


Cite this: *RSC Adv.*, 2023, 13, 21754

Synthesis of AgBr/Ti₃C₂@TiO₂ ternary composite for photocatalytic dehydrogenation of 1,4-dihydropyridine and photocatalytic degradation of tetracycline hydrochloride

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In this work, AgBr/Ti₃C₂@TiO₂ ternary composite photocatalyst was prepared by a solvothermal and precipitation method with the aims of introducing Ti₃C₂ as a cocatalyst and TiO₂ as a compositing semiconductor. The crystal structure, morphology, elemental state, functional groups and photoelectrochemical properties were studied by XRD, SEM, TEM, XPS, FT-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 ($\lambda > 400$ nm). The AgBr/Ti₃C₂@TiO₂ composite photocatalyst showed enhanced photocatalytic performance in both photocatalytic reactions. The photocatalytic activity of the composite photocatalyst is dependent on the proportional content of Ti₃C₂@TiO₂. With optimized Ti₃C₂@TiO₂ proportion, the photocatalytic ability of the AgBr/Ti₃C₂@TiO₂ composite was 24.5 times as high as that of Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂ composite should be due to the formation of a p–n heterojunction structure between AgBr and Ti₃C₂@TiO₂ and the excellent electronic properties of Ti₃C₂, 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 ($\cdot\text{O}_2^-$) was the main active species. In addition, the composite photocatalyst also displayed good stability, indicating its reutilization in practical application.

Received 2nd April 2023

Accepted 10th July 2023

DOI: 10.1039/d3ra02164e

rsc.li/rsc-advances

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 TiO₂,^{6,7} ZnO,⁸ CdS,^{9,10} and g-C₃N₄.^{11,12} Among these photocatalysts, TiO₂ 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 TiO₂ 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 ($\sim 5\%$).^{14,15} The method to overcome this shortcoming is to modify TiO₂ 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 Ag⁰ 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 TiO₂ 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/TiO₂ 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 CO₂.²² Cui *et al.* successfully prepared AgBr nanoparticles modified TiO₂ nanotube arrays (AgBr/TiO₂ NTAs) photoelectrode by anodic oxidation and ultrasonic assisted precipitation. The enhance photocatalytic activity of the AgBr/TiO₂ 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 ion²⁸ and dye adsorption²⁹ and other fields. Because of the excellent conductivity and well visible light absorption capacity of Ti₃C₂ 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 TiO₂ nanoparticles *in situ* on Ti₃C₂ MXene with good electrical conductivity. The photocatalytic reduction of CO₂ to CH₄ (0.22 μmol h⁻¹) by the optimized TiO₂/Ti₃C₂ composite is 3.7 times higher than that of commercial TiO₂ (P25).³⁰ Moreover, Li *et al.* modified carbon nitride (CN) with Ti₃C₂ 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 TiO₂ and simultaneously introducing Ti₃C₂ as a cocatalyst. In this study, Ti₃C₂@TiO₂ was prepared by *in situ* growth of TiO₂ on Ti₃C₂ under solvothermal treatment, and a series of AgBr/Ti₃C₂@TiO₂ composites were prepared by precipitation method. The *in situ* preparation of Ti₃C₂@TiO₂ makes Ti₃C₂ and TiO₂ closely contact, and improves the separation efficiency of photogenerated electron hole pairs. The photocatalytic performance of the AgBr/Ti₃C₂@TiO₂ photocatalyst was evaluated by the photodehydrogenation of 1,4-DHP and photodegradation of TCH under visible light irradiation. The AgBr/Ti₃C₂@TiO₂ photocatalyst showed enhanced photocatalytic performance in both photocatalytic reactions. The photocatalytic performance of the AgBr/Ti₃C₂@TiO₂ composite with optimized composition is 3.9 and 24.5 times higher than that of pure AgBr and Ti₃C₂@TiO₂, respectively, for photodehydrogenation of 1,4-DHP and 1.9 and 5.9 times higher than that of pure AgBr and Ti₃C₂@TiO₂ 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 AgNO₃ was dissolved in 50 mL of deionized water to obtain AgNO₃ 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 Ti₃C₂

Typically, 0.5 g Ti₃AlC₂ 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 Ti₃C₂.

2.3. Preparation of Ti₃C₂@TiO₂ by *in situ* solvothermal method

First, 0.3 g Ti₃C₂, which was obtained from HF etching of Ti₃AlC₂, 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 Ti₃C₂@TiO₂ sample.

2.4. Preparation of AgBr/Ti₃C₂@TiO₂ composites

Solution A was prepared by dissolving 0.1808 g AgNO₃ and dispersing 0.0225 g Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂ composite. This sample was denoted as AgBr/Ti₃C₂@TiO₂-10%, for the mass percentage of Ti₃C₂@TiO₂ was accounting for 10% of the sample. Other AgBr/Ti₃C₂@TiO₂ composite samples with different proportions of Ti₃C₂@TiO₂ (10%, 20%, 30%, 40%, 50%, 60%, 70%) were prepared by changing the amount of each sample. The obtained AgBr/Ti₃C₂@TiO₂ samples were denoted as AgBr/Ti₃C₂@TiO₂-x% (x% referred to the mass percentage of Ti₃C₂@TiO₂).

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/Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂

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 Ti₃AlC₂, Ti₃C₂, Ti₃C₂@TiO₂, AgBr and AgBr/Ti₃C₂@TiO₂ composites are shown in Fig. 1. Ti₃C₂ was obtained by etching Ti₃AlC₂ with HF, removing Al layer and retaining Ti and C layers, the XRD diffraction pattern of the precursor Ti₃AlC₂ shows that there was a main diffraction peak at $2\theta = 39.3^\circ$. After reacting with HF, the diffraction pattern had undergone the following significant changes: firstly, the peak observed at the diffraction angle of $2\theta = 39.3^\circ$ 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 Ti₃AlC₂ has been transformed into Ti₃C₂.^{32,33} The characteristic peaks of multilayer Ti₃C₂ 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} Ti₃C₂@TiO₂ composites were obtained by *in situ* growth of TiO₂ on Ti₃C₂ after solvothermal treatment of Ti₃C₂ 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 TiO₂ (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 Ti₃C₂@TiO₂ correspond to the (002), (004), (006), (101) and (110) crystal planes of Ti₃C₂, respectively. These results indicate that Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂ 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 Ag⁰ (JCPDS no. 65-2871)^{33,37} (Fig. 1B). With the increase of Ti₃C₂@TiO₂ 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 Ti₃C₂ solution, Ag⁺ can be partially reduced to Ag⁰.^{33,38} It is worth noting that the XRD peaks of Ti₃C₂ and TiO₂ were not observed in the XRD patterns of AgBr/Ti₃C₂@TiO₂ 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, Ti₃AlC₂ transforms from a dense, layered ternary carbide structure to an accordion-like structure of Ti₃C₂.³⁵ After co-heat treatment of Ti₃C₂ and isopropanol (IPA) in a reactor, TiO₂ nanosheets with a size of about 100 nm were *in situ* grown on the surface of multilayer Ti₃C₂ to form Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂-10% samples showed better dispersibility and smaller size (Fig. 2E). With the increase of Ti₃C₂@TiO₂ 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 Ti₃C₂@TiO₂ not only affects the morphology and size of AgBr particles, but also prevents the agglomeration of AgBr polyhedral.

