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Synthesis of $AgBr/Ti_3C_2@TiO_2$ ternary composite for photocatalytic dehydrogenation of 1,4-dihydropyridine and photocatalytic degradation of tetracycline hydrochloride

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In this work, $AgBr/Ti_3C_2@TiO_2$ ternary composite photocatalyst was prepared by a solvothermal and precipitation method with the aims of introducing Ti_3C_2 as a cocatalyst and TiO_2 as a compositing semiconductor. The crystal structure, morphology, elemental state, functional groups and photoelectrochemical properties were studied by XRD, SEM, TEM, XPS, FI-IR and EIS. The photocatalytic performances of the composites were investigated by the photodehydrogenation of diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (1,4-DHP) and the photodegradation of tetracycline hydrochloride (TCH) under visible light irradiation (λ > 400 nm). The $AgBr/Ti_3C_2@TiO_2$ composite photocatalyst showed enhanced photocatalytic performance in both photocatalytic reactions. The photocatalytic activity of the composite photocatalyst is dependent on the proportional content of $Ti_3C_2@TiO_2$. With optimized $Ti_3C_2@TiO_2$ proportion, the photocatalytic ability of the $AgBr/Ti_3C_2@TiO_2$ composite was 24.5 times as high as that of $Ti_3C_2@TiO_2$ for photodehydrogenation of 1,4-DHP and 1.9 times as high as that of pure AgBr for photodegradation of TCH. The enhanced photocatalytic performance of the $AgBr/Ti_3C_2@TiO_2$ composite should be due to the formation of a p–n heterojunction structure between AgBr and $Ti_3C_2@TiO_2$ and the excellent electronic properties of Ti_3C_2, which enhanced the visible light absorption capacity, lowered the internal resistance, speeded up the charge transfer and reduced the recombination efficiency of photo-generated carriers. Mechanism studies showed that superoxide free radical ($^{\bullet}O_2^-$) was the main active species. In addition, the composite photocatalyst also displayed good stability, indicating its reutilization in practical application.

1. Introduction

With the rapid development of industrialization and urbanization, environmental pollution and the energy crisis have received extensive attention in the past decades.[1–3] In order to solve these problems, inexhaustible solar-driven photocatalysis is considered to be a potential green method to produce photoinduced carriers with redox ability by using semiconductors as photocatalysts.[4,5] So far, many photocatalysts have been reported in this field, such as TiO_2,[6,7] ZnO,[8] CdS[9,10] and $g\text{-}C_3N_4$.[11,12] Among these photocatalysts, TiO_2 has gained a lot of attention due to its high photocatalytic ability and good chemical stability. What's more, it is also low in price and easy to obtain, safe and harmless.[13] However, the practical application of TiO_2 as a photocatalyst is limited because it can only be excited by UV light that accounts for only a small fraction of the natural sunlight (~5%).[14,15] The method to overcome this shortcoming is to modify TiO_2 with narrow band gap semiconductors. Under light irradiation, the photogenerated charge carriers can move from one semiconductor to another, thereby enhancing the photocatalytic activity.[16–18]

AgBr is an important photosensitive semiconductor for traditional use. It is an n-type semiconductor with a narrow band gap of ~2.64 eV and is very active under visible light excitation.[17] Unfortunately, the pure AgBr is quite unstable, and the photoinduced electrons will combine with Ag^+ to form Ag^0 clusters, resulting in the undesirable and uncontrolled photolysis of AgBr, which leads to the low reusability of AgBr in photocatalytic reaction.[19–21] Therefore, the composite of AgBr and TiO_2 can enhance the photocatalytic performance and improve the photocatalytic stability by reducing the band gap and prolonging the life of photoinduced electron–hole pairs. Abou Asi *et al.* prepared $AgBr/TiO_2$ nanocomposite by a deposition–precipitation method with the addition of cetyltrimethylammonium bromide, and evaluated the photocatalytic

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activity by the reduction of CO_2.[22] Cui *et al.* successfully prepared AgBr nanoparticles modified TiO_2 nanotube arrays ($AgBr/TiO_2$ NTAs) photoelectrode by anodic oxidation and ultrasonic assisted precipitation. The enhance photocatalytic activity of the $AgBr/TiO_2$ NTAs materials was evaluated by the degradation of 4-chlorophenol (4-CP) under visible light irradiation, and 92.6% of 4-CP degradation was obtained within 140 min of Xenon illumination.[23]

MXene, a new family of 2D transition metal carbides and/or nitrides, has attracted widespread interest since its first appearance in 2011.[24] Up to now, MXenes has been widely studied and applied in energy storage and conversion,[25] catalysis,[26] sensor,[27] heavy metal ion[28] and dye adsorption[29] and other fields. Because of the excellent conductivity and well visible light absorption capacity of Ti_3C_2 MXene, it has been clearly proved to be an efficient cocatalyst for improving photocatalytic activity, which can effectively promote the separation and transfer of photogenerated electrons. For example, Low *et al.* used the calcination method to grow TiO_2 nanoparticles *in situ* on Ti_3C_2 MXene with good electrical conductivity. The photocatalytic reduction of CO_2 to CH_4 (0.22 μmol h^{-1}) by the optimized TiO_2/Ti_3C_2 composite is 3.7 times higher than that of commercial TiO_2 (P25).[30] Moreover, Li *et al.* modified carbon nitride (CN) with Ti_3C_2 and found that compared with the original CN, the modified CN showed significantly improved photocatalytic activity for U(VI) reduction.[2]

To the best of our knowledge, there is no report about the enhancement of the photocatalytic performance of AgBr by compositing with TiO_2 and simultaneously introducing Ti_3C_2 as a cocatalyst. In this study, $Ti_3C_2@TiO_2$ was prepared by *in situ* growth of TiO_2 on Ti_3C_2 under solvothermal treatment, and a series of $AgBr/Ti_3C_2@TiO_2$ composites were prepared by precipitation method. The *in situ* preparation of $Ti_3C_2@TiO_2$ makes Ti_3C_2 and TiO_2 closely contact, and improves the separation efficiency of photogenerated electron hole pairs. The photocatalytic performance of the $AgBr/Ti_3C_2@TiO_2$ photocatalyst was evaluated by the photodehydrogenation of 1,4-DHP and photodegradation of TCH under visible light irradiation. The $AgBr/Ti_3C_2@TiO_2$ photocatalyst showed enhanced photocatalytic performance in both photocatalytic reactions. The photocatalytic performance of the $AgBr/Ti_3C_2@TiO_2$ composite with optimized composition is 3.9 and 24.5 times higher than that of pure AgBr and $Ti_3C_2@TiO_2$, respectively, for photodehydrogenation of 1,4-DHP and 1.9 and 5.9 times higher than that of pure AgBr and $Ti_3C_2@TiO_2$ for photodegradation of TCH. The composite photocatalyst were stable under light irradiation. The relative dehydrogenation efficiency of 1,4-DHP photolysis and the relative degradation efficiency of TCH degradation remained above 86% after four cycles.

2. Experimental

2.1. Preparation of AgBr powder

First, 1.0 g $AgNO_3$ was dissolved in 50 mL of deionized water to obtain $AgNO_3$ solution (solution A), 0.70 g KBr was mixed with 25 mL deionized water and dissolved to prepare KBr solution (solution B). Then, the solution B was added dropwise the solution A under magnetically stirring, and the mixed solution was stirred in the dark for 0.5 h. After centrifugation and washing, the AgBr precipitate was collected and dried at 60 °C.

2.2. Preparation of layered Ti_3C_2

Typically, 0.5 g Ti_3AlC_2 powder was added to 10 mL 30 wt% HF (within 5 min) and the reaction was allowed to proceed at room temperature for 5 h to remove the element of Al. The resulting powder was collected by centrifugation (3500 rpm, 5 min per cycle) and washed 5 times with deionized water. Then, the black precipitate was dried at 80 °C for 24 h to obtain multilayered Ti_3C_2.

2.3. Preparation of $Ti_3C_2@TiO_2$ by *in situ* solvothermal method

First, 0.3 g Ti_3C_2, which was obtained from HF etching of Ti_3AlC_2, was mixed with 30 mL isopropanol (IPA). After sonication for 10 min, the mixture was poured into a 100 mL Teflon-lined reactor and heated at 150 °C for 24 h. The precipitate was centrifuged, repeatedly washed until the pH value of the eluate was about 6, and then dried at 60 °C to obtain $Ti_3C_2@TiO_2$ sample.

2.4. Preparation of $AgBr/Ti_3C_2@TiO_2$ composites

Solution A was prepared by dissolving 0.1808 g $AgNO_3$ and dispersing 0.0225 g $Ti_3C_2@TiO_2$ to 50 mL deionized water. Solution B was prepared by dissolving 0.1267 g KBr to 25 mL of deionized water. Then, solution B was added dropwise to solution A under magnetic stirring. After further stirred for 2 h, the reaction mixture was centrifuged, filtered and dried at 60 °C to obtain $AgBr/Ti_3C_2@TiO_2$ composite. This sample was denoted as $AgBr/Ti_3C_2@TiO_2$-10%, for the mass percentage of $Ti_3C_2@TiO_2$ was accounting for 10% of the sample. Other $AgBr/Ti_3C_2@TiO_2$ composite samples with different proportions of $Ti_3C_2@TiO_2$ (10%, 20%, 30%, 40%, 50%, 60%, 70%) were prepared by changing the amount of each sample. The obtained $AgBr/Ti_3C_2@TiO_2$ samples were denoted as $AgBr/Ti_3C_2@TiO_2$-*x*% (*x*% referred to the mass percentage of $Ti_3C_2@TiO_2$).

