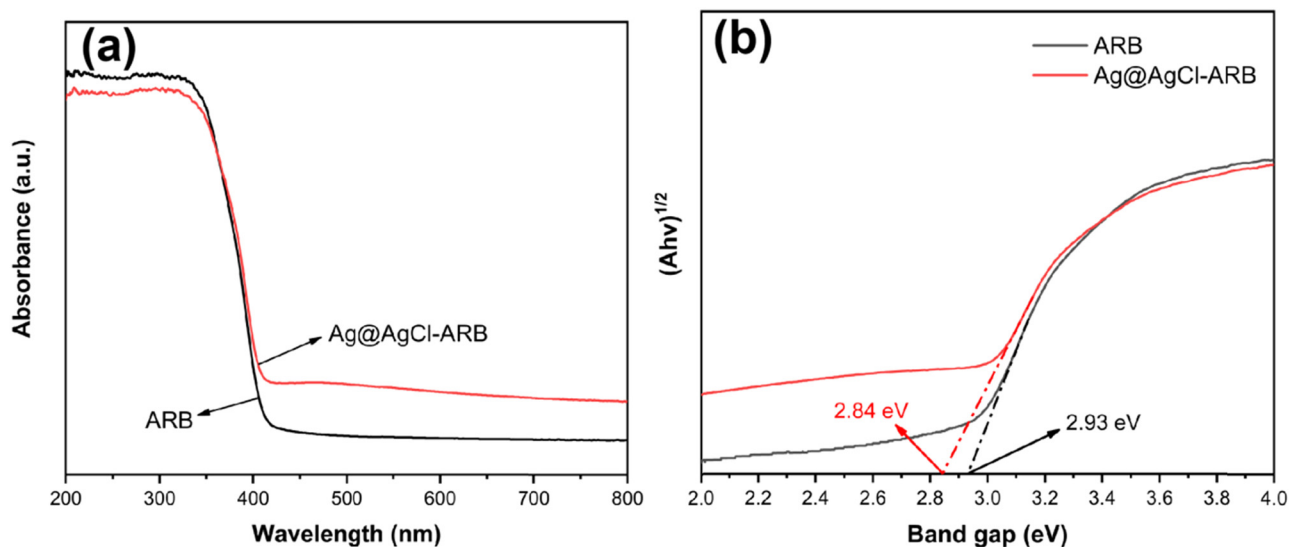


Figure 6: UV-visible absorption spectra (a) and band gap (b) of the samples.