The microstructure of AgBr/Ti₃C₂@TiO₂-40% composite was further analyzed by TEM and HRTEM. As shown in Fig. 3A and B, AgBr is in close contact with the Ti₃C₂@TiO₂ sheets. According to Fig. 3C, the lattice fringe spacing of 0.189 nm and 0.204 nm correspond to the TiO₂ (200) and AgBr (200) crystal planes, respectively. The lattice fringe spacings of 0.189 nm and 0.230 nm belong to TiO₂ (200) and Ti₃C₂ (103) crystal planes, respectively³¹ (Fig. 3E). Furthermore, the lattice fringes at

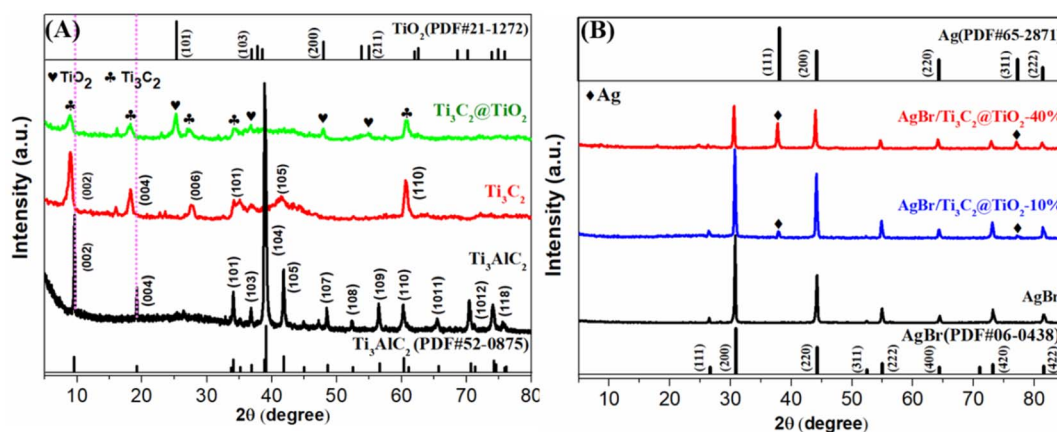


Fig. 1 XRD patterns of Ti₃AlC₂, Ti₃C₂ and Ti₃C₂@TiO₂ (A), AgBr and AgBr/Ti₃C₂@TiO₂ composites (B).



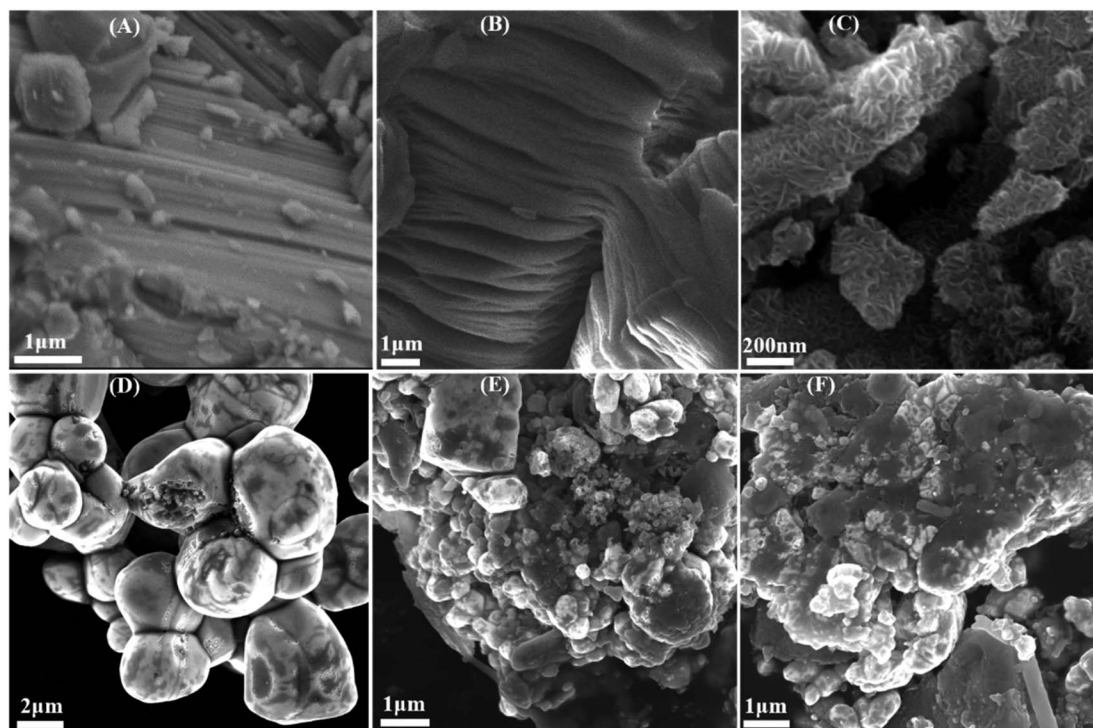


Fig. 2 SEM images of Ti_3AlC_2 (A), Ti_3C_2 (B), $\text{Ti}_3\text{C}_2@\text{TiO}_2$ (C), AgBr (D), AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -10% (E), AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -40% (F).

0.214 nm and 0.204 nm correspond to Ti_3C_2 (005) and Ag (200) crystal planes, respectively⁴¹ (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/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -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/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -40% sample. Fig. 5B–