2.5. Characterization

The crystal structure, morphology, and elemental composition were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrometer (FT-IR). An electrochemical workstation equipped with a three-electrode system was used to measure the electrochemical characteristics of the samples.

2.6. Photocatalytic performance evaluation

The photocatalytic performance of $AgBr/Ti_3C_2@TiO_2$ was evaluated by the photodehydrogenation of 1,4-DHP and photodegradation of TCH under the irradiation of visible light. The light was provided by a 70 W metal halide lamp equipped with a 400 nm cutoff filter. Typically, 50 mg of $AgBr/Ti_3C_2@TiO_2$

composite was dispersed into 50 mL of 0.1 mM 1,4-DHP or 20 mg L^{-1} TCH solution. In order to obtain adsorption–desorption equilibrium, the mixture was magnetically stirred for 30 min before illumination. The extent of the reaction was spectroscopically monitored by measuring the residual concentrations of 1,4-DHP and TCH at wavelengths of 374 and 357 nm, respectively.

3. Results and discussion

The XRD patterns of Ti_3AlC_2, Ti_3C_2, Ti_3C_2@TiO_2, AgBr and AgBr/Ti_3C_2@TiO_2 composites are shown in Fig. 1. Ti_3C_2 was obtained by etching Ti_3AlC_2 with HF, removing Al layer and retaining Ti and C layers, the XRD diffraction pattern of the precursor Ti_3AlC_2 shows that there was a main diffraction peak at $2\theta = 39.3°$. After reacting with HF, the diffraction pattern had undergone the following significant changes: firstly, the peak observed at the diffraction angle of $2\theta = 39.3°$ almost disappeared, indicating that the Al layer was successfully removed by etching.[31] Secondly, at the low diffraction angle, because of the expansion of the interlayer distance, the peaks at (002) and (004) move to a low angle and become wider and weaker, indicating that Ti_3AlC_2 has been transformed into Ti_3C_2.[32,33] The characteristic peaks of multilayer Ti_3C_2 appear at 2θ values of 8.94° (002), 18.29° (006), 27.66° (008), 34.53° (101), 41.78° (105) and 60.62° (110), which are consistent with the literature.[34,35] Ti_3C_2@TiO_2 composites were obtained by *in situ* growth of TiO_2 on Ti_3C_2 after solvothermal treatment of Ti_3C_2 and isopropanol (IPA) in a reactor. The characteristic peaks at 25.28°, 36.95°, 48.04° and 55.06° were attributed to the (101), (103), (200) and (211) crystal planes of anatase TiO_2 (JCPDS no. 21-1272).[36] And the characteristic peaks with 2θ values of 8.94°, 18.29°, 27.66°, 34.53° and 60.62° in Ti_3C_2@TiO_2 correspond to the (002), (004), (006), (101) and (110) crystal planes of Ti_3C_2, respectively. These results indicate that Ti_3C_2@TiO_2 composites were successfully synthesized (Fig. 1A). It can be noted from Fig. 1B that the diffraction peaks of AgBr can be attributed to the face-centered cubic crystal phase of AgBr, and the 2θ values are 26.72° (111), 30.96° (200), 44.34° (220), 52.48° (311), 55.04° (222), 64.47° (400), 71.09° (331), 73.26° (420) and 81.61° (422), respectively.[17] It is consistent with the standard data of AgBr (JCPDS no. 06-0438). As for the AgBr/Ti_3C_2@TiO_2 composites, except for the XRD patterns of AgBr, another two peaks appeared at 2θ values of 39.12° and 77.39°, which should be ascribed to the (111) and (311) crystal planes of Ag^0 (JCPDS no. 65-2871)[33,37] (Fig. 1B). With the increase of Ti_3C_2@TiO_2 content, the diffraction peaks of AgBr in the ternary composites gradually weakened, and the diffraction peaks of (111) and (311) crystal planes of Ag increased. Due to the existence of low-valent Ti with strong reducing activity in Ti_3C_2 solution, Ag^+ can be partially reduced to Ag^0.[33,38] It is worth noting that the XRD peaks of Ti_3C_2 and TiO_2 were not observed in the XRD patterns of AgBr/Ti_3C_2@TiO_2 composites, which may have resulted from their low degree of crystallization in the composite samples.[39,40]

As shown in Fig. 2A and B, due to the exothermic reaction of HF, Ti_3AlC_2 transforms from a dense, layered ternary carbide structure to an accordion-like structure of Ti_3C_2.[35] After co-heat treatment of Ti_3C_2 and isopropanol (IPA) in a reactor, TiO_2 nanosheets with a size of about 100 nm were *in situ* grown on the surface of multilayer Ti_3C_2 to form Ti_3C_2@TiO_2 composites (Fig. 2C). The AgBr sample shows that irregular polyhedrons with a size of about 2–4 μm were clustered together (Fig. 2D). Compared with pure AgBr (Fig. 2D), AgBr particles in AgBr/Ti_3C_2@TiO_2-10% samples showed better dispersibility and smaller size (Fig. 2E). With the increase of Ti_3C_2@TiO_2 content, the shape of irregular polyhedral AgBr particles becomes more dispersed and the particle size becomes smaller (Fig. 2F). These results indicate that the addition of Ti_3C_2@TiO_2 not only affects the morphology and size of AgBr particles, but also prevents the agglomeration of AgBr polyhedral.

The microstructure of AgBr/Ti_3C_2@TiO_2-40% composite was further analyzed by TEM and HRTEM. As shown in Fig. 3A and B, AgBr is in close contact with the Ti_3C_2@TiO_2 sheets. According to Fig. 3C, the lattice fringe spacing of 0.189 nm and 0.204 nm correspond to the TiO_2 (200) and AgBr (200) crystal planes, respectively. The lattice fringe spacings of 0.189 nm and 0.230 nm belong to TiO_2 (200) and Ti_3C_2 (103) crystal planes, respectively[31] (Fig. 3E). Furthermore, the lattice fringes at

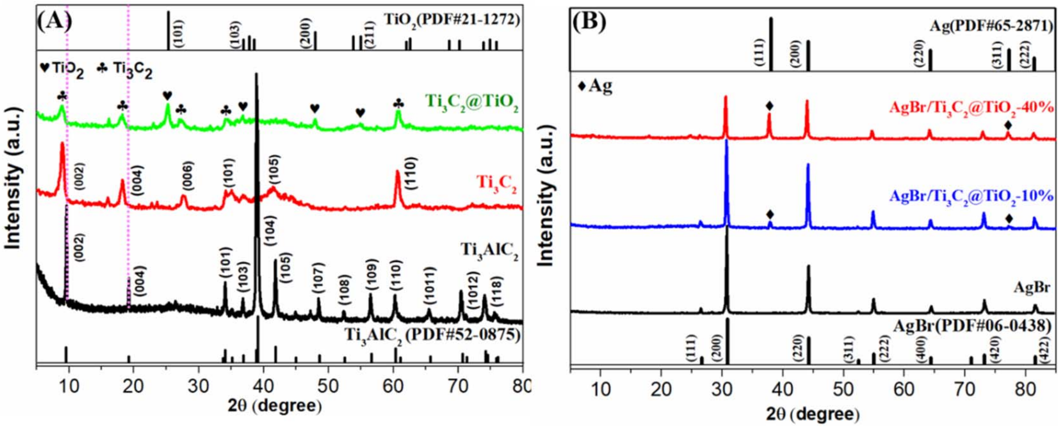

Fig. 1 XRD patterns of Ti_3AlC_2, Ti_3C_2 and Ti_3C_2@TiO_2 (A), AgBr and AgBr/Ti_3C_2@TiO_2 composites (B).