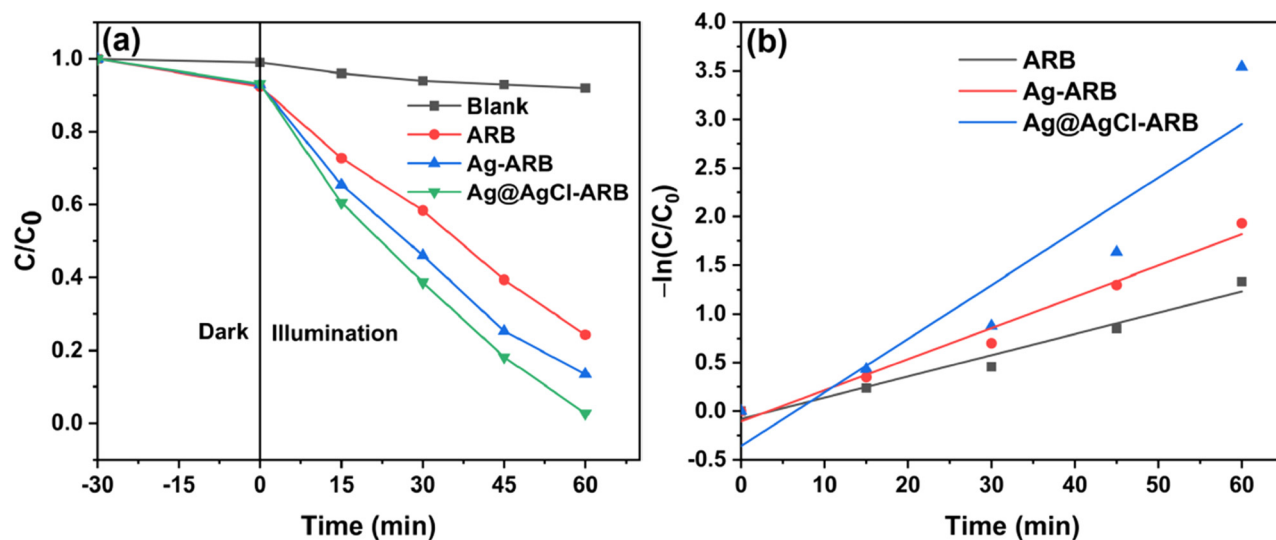


Figure 7: Degradation degree curves (a) and kinetic curves (b) of ARB, Ag-ARB, and Ag@AgCl-ARB.

ARB = 2.93 eV), the E_{CB} and E_{VB} of ARB are -0.15 and 2.78 eV, respectively. ARB consists of anatase, rutile, and brookite, and brookite shows the highest conduction band, followed by anatase and rutile [20,44,52,53]. On the other hand, the E_{CB} and E_{VB} of AgCl are determined to be -0.06 and 3.2 eV [54]. Based on the above content, a possible mechanism of the photogenerated charges separation and transfer for Ag@AgCl-ARB is proposed, as shown in Figure 12. In UV light region, photogenerated charges are generated, as TiO₂ is three phase mixed crystal structure, which can accelerate the migration of

carriers [52,53]. Moreover, the conduction bands of TiO₂ and AgCl are higher than the Fermi level of metallic Ag, and the photogenerated electrons generated in TiO₂ and AgCl will transfer to Ag particles, further inhibiting the recombination [54–57]. In visible light region, due to the SPR effect of Ag, the hot-electrons generated in Ag particles can be transferred to the conduction band of TiO₂ and AgCl, which are captured by O₂ to generate $\cdot O_2^-$ radicals, advancing the photocatalytic activity [58]. On the other hand, the holes will oxidize Cl[−] to form Cl⁰ radicals, which also contributes to the

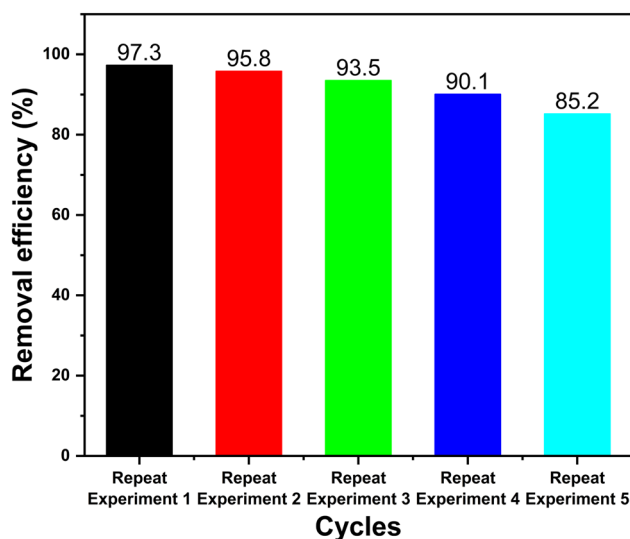


Figure 8: The reuse experiment of Ag@AgCl-ARB photocatalyst for MB degradation.

improvement in the photocatalytic activity [18,59]. Consequently, Ag@AgCl-ARB exhibits the best photocatalytic performance.