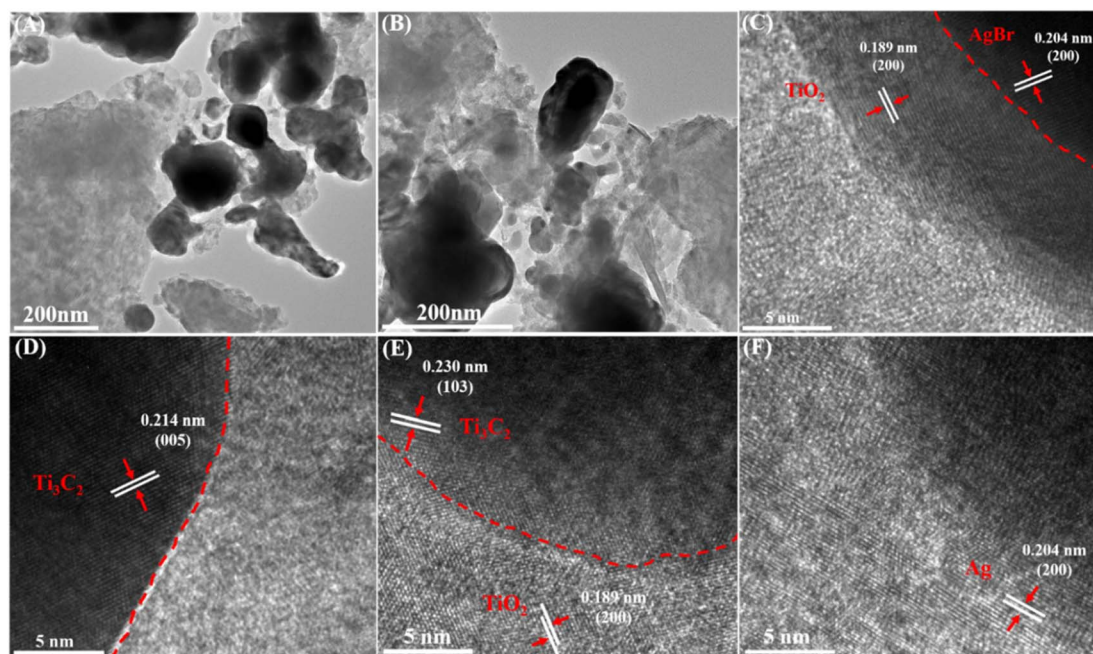


Fig. 3 TEM (A and B) and HRTEM (C, D, E and F) images of AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -40% sample.

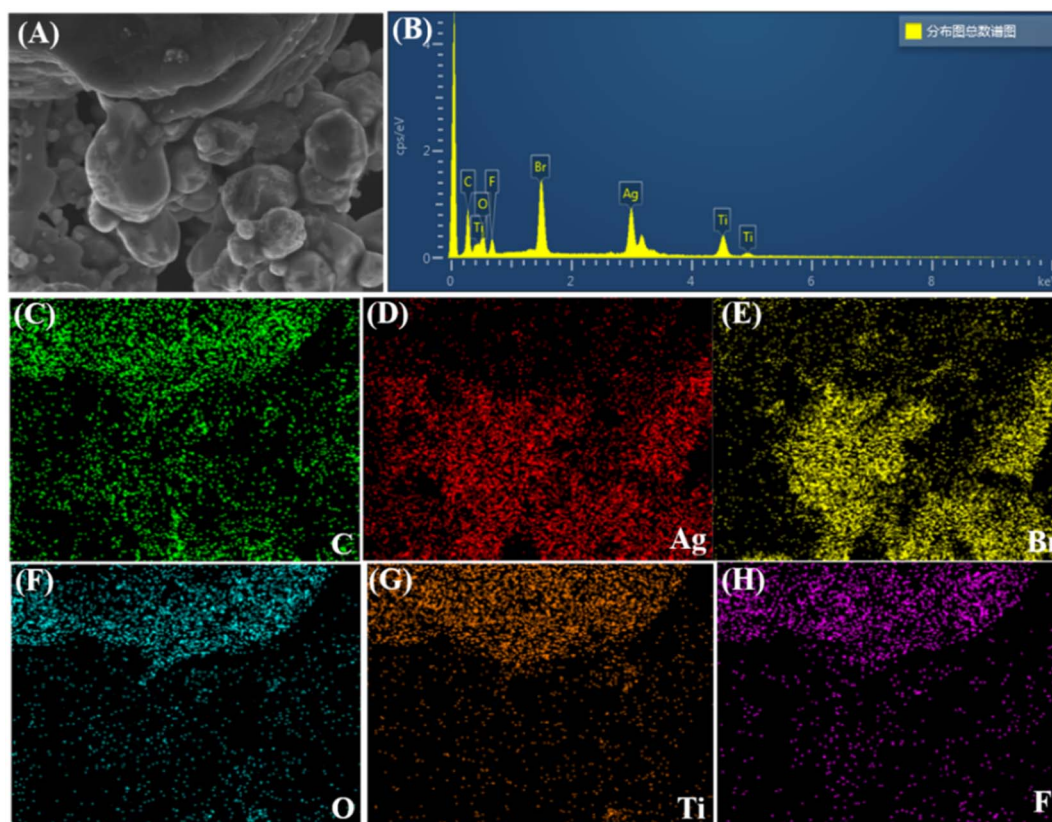


Fig. 4 Selected SEM images (A), the EDS spectrum of the AgBr/Ti₃C₂@TiO₂-10% composite (B), C (C), Ag (D), Br (E), O (F), Ti (G) and F (H) element.

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.

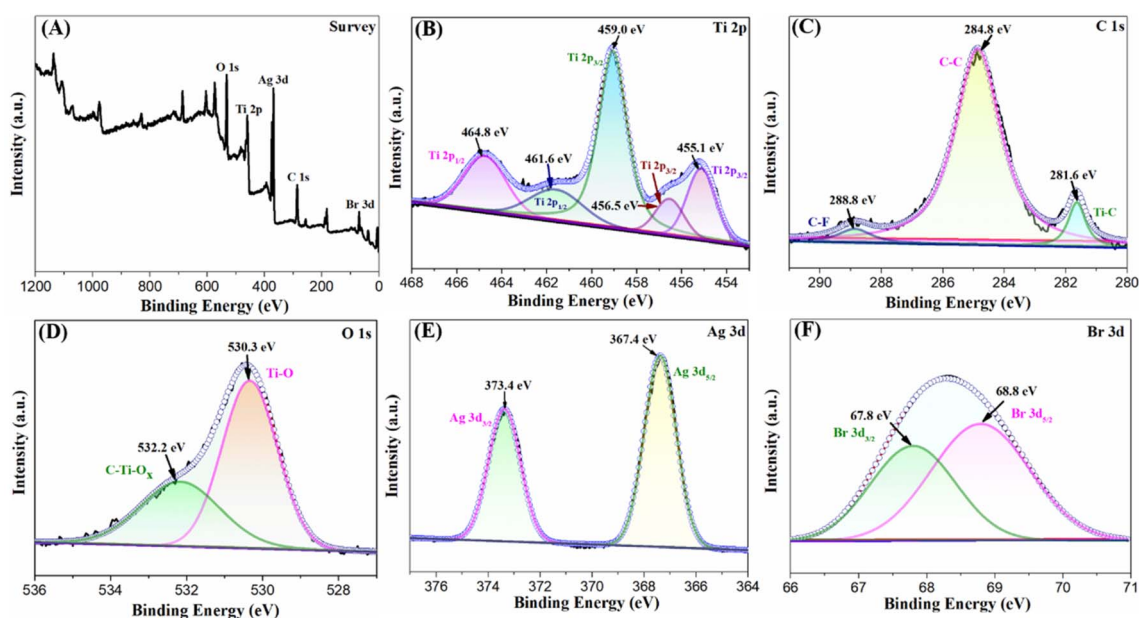


Fig. 5 High-resolution XPS spectra of the AgBr/Ti₃C₂@TiO₂-40%. Full spectrum (A), Ti 2p (B), C 1s (C), O 1s (D), Ag 3d (E) and (F) Br 3d.