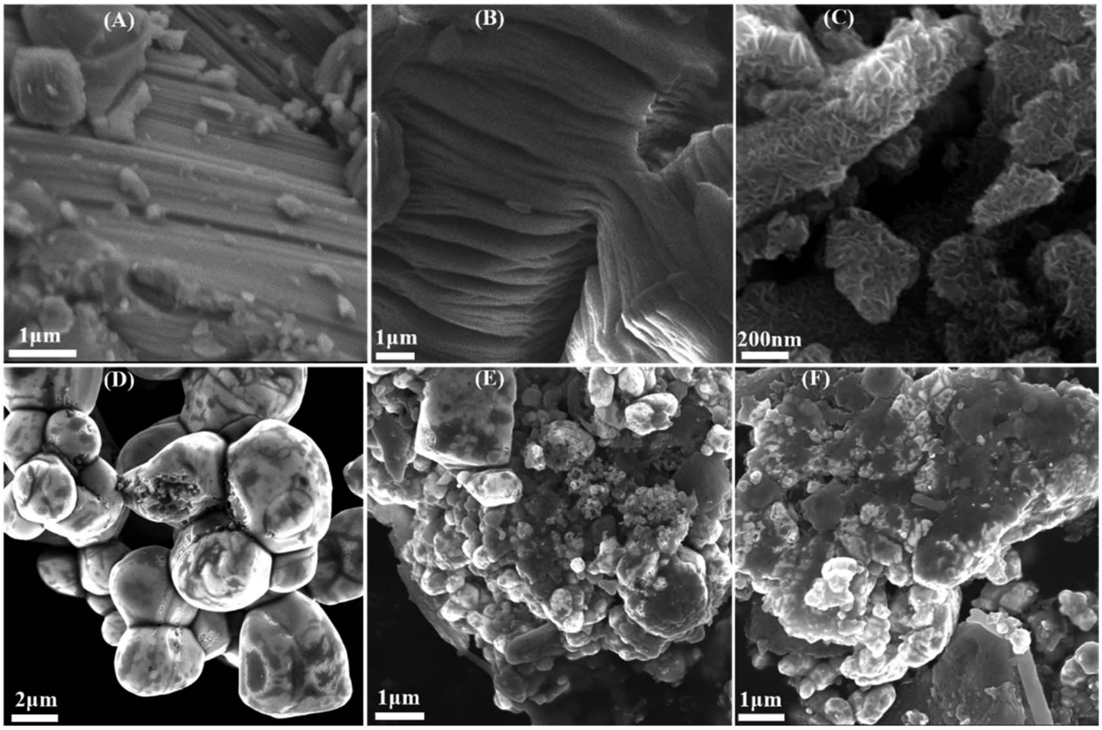

Fig. 2 SEM images of Ti_3AlC_2 (A), Ti_3C_2 (B), $Ti_3C_2@TiO_2$ (C), AgBr (D), AgBr/$Ti_3C_2@TiO_2$-10% (E), AgBr/$Ti_3C_2@TiO_2$-40% (F).

0.214 nm and 0.204 nm correspond to Ti_3C_2 (005) and Ag (200) crystal planes, respectively[41] (Fig. 3D and F). The above data show that after solvothermal method and precipitation method, stable heterojunctions are formed between AgBr and TiO_2, thus improving the photocatalytic performance of the composites.[42]

The element distribution and composition of the composites were detected by elemental mapping image. Fig. 4 shows the elemental scanning spectrum of AgBr/$Ti_3C_2@TiO_2$-10% composites. As can be seen from the figure, the distribution of six elements, namely C, Ag, Br, O, Ti and F. Among them, the element F is the residue of Ti_3AlC_2 etched by HF, so its content is less.

The full XPS spectra (Fig. 5A) shows the characteristic peaks of Ti, C, O, Ag and Br in AgBr/$Ti_3C_2@TiO_2$-40% sample. Fig. 5B–

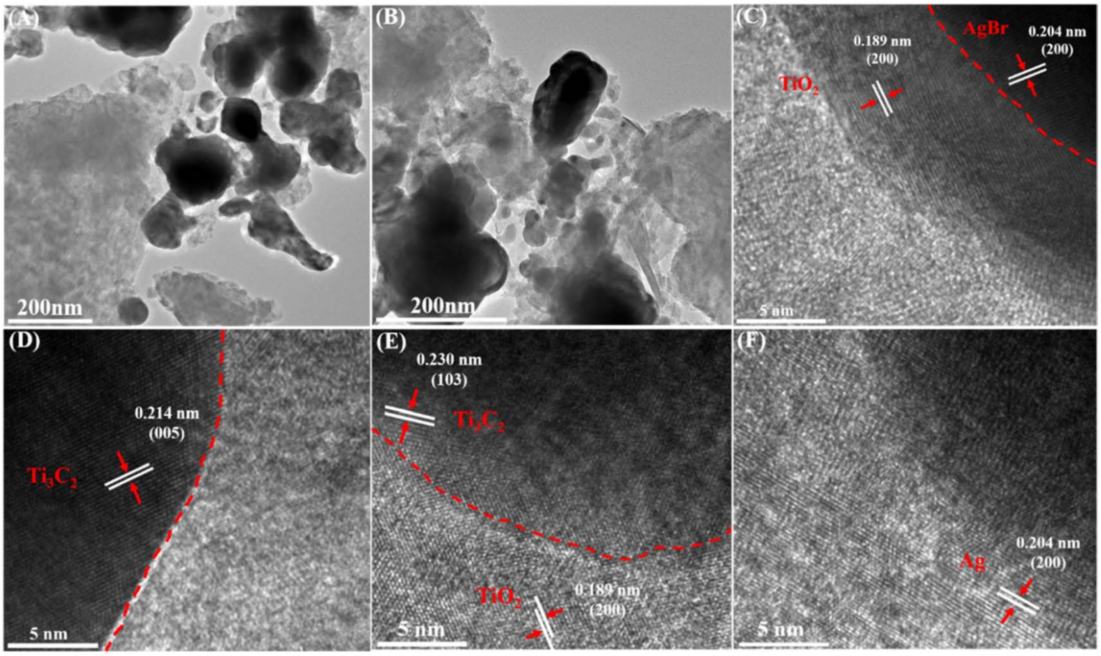

Fig. 3 TEM (A and B) and HRTEM (C, D, E and F) images of AgBr/$Ti_3C_2@TiO_2$-40% sample.

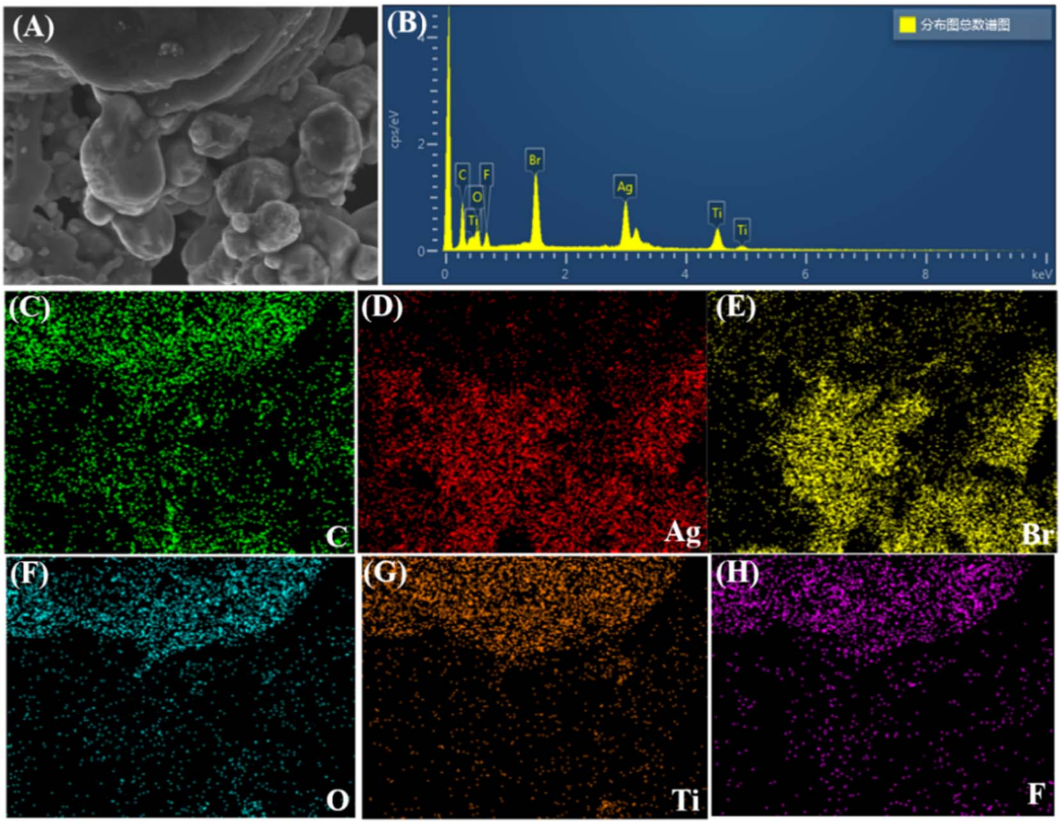

Fig. 4 Selected SEM images (A), the EDS spectrum of the AgBr/Ti_3C_2@TiO_2-10% composite (B), C (C), Ag (D), Br (E), O (F), Ti (G) and F (H) element.

F shows the high-resolution spectra of each element. After carbon correction, curve fitting and background subtraction are carried out. As shown in Fig. 5B, five different peaks can be found in high resolution Ti 2p, of which 455.1 eV, 456.5 eV and 459.0 eV belong to Ti $2p_{3/2}$, 464.8 eV and 461.6 eV attribute to Ti $2p_{1/2}$. Specifically, the peaks at 456.5 eV, 459.0 eV and 464.8 eV can be belonged to Ti–O bond, and the peaks at 455.1 eV and 461.6 eV indicate the existence of Ti–C bond.[43,44] The XPS C 1s spectrum of the composite (Fig. 5C) showed a strong peak at the binding energy of 284.8 eV, corresponding to the C–C bond.