4 Conclusion

ARB and Ag@AgCl-ARB were prepared by one step hydrothermal method. ARB shows a three-phase mixed crystal structure composed of anatase, rutile, and brookite. Ag@AgCl modification does not change the crystal structure of ARB. The formation of Ag@AgCl-ARB heterojunctions is advantageous to the separation of photo-generated charges and the absorption of visible light,

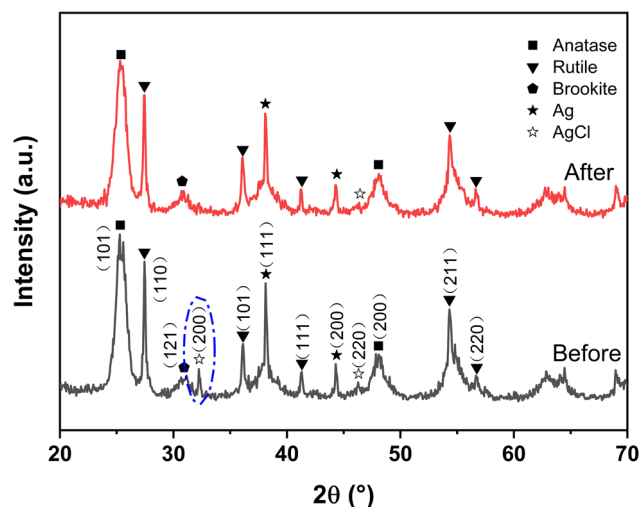


Figure 9: XRD patterns of Ag@AgCl-ARB photocatalyst before and after the photocatalytic experiment.

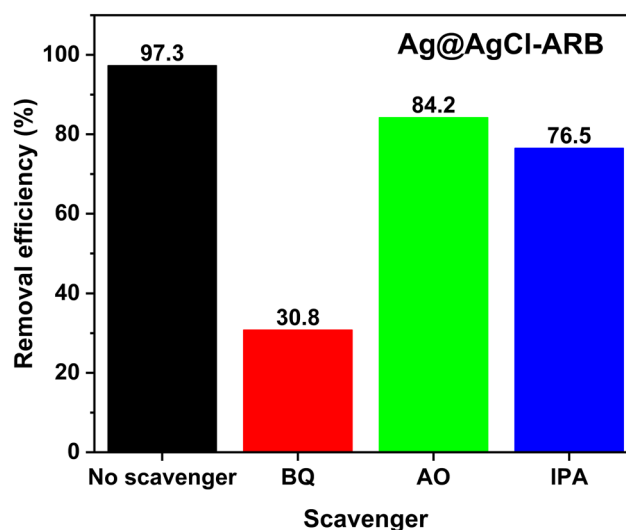


Figure 10: Active species experiment of Ag@AgCl-ARB.