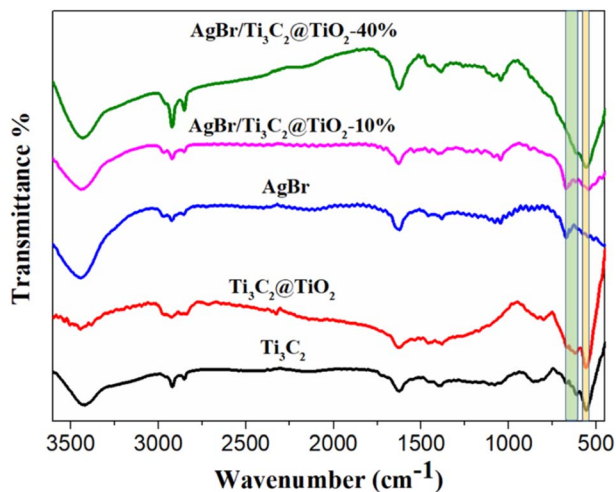


Fig. 6 FT-IR spectra of Ti_3C_2 , $\text{Ti}_3\text{C}_2@\text{TiO}_2$, AgBr, AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -10% and AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -40% samples.

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 , $\text{Ti}_3\text{C}_2@\text{TiO}_2$, AgBr, AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -10% and AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -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 $\text{Ti}_3\text{C}_2@\text{TiO}_2$, 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 $\text{Ti}_3\text{C}_2@\text{TiO}_2$ content, the two characteristic peaks of Ti_3C_2 (at 564 cm^{-1} – 670 cm^{-1}) gradually increased when it was compounded with AgBr.

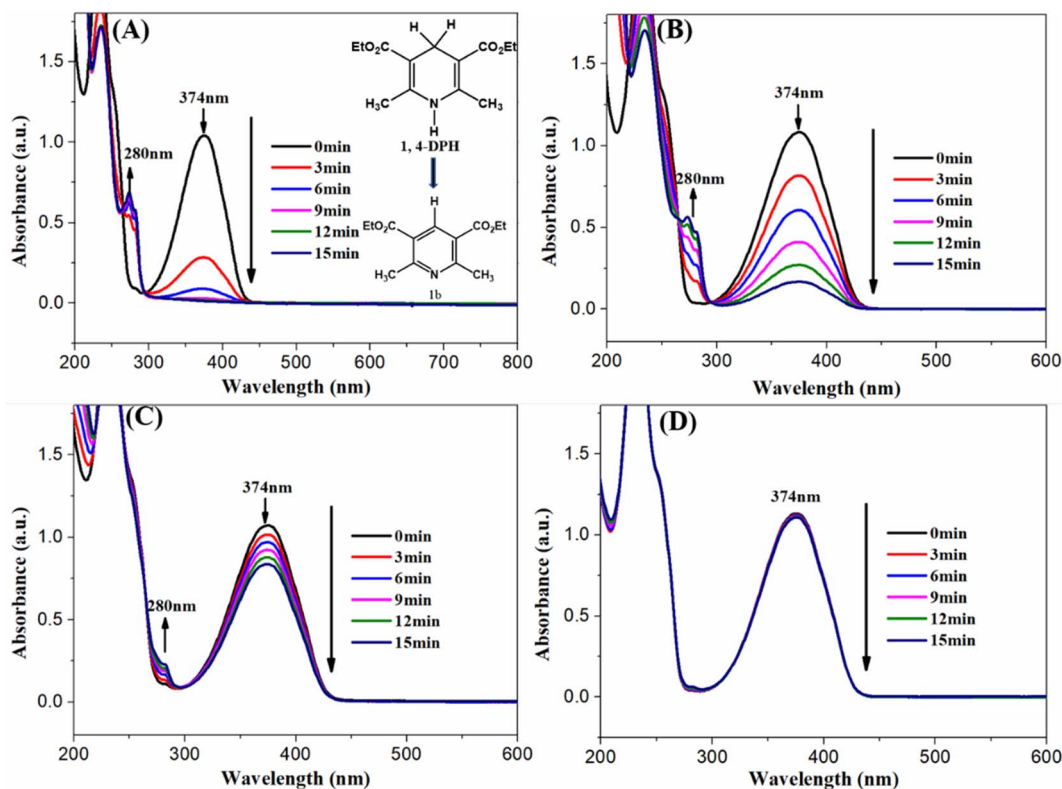


Fig. 7 Under the irradiation of visible light ($\lambda > 400\text{ nm}$), the ultraviolet-visible spectrum changes of 1,4-DHP solution under different photocatalysts. (A) AgBr/ $\text{Ti}_3\text{C}_2@\text{TiO}_2$ -40%, (B) AgBr, (C) $\text{Ti}_3\text{C}_2@\text{TiO}_2$ and (D) no catalyst.



The photocatalytic performance of the prepared AgBr/Ti₃C₂@TiO₂ composite was tested by the dehydrogenation of 1,4-DHP under visible light irradiation ($\lambda > 400$ nm). As shown in Fig. 7A, the absorption peak of 1,4-DHP at 374 nm decreased rapidly, accompanying 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 Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂-40%, AgBr, and Ti₃C₂@TiO₂ respectively. The above results show that the as-prepared AgBr/Ti₃C₂@TiO₂ composites have much better photocatalytic performance for 1,4-DHP photodehydrogenation.

In order to further analyze the influence of Ti₃C₂@TiO₂ content on the photocatalytic properties of AgBr/Ti₃C₂@TiO₂ composites, we prepared a series of AgBr/Ti₃C₂@TiO₂ composites with different Ti₃C₂@TiO₂ content and evaluated their photocatalytic activities by the photodehydrogenation of 1,4-DHP. With the increase of Ti₃C₂@TiO₂ content, the photocatalytic performance of the AgBr/Ti₃C₂@TiO₂ composites first increased and then decreased. All of the composites displayed enhanced photocatalytic ability and the AgBr/Ti₃C₂@TiO₂-40%

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/Ti₃C₂@TiO₂-40% (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 Ti₃C₂@TiO₂ (0.0165 min⁻¹), respectively, further confirming the enhanced photocatalytic ability of AgBr/Ti₃C₂@TiO₂ composites.

Besides the photodehydrogenation of 1,4-DHP, the AgBr/Ti₃C₂@TiO₂ composites was further applied for the photodegradation of TCH under visible light irradiation ($\lambda > 400$ nm). As shown in Fig. 9A, when the catalyst is AgBr/Ti₃C₂@TiO₂-10%, the absorption peak of TCH at 357 nm decreases rapidly, indicating the efficient catalytic degradation of TCH. When AgBr and Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂-10%, AgBr, and Ti₃C₂@TiO₂, respectively. These results show that the photocatalytic performance of AgBr/Ti₃C₂@TiO₂-10% is much better than that of pure AgBr and Ti₃C₂@TiO₂.