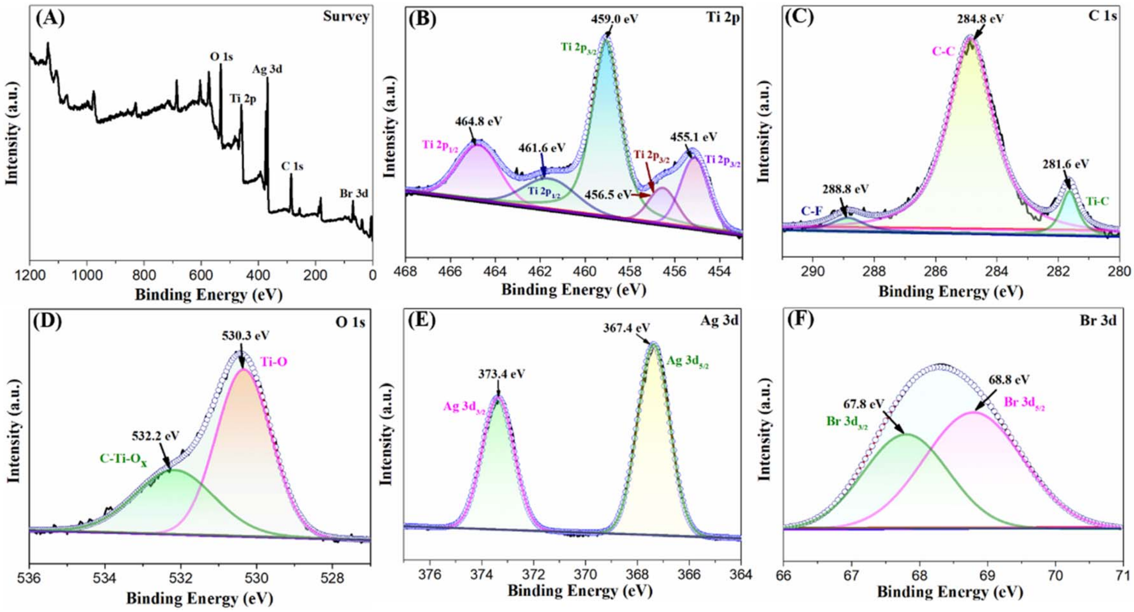

Fig. 5 High-resolution XPS spectra of the AgBr/Ti_3C_2@TiO_2-40%. Full spectrum (A), Ti 2p (B), C 1s (C), O 1s (D), Ag 3d (E) and (F) Br 3d.

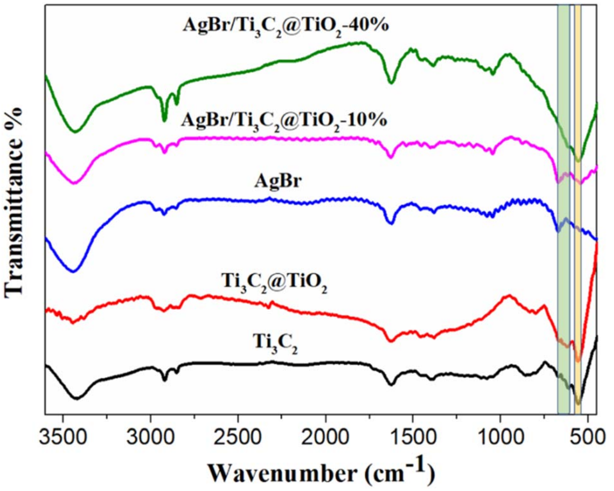

Fig. 6 FT-IR spectra of Ti_3C_2, $Ti_3C_2@TiO_2$, AgBr, AgBr/$Ti_3C_2@TiO_2$-10% and AgBr/$Ti_3C_2@TiO_2$-40% samples.

Two peaks appear at the binding energies of 281.6 eV and 288.8 eV, corresponding to the Ti–C bond and the C–F bond, respectively.[43,45] In addition, the O 1s XPs spectrum showed two distinct peaks at 532.2 eV and 530.3 eV (Fig. 5D), the highest peak at 530.3 eV usually represent the lattice oxygen in TiO_2, which also indicated that TiO_2 was successfully grown *in situ* on Ti_3C_2.[31] Fig. 5E shows the Ag 3d spectrum. There are two peaks at around 367.4 eV and 373.4 eV, which can be attributed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. Other studies have shown that the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks of Ag^+ in AgBr usually locate at about 367.37 and 373.48 eV, and the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks of Ag^0 are usually observed at 367.87 and 376.03 eV.[14] The present Ag 3d data (367.4 eV for Ag $3d_{5/2}$ and 373.4 eV for Ag $3d_{3/2}$) should be the superposition of the 3d binding energy of Ag^0 and Ag^+.[46] However, the peaks in Fig. 5E are difficult to divide into two sets of peaks belonging to Ag^0 and Ag^+, respectively. It may show that Ag^0 particles and AgBr particles have a special composite structure, which is different from any of their individual particles.[37,46] Fig. 5F shows the Br 3d XPS spectrum, the binding energies of 67.8 eV and 68.8 eV correspond to Br $3d_{3/2}$ and Br $3d_{5/2}$, respectively.[47,48]

The functional groups of Ti_3C_2, $Ti_3C_2@TiO_2$, AgBr, AgBr/$Ti_3C_2@TiO_2$-10% and AgBr/$Ti_3C_2@TiO_2$-40% were detected by FT-IR (Fig. 6). The absorption peaks appeared at 3424 cm^{-1} and 1631 cm^{-1}, respectively, corresponding to –OH asymmetric stretching and –OH bending vibration of adsorbed water.[49] Furthermore, the band at about 2850 cm^{-1}–2924 cm^{-1} corresponds to O–H stretching vibration, which reflects the existence of –OH.[50] In $Ti_3C_2@TiO_2$, the peaks at 616 cm^{-1} and 564 cm^{-1} correspond to Ti–O and Ti–C vibrations respectively,[26,51] and the peak at 1393 cm^{-1} corresponds to C–O or C–N.[52] With the increase of $Ti_3C_2@TiO_2$ content, the two characteristic peaks of Ti_3C_2 (at 564 cm^{-1}–670 cm^{-1}) gradually increased when it was compounded with AgBr.

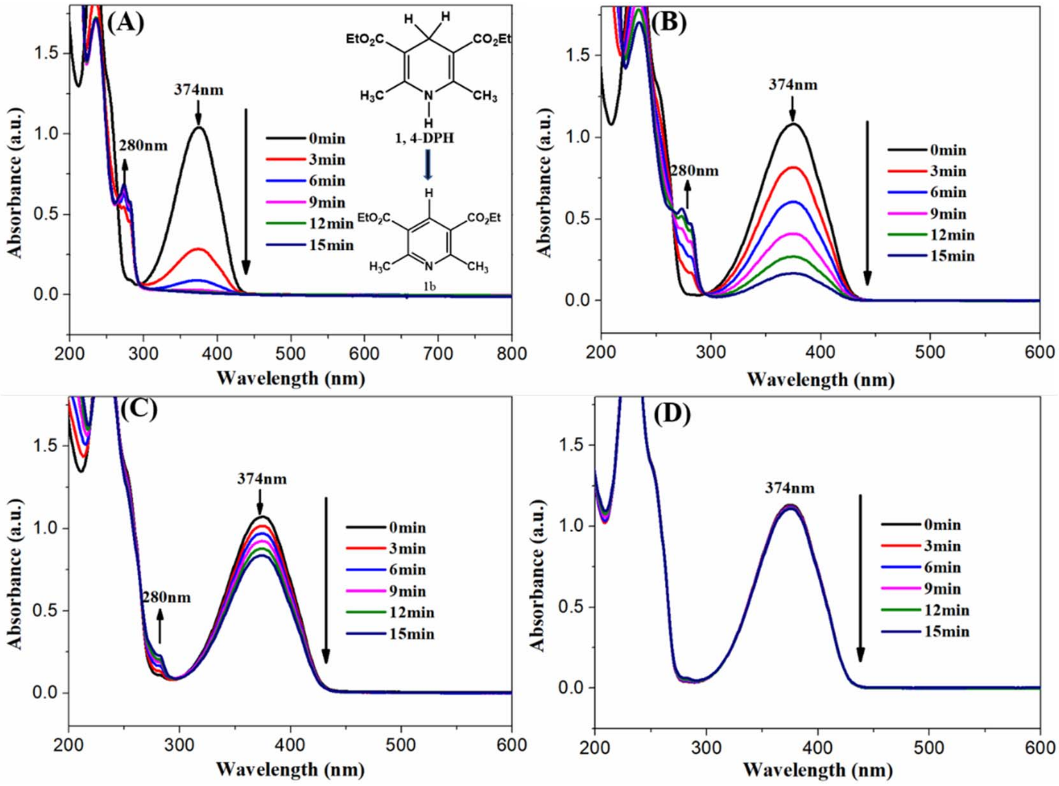

Fig. 7 Under the irradiation of visible light (λ > 400 nm), the ultraviolet-visible spectrum changes of 1,4-DHP solution under different photocatalysts. (A) AgBr/$Ti_3C_2@TiO_2$-40%, (B) AgBr, (C) $Ti_3C_2@TiO_2$ and (D) no catalyst.