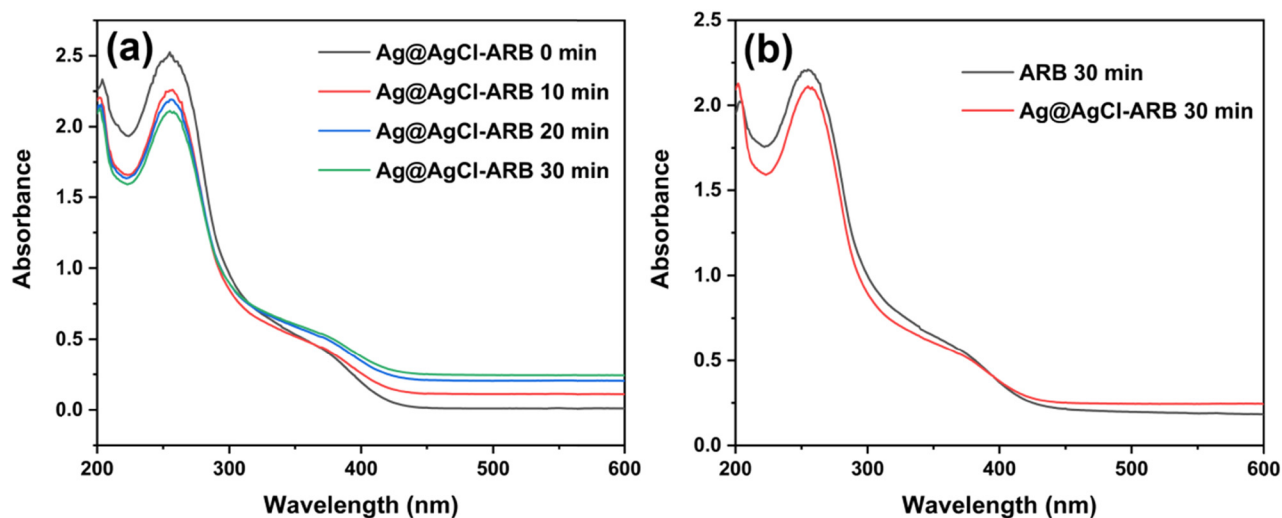


Figure 11: The NBT absorbance curves of Ag@AgCl-ARB with increasing time (a) and the comparison of ARB and Ag@AgCl-ARB (b).

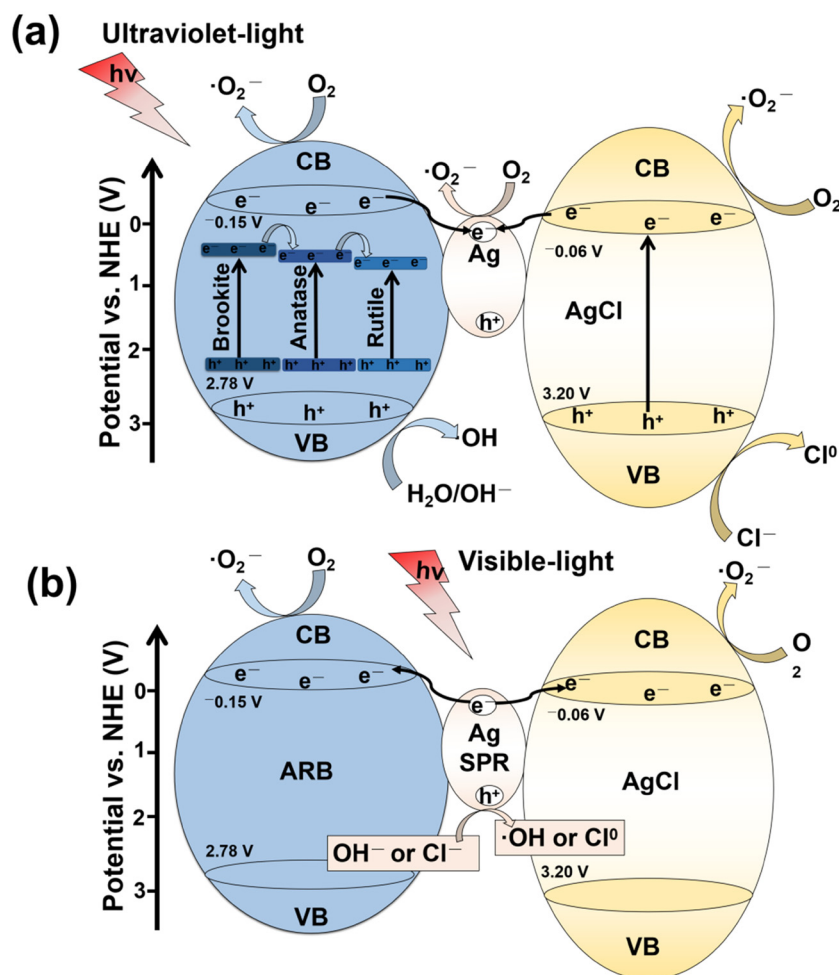


Figure 12: Schematic illustration of the charge separation and transfer in the Ag@AgCl-ARB photocatalysts under ultraviolet light (a) and visible light irradiation (b).

which can be explained by the fact that Ag@AgCl-ARB exhibits the highest photocatalytic activity.

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