Similarly, AgBr/Ti₃C₂@TiO₂ composites with different Ti₃C₂@TiO₂ contents were used to degrade TCH. With increase of Ti₃C₂@TiO₂ content, the photodegradation efficiency of AgBr/Ti₃C₂@TiO₂ composites increased first and then decreased. The

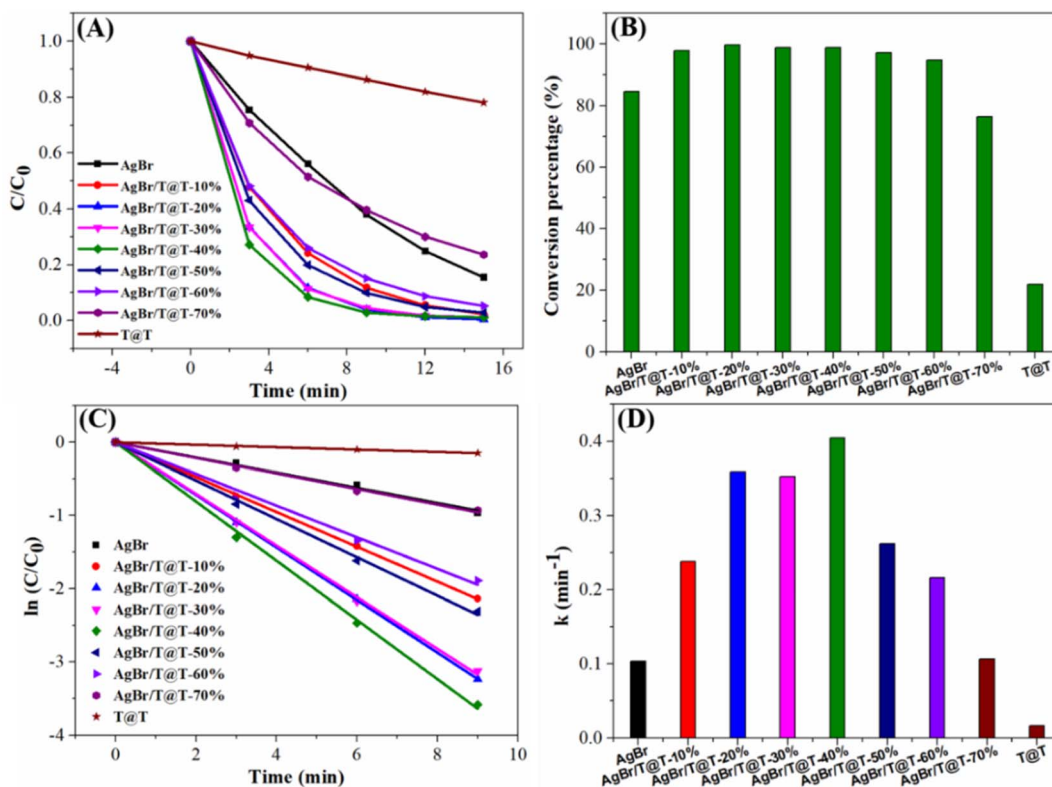


Fig. 8 AgBr, Ti₃C₂@TiO₂ (T@T for short) and AgBr/Ti₃C₂@TiO₂-x% (AgBr/T@T-x% for short) photocatalytic oxidation of 1,4-DHP under visible light: (A) kinetic diagram, (B) degradation efficiency graph, (C) the linear kinetic fitting graph, (D) apparent rate constant.



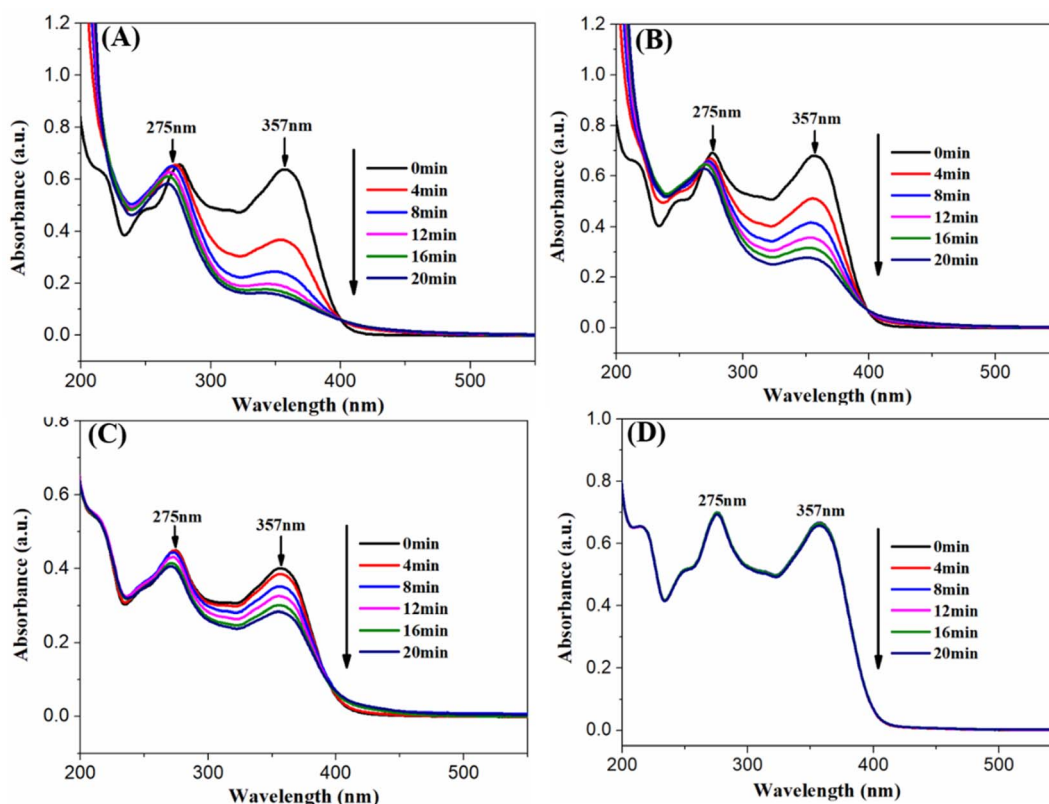


Fig. 9 Under the irradiation of visible light ($\lambda > 400$ nm), the ultraviolet-visible spectrum changes of TCH solution under different photocatalysts. (A) AgBr/Ti₃C₂@TiO₂-10%, (B) AgBr, (C) Ti₃C₂@TiO₂ and (D) no catalyst.