The photocatalytic performance of the prepared AgBr/Ti_3C_2@TiO_2 composite was tested by the dehydrogenation of 1,4-DHP under visible light irradiation (λ > 400 nm). As shown in Fig. 7A, the absorption peak of 1,4-DHP at 374 nm decreased rapidly, companying with the rapid increase at 280 nm. According to the previous literature, the simultaneous peak intensity decrease at 374 nm and increase at 280 nm indicates the dehydrogenation of 1,4-DHP,[53–55] namely the conversion of 1,4-DHP to its pyridine derivatives (Fig. 7A, inset). When AgBr and Ti_3C_2@TiO_2 were used as photocatalyst, the changes of the peak intensity at 374 and 280 nm were also observed, but the changes were much slower (Fig. 7B and C). When no catalyst was added and only irradiated under visible light, the changes of the two peaks were hardly observed. After 9 min irradiation under visible light, the conversion rate of 1,4-DHP were 98.9%, 84.5%, and 21.9% in the presence of AgBr/Ti_3C_2@TiO_2-40%, AgBr, and Ti_3C_2@TiO_2 respectively. The above results show that the as-prepared AgBr/Ti_3C_2@TiO_2 composites have much better photocatalytic performance for 1,4-DHP photodehydrogenation.

In order to further analyze the influence of Ti_3C_2@TiO_2 content on the photocatalytic properties of AgBr/Ti_3C_2@TiO_2 composites, we prepared a series of AgBr/Ti_3C_2@TiO_2 composites with different Ti_3C_2@TiO_2 content and evaluated their photocatalytic activities by the photodehydrogenation of 1,4-DHP. With the increase of Ti_3C_2@TiO_2 content, the photocatalytic performance of the AgBr/Ti_3C_2@TiO_2 composites first increased and then decreased. All of the composites displayed enhanced photocatalytic ability and the AgBr/Ti_3C_2@TiO_2-40% composite showed the highest photocatalytic activity (Fig. 8A and B). The rate constants of the photocatalyst for 1,4-DHP dehydrogenation are obtained by plotting ln(C/C_0) *versus* illumination time (Fig. 8C) and compared in Fig. 8D. The rate constant of AgBr/Ti_3C_2@TiO_2-40% (0.4044 min^{-1}) is the highest, which is about 3.9 times and 24.5 times as high as that of pure AgBr (0.1035 min^{-1}) and Ti_3C_2@TiO_2 (0.0165 min^{-1}), respectively, further confirming the enhanced photocatalytic ability of AgBr/Ti_3C_2@TiO_2 composites.

Besides the photodehydrogenation of 1,4-DHP, the AgBr/Ti_3C_2@TiO_2 composites was further applied for the photodegradation of TCH under visible light irradiation (λ > 400 nm). As shown in Fig. 9A, when the catalyst is AgBr/Ti_3C_2@TiO_2-10%, the absorption peak of TCH at 357 nm decreases rapidly, indicating the efficient catalytic degradation of TCH. When AgBr and Ti_3C_2@TiO_2 were used as photocatalyst, the changes of the peak intensity at 357 nm were also observed, but the changes were much slower (Fig. 9B and C). No obvious changes could be observed without any catalyst (Fig. 9D). After 20 min irradiation under visible light, the degradation rate of TCH were 76.5%, 59.6%, and 31.9% in the presence of AgBr/Ti_3C_2@TiO_2-10%, AgBr, and Ti_3C_2@TiO_2, respectively. These results show that the photocatalytic performance of AgBr/Ti_3C_2@TiO_2-10% is much better than that of pure AgBr and Ti_3C_2@TiO_2.

Similarly, AgBr/Ti_3C_2@TiO_2 composites with different Ti_3C_2@TiO_2 contents were used to degrade TCH. With increase of Ti_3C_2@TiO_2 content, the photodegradation efficiency of AgBr/Ti_3C_2@TiO_2 composites increased first and then decreased. The

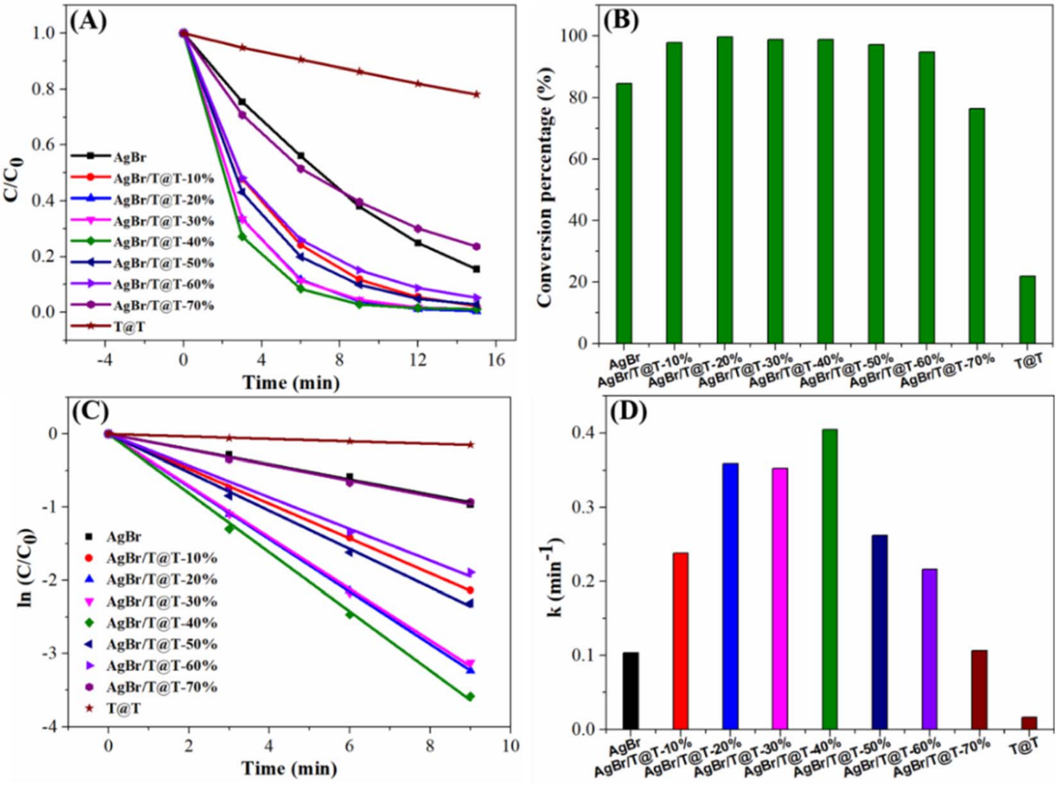

Fig. 8 AgBr, Ti_3C_2@TiO_2 (T@T for short) and AgBr/Ti_3C_2@TiO_2-x% (AgBr/T@T-x% for short) photocatalytic oxidation of 1,4-DHP under visible light: (A) kinetic diagram, (B) degradation efficiency graph, (C) the linear kinetic fitting graph, (D) apparent rate constant.

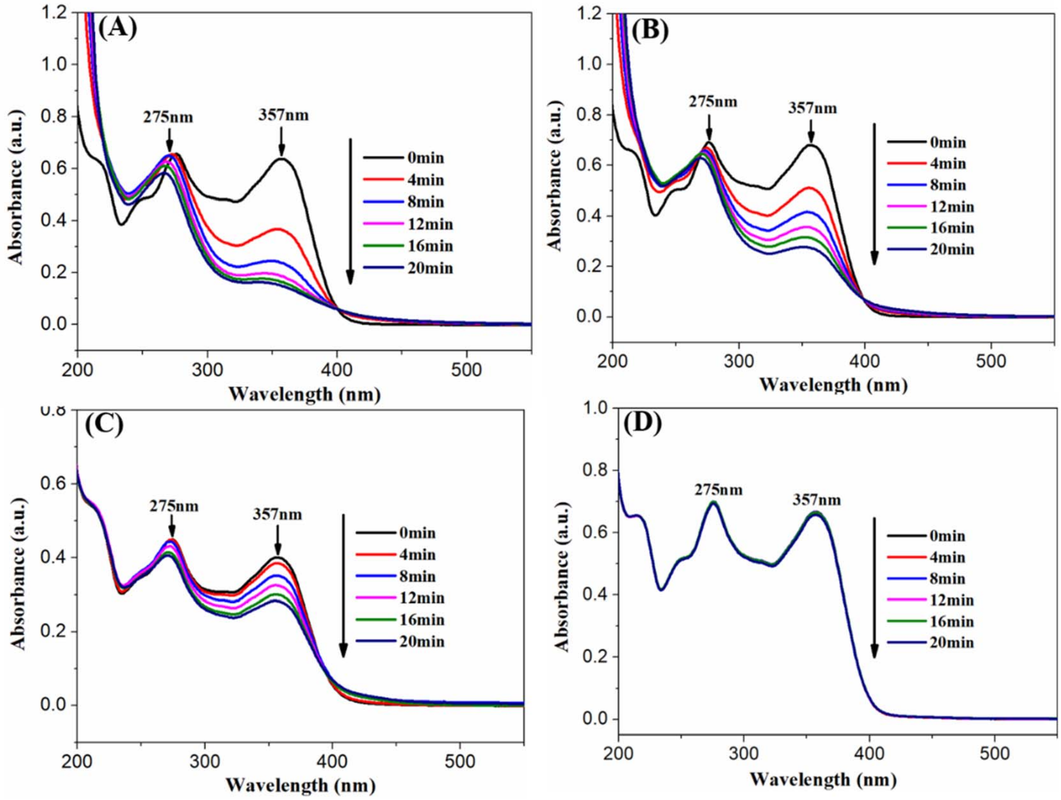

Fig. 9 Under the irradiation of visible light (λ > 400 nm), the ultraviolet-visible spectrum changes of TCH solution under different photocatalysts. (A) AgBr/Ti_3C_2@TiO_2-10%, (B) AgBr, (C) Ti_3C_2@TiO_2 and (D) no catalyst.

photo-degradation results of TCH show that under visible light, the conversion rate of AgBr/Ti_3C_2@TiO_2-10% to TCH reaches 76.5% within 20 min, showing the highest photocatalytic activity (Fig. 10A and B). The photodegradation rate constant of TCH (Fig. 10D) is obtained by plotting $\ln(C/C_0)$ *vs.* time in Fig. 10C. Among them, the rate constant of AgBr/Ti_3C_2@TiO_2-10% is the highest (0.1027 min^{-1}), which is about 1.9 times and 5.9 times as high as that of pure AgBr (0.0540 min^{-1}) and Ti_3C_2@TiO_2 (0.0174 min^{-1}), respectively. The above data show that AgBr/Ti_3C_2@TiO_2 composite also has good photocatalytic performance for TCH degradation.

The UV-vis DRS spectra of the materials are shown in Fig. 11A. In comparison with pure AgBr, with an increase of Ti_3C_2@TiO_2 content, the light absorption ability of the composites gradually increases.[45,56] The fast charge transfer properties of the prepared materials were analyzed by PL spectroscopy. As shown in Fig. 11B, compared with the pure AgBr, pure Ti_3C_2 and Ti_3C_2@TiO_2 samples, the emission peaks of the AgBr/Ti_3C_2@TiO_2 composite are of weaker intensity, indicating the beneficial effect of the heterojunction to promote the separation efficiency of photo-induced electron–hole pairs.[35,57] Electrochemical impedance spectroscopy (EIS) tests is used to study the electrochemical performance. Fig. 11C shows the Nyquist diagram of EIS of AgBr, Ti_3C_2@TiO_2 and AgBr/Ti_3C_2@TiO_2 photocatalysts. In general, the arc radius in the Nyquist diagram describes the reaction rate at the electrode surface, the smaller the radius, the lower the corresponding electron transfer resistance, the higher the charge transfer and separation efficiency.[58] The arc radii of AgBr/Ti_3C_2@TiO_2 composites are much smaller than that of pure AgBr and Ti_3C_2@TiO_2, which indicates that more efficient photogenerated charge carrier's separation, lower internal resistance and faster transfer of charge carriers can occur on the surface of AgBr/Ti_3C_2@TiO_2 composites. These results demonstrate that AgBr is successfully compounded with Ti_3C_2@TiO_2 and has good photogenerated charge carrier separation efficiency. Fig. 11D–F shows the Mott–Schottky curves of AgBr, Ti_3C_2@TiO_2 and AgBr/Ti_3C_2@TiO_2-10% materials. As can be seen from the figure that AgBr is considered as an n-type semiconductor because of its positive slope (Fig. 11D). Although TiO_2 is also an n-type semiconductor,[59] its Mott–Schottky diagram slope of Ti_3C_2@TiO_2 composite material is negative after *in situ* growth on Ti_3C_2 by solvothermal method, and it has the potential of a p-type semiconductor[2,23] (Fig. 11E). More importantly, the Mott–Schottky diagram of AgBr/Ti_3C_2@TiO_2-10% composite shows an inverted "V-shape" as shown in Fig. 11F, which indicates that the p–n junction structure has been successfully formed.

Using AgBr/Ti_3C_2@TiO_2 composite catalyst, four repeated experiments were carried out to determine the photodehydrogenation of 1,4-DHP and the photodegradation of TCH separately to evaluate the stability of the prepared photocatalyst. After four cycles, the relative hydrogenation efficiency of 1,4-DHP was 86.2% (Fig. 12A and B), and the relative degradation efficiency of TCH was 93.8% (Fig. 12C and D). Part of the

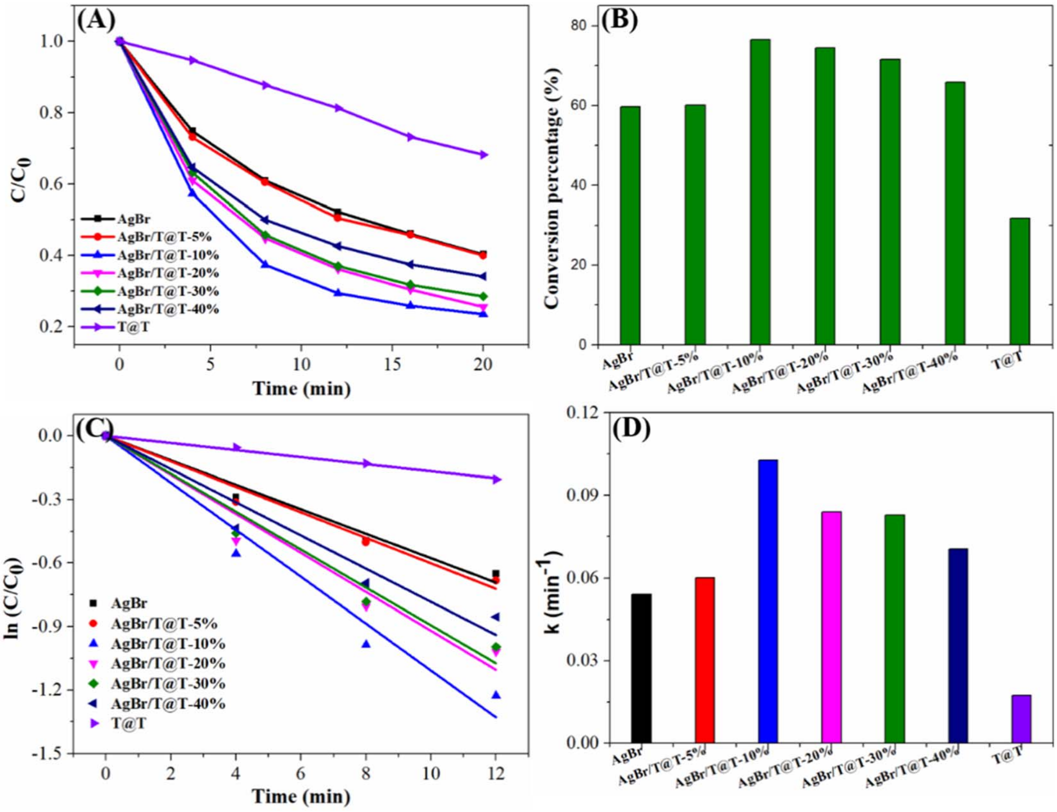

Fig. 10 AgBr, $Ti_3C_2@TiO_2$ (T@T for short) and $AgBr/Ti_3C_2@TiO_2$-*x*% (AgBr/T@T-*x*% for short) photocatalytic degradation of TCH under visible light: (A) kinetic diagram, (B) degradation efficiency graph, (C) the linear kinetic fitting graph, (D) apparent rate constant.

reason for the decrease in efficiency may be due to the loss of the catalyst during the cycle. Therefore, $AgBr/Ti_3C_2@TiO_2$ composite has good photocatalytic stability and potential practical application.

Active species capture experiment was conducted to explore the three main active species in photocatalytic reaction,[60] ammonium oxalate (AO), benzoquinone (BQ) and isopropanol (IPA) were used as scavengers for h^+, $^{\bullet}O_2^-$ and $^{\bullet}OH$, respectively.[53] As shown in Fig. 13, the addition of IPA slightly decreased the degradation of TCH but has little effect on the dehydrogenation of 1,4-DHP, the addition of AO has a little effect on the degradation of TCH, but slightly decreased the dehydrogenation of 1,4-DHP. When BQ was added to the reaction system, the degradation of TCH was obviously inhibited (Fig. 13A), indicating the major role of $^{\bullet}O_2^-$ in TCH degradation. The addition of BQ has significant influence on absorption spectrum of 1,4-DHP (data not shown), so BQ is not suitable for the detection of $^{\bullet}O_2^-$ radicals in the reaction system of 1,4-DHP. It was generally thought that the dissolved oxygen (O_2) in the reaction solution accepted photo-excited electrons from the conduction band of a semiconductor to produced $^{\bullet}O_2^-$ ($O_2 + e^- \rightarrow {}^{\bullet}O_2^-$).[61] Therefore, the removal of O_2 from the 1,4-DHP reaction system would affect the photodehydrogenation of 1,4-DHP, if $^{\bullet}O_2^-$ was involved in the dehydrogenation process. With this in mind, we carried out the photodehydrogenation of 1,4-DHP under a nitrogen atmosphere. The dissolved O_2 was removed from the reaction by nitrogen bubbling. The removal of O_2 apparently suppressed the dehydrogenation of 1,4-DHP (Fig. 13B). This results suggested that $^{\bullet}O_2^-$ was also played important role in 1,4-DHP dehydrogenation, just as in TCH degradation.