photo-degradation results of TCH show that under visible light, the conversion rate of AgBr/Ti₃C₂@TiO₂-10% 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/Ti₃C₂@TiO₂-10% 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 Ti₃C₂@TiO₂ (0.0174 min^{-1}), respectively. The above data show that AgBr/Ti₃C₂@TiO₂ 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 Ti₃C₂@TiO₂ 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 Ti₃C₂ and Ti₃C₂@TiO₂ samples, the emission peaks of the AgBr/Ti₃C₂@TiO₂ 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, Ti₃C₂@TiO₂ and AgBr/Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂ composites are much smaller than that of pure AgBr and Ti₃C₂@TiO₂, 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/Ti₃C₂@TiO₂ composites. These results demonstrate that AgBr is successfully compounded with Ti₃C₂@TiO₂ and has good photogenerated charge carrier separation efficiency. Fig. 11D–F shows the Mott–Schottky curves of AgBr, Ti₃C₂@TiO₂ and AgBr/Ti₃C₂@TiO₂-10% 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 TiO₂ is also an n-type semiconductor,⁵⁹ its Mott–Schottky diagram slope of Ti₃C₂@TiO₂ composite material is negative after *in situ* growth on Ti₃C₂ 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/Ti₃C₂@TiO₂-10% 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/Ti₃C₂@TiO₂ composite catalyst, four repeated experiments were carried out to determine the photo-dehydrogenation 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



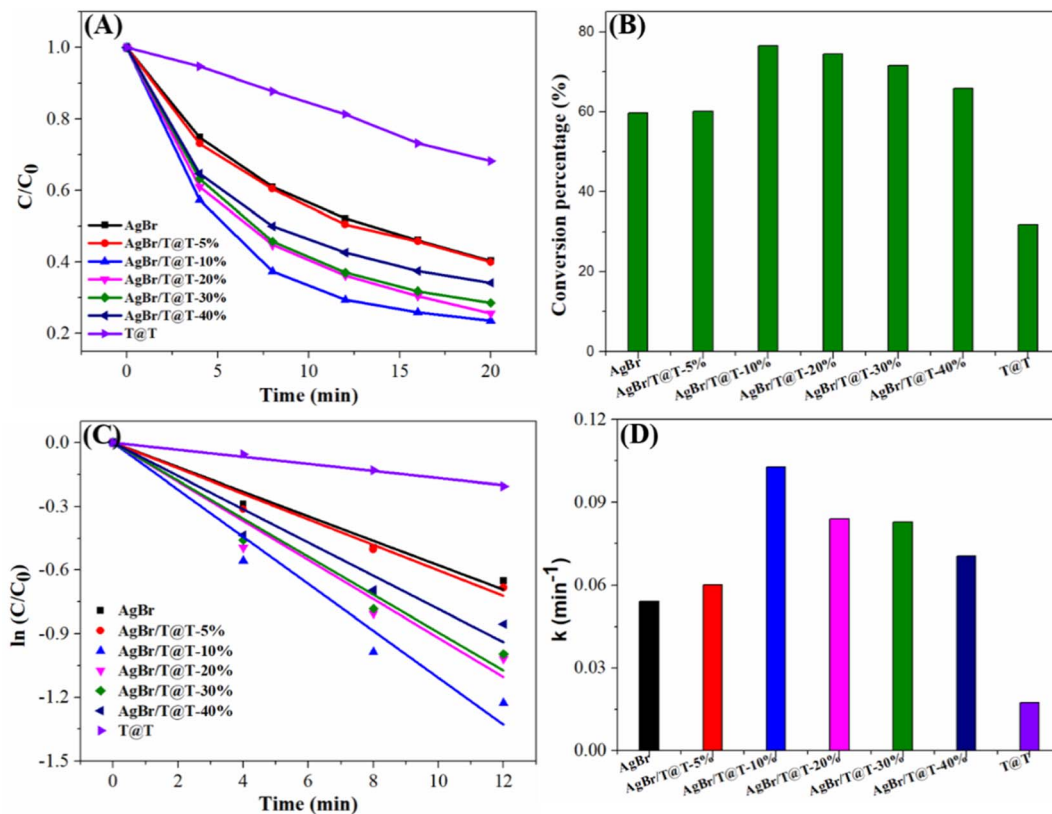


Fig. 10 AgBr, $\text{Ti}_3\text{C}_2\text{@TiO}_2$ (T@T for short) and AgBr/ $\text{Ti}_3\text{C}_2\text{@TiO}_2$ -x% (AgBr/T@T-x% for short) photocatalytic degradation of TCH under visible light: (A) kinetic diagram, (B) degradation efficiency graph, (C) the linear kinetic fitting graph, (D) apparent rate constant.

reason for the decrease in efficiency may be due to the loss of the catalyst during the cycle. Therefore, AgBr/ $\text{Ti}_3\text{C}_2\text{@TiO}_2$ 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^+ , O_2^- and OH^\cdot , 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 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 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 O_2^- ($\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$).⁶¹ Therefore, the removal of O_2 from the 1,4-DHP reaction system would affect the photodehydrogenation of 1,4-DHP, if 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 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 O_2^- in the AgBr/ $\text{Ti}_3\text{C}_2\text{@TiO}_2$ composite involved photocatalytic system. DMPO was used as a radical trap. As shown in Fig. 13C, the DMPO- O_2^- characteristic peak was observed under visible light irradiation,⁶² but not observed in dark condition. The production of OH^\cdot by AgBr/ $\text{Ti}_3\text{C}_2\text{@TiO}_2$ 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 terphenylic acid (TA-OH), confirmed the generation of OH^\cdot on the surface of AgBr/ $\text{Ti}_3\text{C}_2\text{@TiO}_2$ 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 photo-generated 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