EPR technique was employed to further detect the generation of $^{\bullet}O_2^-$ in the $AgBr/Ti_3C_2@TiO_2$ composite involved photocatalytic system. DMPO was used as a radical trap. As shown in Fig. 13C, the DMPO-$^{\bullet}O_2^-$ characteristic peak was observed under visible light irradiation,[62] but not observed in dark condition. The production of $^{\bullet}OH$ by $AgBr/Ti_3C_2@TiO_2$ composite during the photocatalysis process was probed by fluorescence technique.[63] The fluorescence absorption peak around 425 nm obviously increased with visible-light irradiation time (Fig. 13D), indicating the formation of hydroxyl terephthalic acid (TA-OH), confirmed the generation of $^{\bullet}OH$ on the surface of $AgBr/Ti_3C_2@TiO_2$ composites.[53]

According to the results of active species capture experiment, EPR trapping experiment and terephthalic acid-based fluorescence experiment, a possible photocatalytic reaction mechanism was proposed (Fig. 14).

Under the excitation of visible light, AgBr with narrow band gap (2.6 eV) absorbs photons and produces photogenerated electron–hole pairs (eqn (1)). According to theoretical analysis, the conduction band (CB) potential of AgBr is more negative than the CB potential of TiO_2 and the Fermi

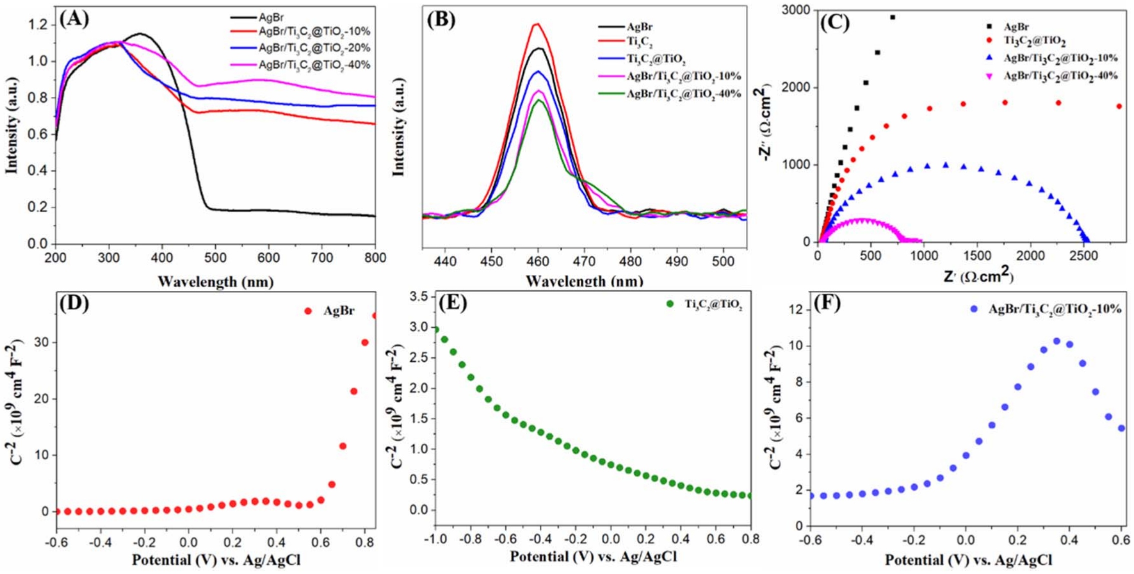

Fig. 11 UV-vis DRS of the as-prepared samples (A), PL spectra (B), EIS Nyquist plots of samples (C), Mott–Schottky plots of AgBr (D), Ti_3C_2@TiO_2 (E) and AgBr/Ti_3C_2@TiO_2-10% (F).

level of Ag^0 nanoparticles.[64–66] Therefore, the electrons on the CB of AgBr can rapidly transfer to the CB of TiO_2 (eqn (2)) or be captured by Ag^0 nanoparticles through Schottky barrier (eqn (3)).[67] The electrons on the CB of TiO_2 can further transfer to Ti_3C_2 (eqn (4)), since the CB potentials of TiO_2 is more negative than the Fermi level of the Ti_3C_2.[30,68,69] Thus, the photoinduced charge carriers on AgBr is efficiently separated, and the photocatalytic activity of AgBr is improved by

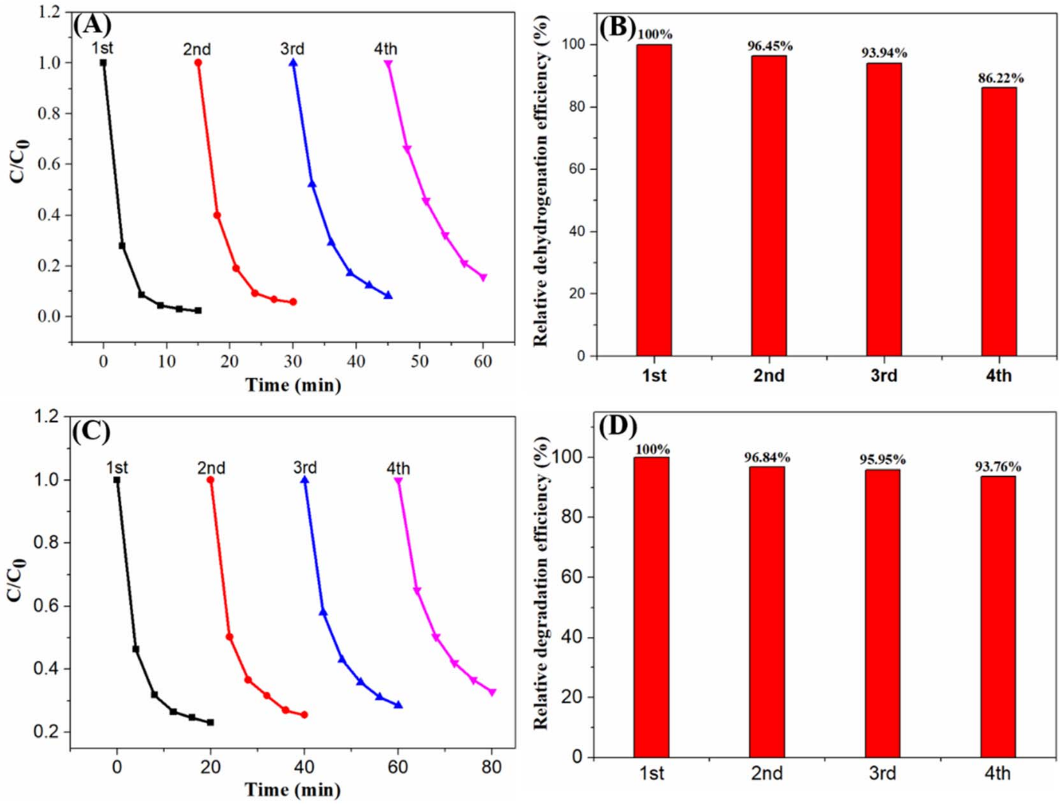

Fig. 12 Cyclic kinetics curve and relative dehydrogenation efficiency of 1,4-DHP by AgBr/Ti_3C_2@TiO_2-40% (A and B); cyclic kinetics curve and relative degradation efficiency of TCH by AgBr/Ti_3C_2@TiO_2-10% (C and D).