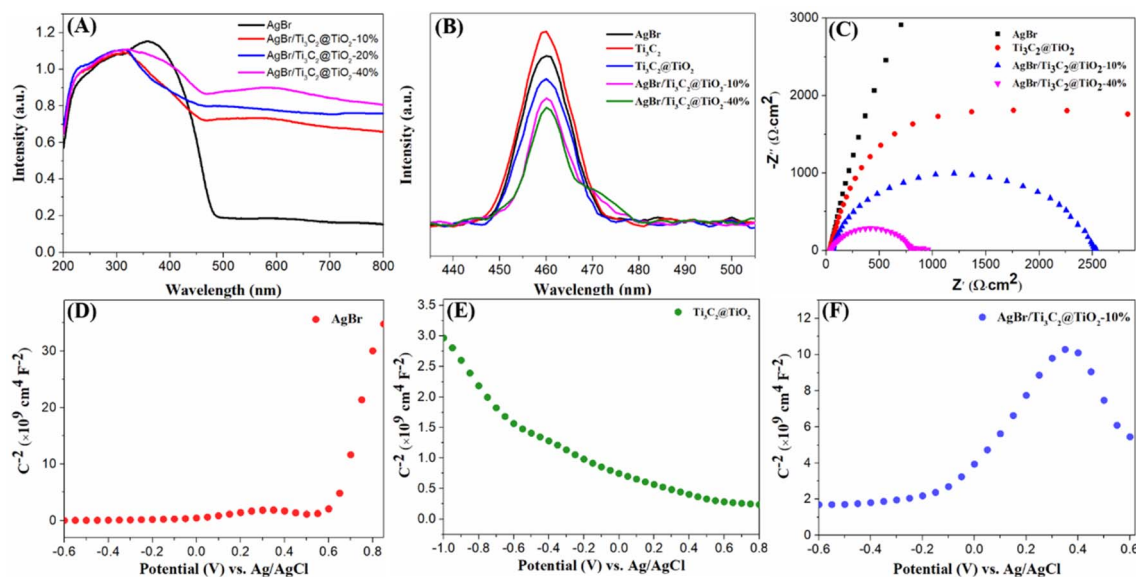


Fig. 11 UV-vis DRS of the as-prepared samples (A), PL spectra (B), EIS Nyquist plots of samples (C), Mott-Schottky plots of AgBr (D), Ti₃C₂@TiO₂ (E) and AgBr/Ti₃C₂@TiO₂-10% (F).

level of Ag⁰ nanoparticles.^{64–66} Therefore, the electrons on the CB of AgBr can rapidly transfer to the CB of TiO₂ (eqn (2)) or be captured by Ag⁰ nanoparticles through Schottky barrier (eqn (3)).⁶⁷ The electrons on the CB of TiO₂ can further

transfer to Ti₃C₂ (eqn (4)), since the CB potentials of TiO₂ is more negative than the Fermi level of the Ti₃C₂.^{30,68,69} Thus, the photoinduced charge carriers on AgBr is efficiently separated, and the photocatalytic activity of AgBr is improved by

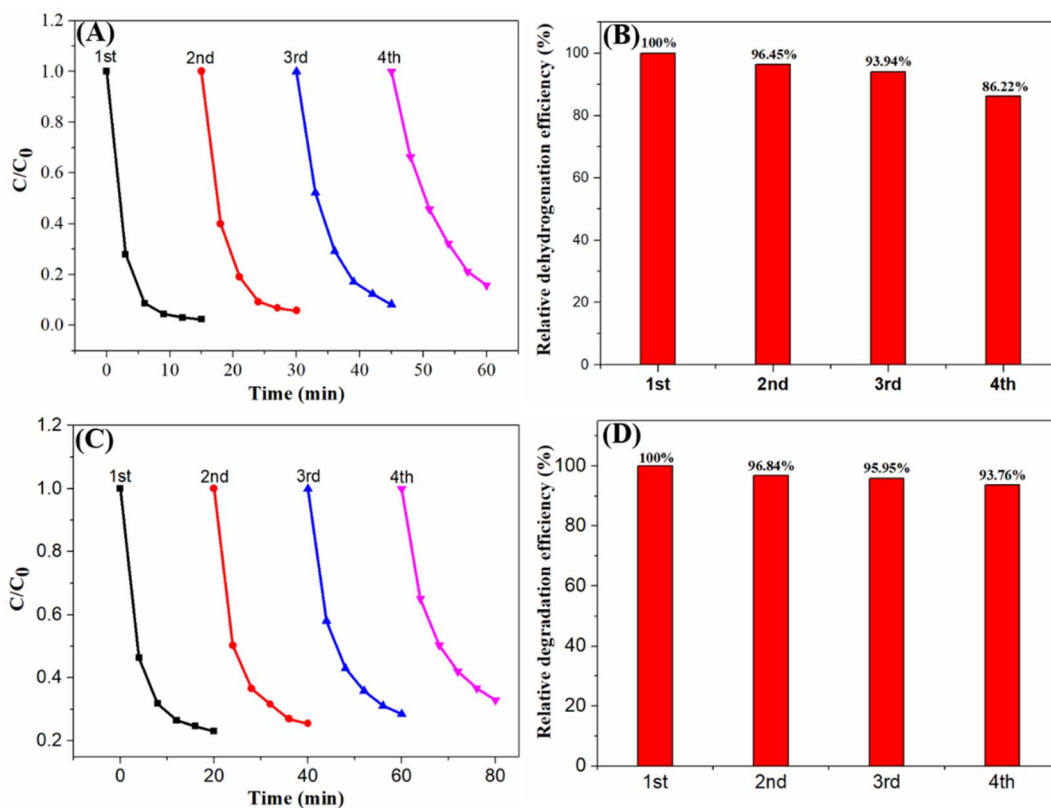


Fig. 12 Cyclic kinetics curve and relative dehydrogenation efficiency of 1,4-DHP by AgBr/Ti₃C₂@TiO₂-40% (A and B); cyclic kinetics curve and relative degradation efficiency of TCH by AgBr/Ti₃C₂@TiO₂-10% (C and D).



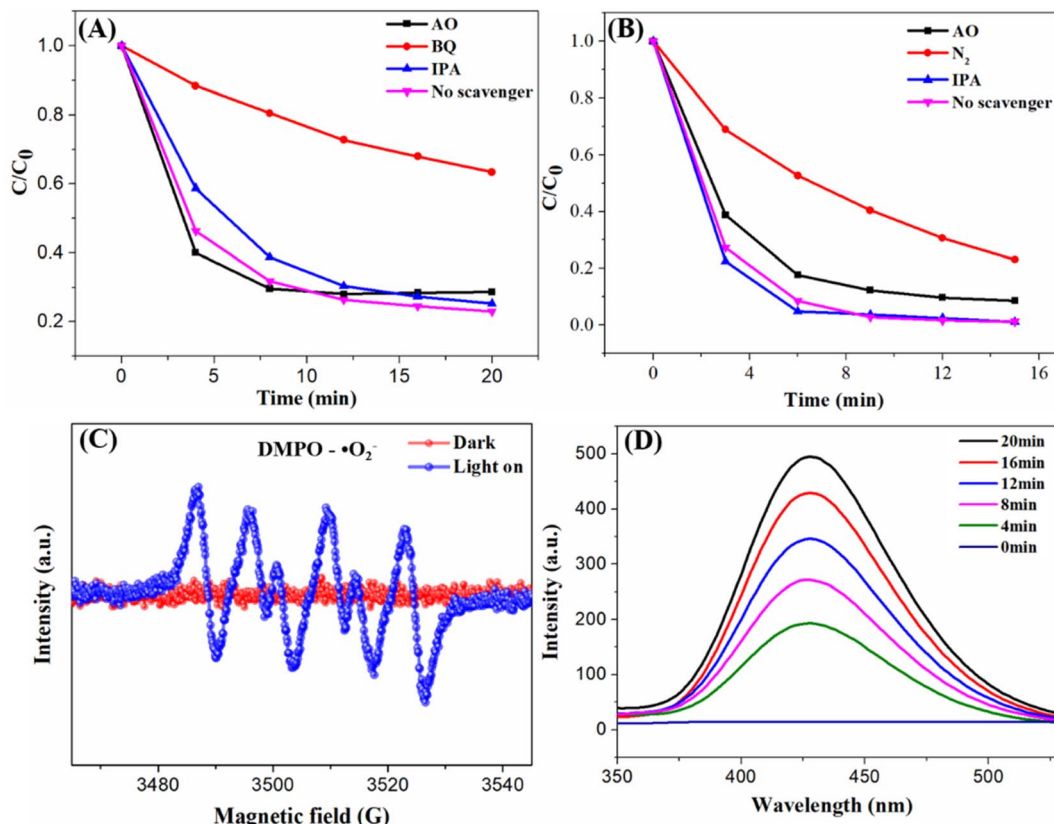
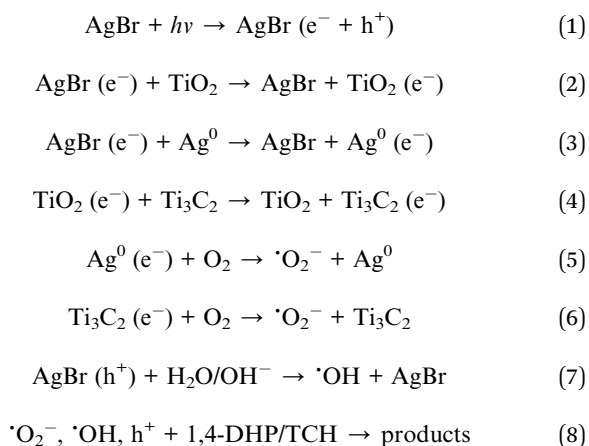


Fig. 13 The effect of certain selected scavengers on the photooxidation of TCH (A) and 1,4-DHP (B) under visible light ($\lambda > 400$ nm) irradiation, EPR signals of AgBr/Ti₃C₂@TiO₂ under dark and visible light irradiation (C) and fluorescence spectra of 0.5 mM alkaline terephthalic acid (TA) solution in the presence of AgBr/Ti₃C₂@TiO₂ composite under visible light irradiation (D).

compositing with Ti₃C₂@TiO₂. The electrons transferred to Ag⁰ and Ti₃C₂ are subsequently captured by O₂ to produce $\cdot O_2^-$ (eqn (5) and (6)). At the same time, the h^+ left on the valence band (VB) of AgBr can convert H₂O and OH⁻ (H₂O/OH⁻) to $\cdot OH$ (eqn (7)). The produced $\cdot O_2^-$, $\cdot OH$ and h^+ may all be utilized as oxidizer for 1,4-DHP dehydrogenation and TCH degradation (eqn (8)).



It is worth pointing out that the main active species are $\cdot O_2^-$ and h^+ for 1,4-DHP dehydrogenation, while $\cdot O_2^-$ and $\cdot OH$ for TCH degradation. In other words, the photogenerated

h^+ in the VB of AgBr can react with H₂O and OH⁻ to produce $\cdot OH$, then the generated $\cdot OH$ is consumed by the oxidation of TCH in the TCH-catalyst system. But for the 1,4-DHP-catalyst system, the generated $\cdot OH$ 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 Ti₃C₂@TiO₂ 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 Ti₃C₂@TiO₂ is different for 1,4-DHP and TCH.

To sum up, under visible light irradiation, The enhanced photocatalytic performance of AgBr/Ti₃C₂@TiO₂ composite should be attributed to the following aspects: (1) the formation of a p-n heterojunction between AgBr and TiO₂ and the introduction of Ti₃C₂ 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, TiO₂ and Ti₃C₂ increases, which also promotes the transfer of photogenerated carriers. (3) Ti₃C₂ and AgBr has good absorption capacity for visible light, which can increase the utilization of visible light by composite materials.



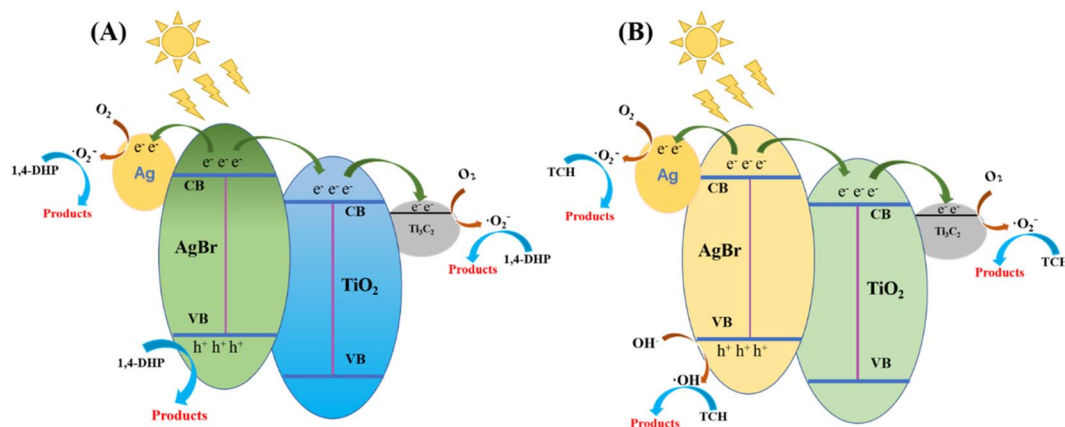


Fig. 14 Hypothetical mechanism diagram of dehydrogenation of 1,4-DHP (A) and photodegradation of TCH (B) by AgBr/Ti₃C₂@TiO₂ composites under visible light ($\lambda > 400$ nm).

4. Conclusions

In conclusion, AgBr/Ti₃C₂@TiO₂ 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/Ti₃C₂@TiO₂ composite photocatalyst showed improved photocatalytic performance compared with AgBr and Ti₃C₂@TiO₂. The photocatalytic performance of the AgBr/Ti₃C₂@TiO₂ composite with optimized composition is 3.9 and 24.5 times higher than that of pure AgBr and Ti₃C₂@TiO₂, respectively, for photodehydrogenation of 1,4-DHP and 1.9 and 5.9 times higher than that of pure AgBr and Ti₃C₂@TiO₂ for photodegradation of TCH. The improvement of photocatalytic performance of AgBr/Ti₃C₂@TiO₂ composite is due to the formation of p-n heterojunction structure between AgBr and Ti₃C₂@TiO₂, and the using of Ti₃C₂ as cocatalyst, which reduced the internal resistance, accelerated charge transfer and improved the separation efficiency of photo-generated carriers. In addition, AgBr/Ti₃C₂@TiO₂ composite photocatalyst also showed good stability in photochemical reaction, indicating that the AgBr/Ti₃C₂@TiO₂ composite has potential application in photooxidation reaction, wastewater treatment and environmental remediation.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by the Opening Project of Key Laboratory of Green Chemistry of Sichuan Institutes of Higher Education (LZJ2002) and the Open Project of Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province (CSPC2016-3-2).

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