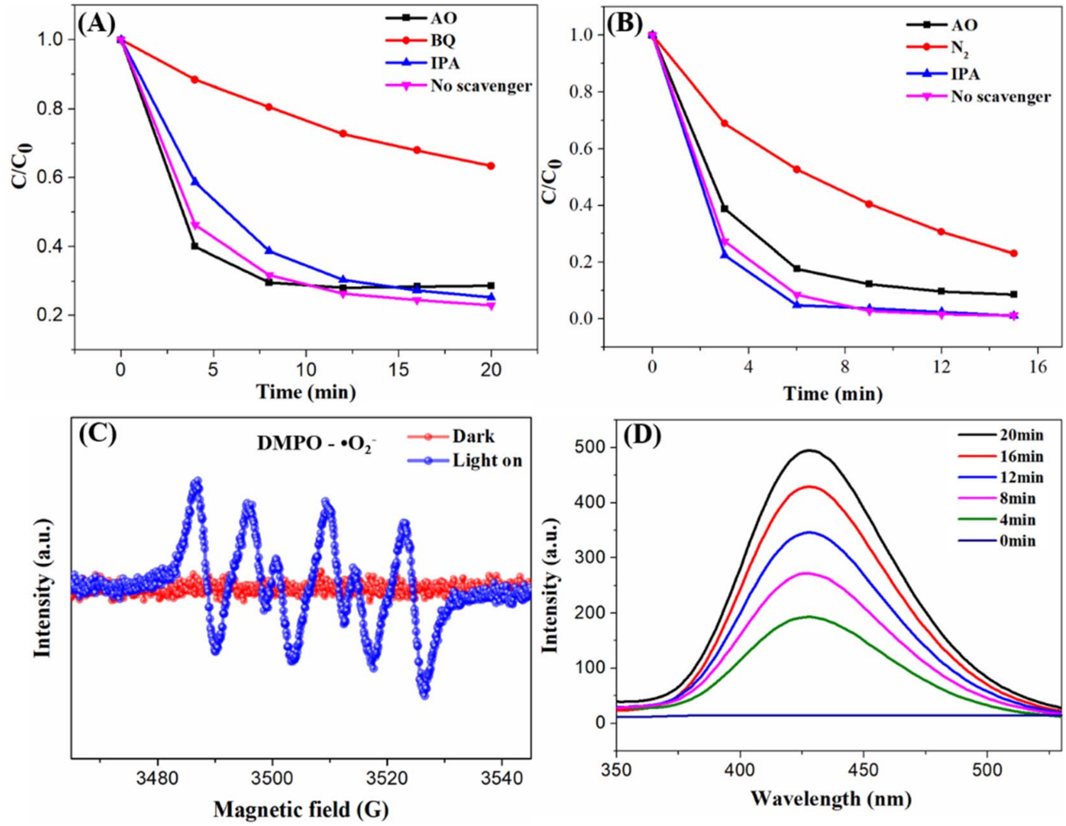

Fig. 13 The effect of certain selected scavengers on the photooxidation of TCH (A) and 1,4-DHP (B) under visible light ($\lambda > 400$ nm) irradiation, EPR signals of AgBr/Ti_3C_2@TiO_2 under dark and visible light irradiation (C) and fluorescence spectra of 0.5 mM alkaline terephthalic acid (TA) solution in the presence of AgBr/Ti_3C_2@TiO_2 composite under visible light irradiation (D).

compositing with Ti_3C_2@TiO_2. The electrons transferred to Ag^0 and Ti_3C_2 are subsequently captured by O_2 to produce $^{\bullet}O_2^-$ (eqn (5) and (6)). At the same time, the h^+ left on the valence band (VB) of AgBr can convert H_2O and OH^- (H_2O/OH^-) to $^{\bullet}OH$ (eqn (7)). The produced $^{\bullet}O_2^-$, $^{\bullet}OH$ and h^+ may all be utilized as oxidizer for 1,4-DHP dehydrogenation and TCH degradation (eqn (8)).

$$\mathrm{AgBr} + h\nu \rightarrow \mathrm{AgBr}\ (e^- + h^+) \tag{1}$$

$$\mathrm{AgBr}\ (e^-) + \mathrm{TiO_2} \rightarrow \mathrm{AgBr} + \mathrm{TiO_2}\ (e^-) \tag{2}$$

$$\mathrm{AgBr}\ (e^-) + \mathrm{Ag^0} \rightarrow \mathrm{AgBr} + \mathrm{Ag^0}\ (e^-) \tag{3}$$

$$\mathrm{TiO_2}\ (e^-) + \mathrm{Ti_3C_2} \rightarrow \mathrm{TiO_2} + \mathrm{Ti_3C_2}\ (e^-) \tag{4}$$

$$\mathrm{Ag^0}\ (e^-) + \mathrm{O_2} \rightarrow {}^{\bullet}\mathrm{O_2}^- + \mathrm{Ag^0} \tag{5}$$

$$\mathrm{Ti_3C_2}\ (e^-) + \mathrm{O_2} \rightarrow {}^{\bullet}\mathrm{O_2}^- + \mathrm{Ti_3C_2} \tag{6}$$

$$\mathrm{AgBr}\ (h^+) + \mathrm{H_2O/OH^-} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{AgBr} \tag{7}$$

$$^{\bullet}\mathrm{O_2}^-,\ {}^{\bullet}\mathrm{OH},\ h^+ + \text{1,4-DHP/TCH} \rightarrow \text{products} \tag{8}$$

It is worth pointing out that the main active species are $^{\bullet}O_2^-$ and h^+ for 1,4-DHP dehydrogenation, while $^{\bullet}O_2^-$ and $^{\bullet}OH$ for TCH degradation. In other words, the photogenerated h^+ in the VB of AgBr can react with H_2O and OH^- to produce $^{\bullet}OH$, then the generated $^{\bullet}OH$ is consumed by the oxidation of TCH in the TCH-catalyst system. But for the 1,4-DHP-catalyst system, the generated $^{\bullet}OH$ cannot be consumed by 1,4-DHP, which will influence the separation of photogenerated electron–hole pairs. The transfer of electrons in the CB of AgBr to separate it from the photogenerated holes in the VB of AgBr is more urgent in the 1,4-DHP-catalysts system. Therefore, the introduction of Ti_3C_2@TiO_2 into AgBr is more pronounced to enhance the catalytic activity of AgBr for 1,4-DHP oxidation. This maybe also one of the reasons that the optimal proportion of Ti_3C_2@TiO_2 is different for 1,4-DHP and TCH.

To sum up, under visible light irradiation, The enhanced photocatalytic performance of AgBr/Ti_3C_2@TiO_2 composite should be attributed to the following aspects: (1) the formation of a p–n heterojunction between AgBr and TiO_2 and the introduction of Ti_3C_2 as an electron transport medium and acceptor can rapidly transfer electrons, thus enhancing the separation rate of photo-generated electron–hole pairs; (2) as the size of AgBr particles in the composite decreases, the specific surface area of the composite increases, and the contact area between the interfaces of AgBr, TiO_2 and Ti_3C_2 increases, which also promotes the transfer of photogenerated carriers. (3) Ti_3C_2 and AgBr has good absorption capacity for visible light, which can increase the utilization of visible light by composite materials.

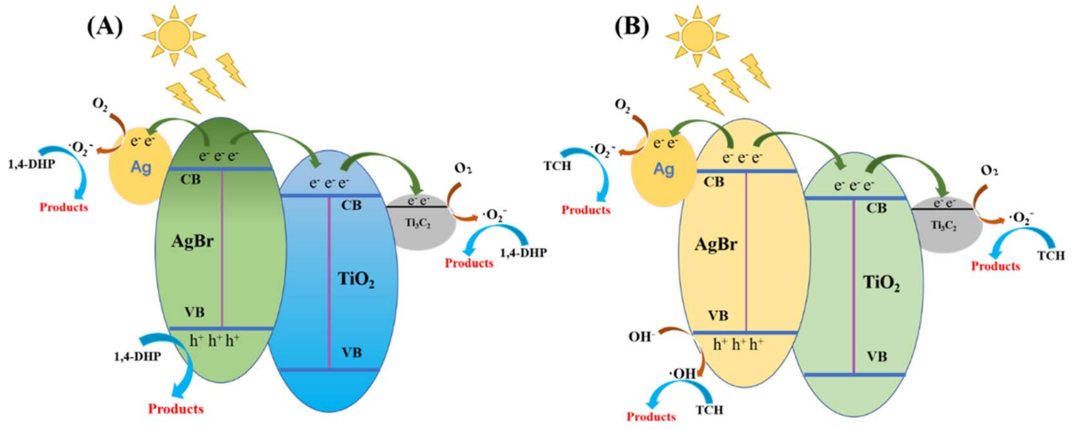

Fig. 14 Hypothetical mechanism diagram of dehydrogenation of 1,4-DHP (A) and photodegradation of TCH (B) by AgBr/Ti_3C_2@TiO_2 composites under visible light (λ > 400 nm).

4. Conclusions

In conclusion, AgBr/Ti_3C_2@TiO_2 composite photocatalyst was prepared by solvothermal and precipitation method and the photocatalytic performance of the composite was evaluated by the photodehydrogenation of 1,4-DHP and photodegradation of TCH under visible light irradiation. The AgBr/Ti_3C_2@TiO_2 composite photocatalyst showed improved photocatalytic performance compared with AgBr and Ti_3C_2@TiO_2. The photocatalytic performance of the AgBr/Ti_3C_2@TiO_2 composite with optimized composition is 3.9 and 24.5 times higher than that of pure AgBr and Ti_3C_2@TiO_2, respectively, for photodehydrogenation of 1,4-DHP and 1.9 and 5.9 times higher than that of pure AgBr and Ti_3C_2@TiO_2 for photodegradation of TCH. The improvement of photocatalytic performance of AgBr/Ti_3C_2@TiO_2 composite is due to the formation of p–n heterojunction structure between AgBr and Ti_3C_2@TiO_2, and the using of Ti_3C_2 as cocatalyst, which reduced the internal resistance, accelerated charge transfer and improved the separation efficiency of photogenerated carriers. In addition, AgBr/Ti_3C_2@TiO_2 composite photocatalyst also showed good stability in photochemical reaction, indicating that the AgBr/Ti_3C_2@TiO_2 composite has potential application in photooxidation reaction, wastewater treatment and environmental remediation.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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