TiO$_2$-Based photocatalyst modified with a covalent triazine-based framework organocatalyst for carbamazepine photodegradation

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A novel fluorine-doped TiO$_2$ (TiO$_{2-x}$F$_x$) heterojunction semiconductor photocatalyst was synthesised using covalent triazine-based frameworks (CTFs) at different weight ratios. X-ray photoelectron spectroscopy revealed that doping with CTFs shifts the value of the TiO$_{2-x}$F$_x$ catalyst to a lower binding energy, which led to the bandgap narrowing. From the results of the photocatalytic activity and Fourier-transform infrared spectroscopy, a rise in carbamazepine (CBZ) adsorption under dark conditions and an increased intensity of characteristic triazine units after exfoliation were observed, which indicated that the addition of nanosheet CTFs would increase the number of active sites. Furthermore, the results showed that the TiO$_{2-x}$F$_x$/CTFs photocatalyst was almost 5.5 times better than pure TiO$_{2-x}$F$_x$ in the removal of CBZ under visible light owing to the narrowed bandgap, the increased active sites, the quick separation of photo-generated carriers, and improved light absorption. A mechanism for photodegradation of CBZ with the TiO$_{2-x}$F$_x$/CTFs photocatalyst was proposed.

Introduction

TiO$_2$-Based semiconductor photocatalysts have been widely studied owing to their low toxicity, low-cost, and high physicochemical stability. However, the main disadvantages of TiO$_2$-based photocatalysts are their wide bandgaps (3.0 eV for rutile and 3.2 eV for anatase), and high electron–hole pair recombination rates. Therefore, doping with metal or nonmetal elements, such as transition metals and nonmetal anions, has been introduced to avoid these disadvantages. However, anionic dopants such as N-doped TiO$_2$ reduce the photocatalytic activity if the nitrogen content exceeds a certain value. It was observed that F-doped TiO$_2$ only had a slight effect on narrowing the bandgap. Transition-metal cations inefficiently separate electron and hole pairs, as they present recombination centres for photocatalytic carriers. Moreover, metal doping can have the drawback of thermal instability. Therefore, the synergistic effect with other organic semiconductor catalysts, such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), can lower the bandgap and lower contamination.

Among multiple attractive organic semiconductors photocatalysts, covalent triazine-based frameworks (CTFs), which possess a wide visible-light adsorption band, a tunable band structure, high chemical and thermal stability, low toxicity, a relatively narrow bandgap (2.4 eV), and cheap, have been considered as a suitable co-catalyst for TiO$_2$-based photocatalysts. However, CTFs have similar problems, such as fast photogenerated carrier recombination, to other photocatalysts. The synthesis of heterostructures could enhance the separation of the electron–hole pairs, thus improving the photocatalytic performance.

In this work, we have modified TiO$_{2-x}$F$_x$ with CTFs using different weight ratios. The synergistic effect of TiO$_{2-x}$F$_x$/CTFs was investigated through photocatalytic degradation of a typical pharmaceutical carbamazepine (CBZ) under simulated sunlight irradiation ($\lambda > 420$ nm). Moreover, physicochemical characterisation, such as scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) N$_2$ adsorption–desorption, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were performed and discussed.

Experimental methods

Materials

Tetrabutyl titanate (C$_{16}$H$_{36}$O$_4$Ti), 1,4-dicyanobenzene (DCB), trifluoromethanesulfonic acid (TFMS), N,N-dimethylformamide (DMF), potassium monopersulfate triple salt (PMS, KHSO$_5$·0.5KHSO$_4$·0.5K$_2$SO$_4$), CBZ, methanol, and sodium hydroxide (NaOH) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. Ethanol (EtOH) was obtained from Shanghai Titan Scientific Co., Ltd. Hydrofluoric Acid (HF) was purchased from Kunshan Jincheng Reagent Co., Ltd.
Synthesis of TiO$_2$-$xF_x$

The fluorine-doped TiO$_2$ (TiO$_2$-$xF_x$) nanosheets were fabricated by a simple hydrothermal method. C$_{16}$H$_{36}$O$_4$Ti (50 mL) was dissolved in a HF solution (40 wt%, 10 mL), and the mixture was heated in a Teflon-lined autoclave (100 mL) at 240 °C for 24 h after stirring for 30 min at ambient temperature. The precipitation products were obtained using centrifugation and washed three times with ethanol and ultrapure water. The sky blue photocatalyst was obtained after drying in an oven at 80 °C for 12 h.

Synthesis of CTFs

DCB (98 wt%, 4 mmol) was dissolved in TFMS (2.5 mL) under N$_2$ at 0 °C. Then silica microspheres (0.5 g) were added to the mixture with continuous stirring for 1.5 h at 0 °C. Thereafter, the synthesised products (SiO$_2$@CTFs), were heated to 100 °C for 20 min, obtained by centrifugation, and washed several times with ultrapure water and ethanol. Subsequently, the composite was dried in a vacuum overnight at 60 °C. H-CTF-Na photocatalysts were synthesised with NaOH (0.5 M) under hydrothermal conditions for 5 h at 60 °C. The products were obtained following centrifugation, washing with ultrapure water and ethanol until neutral, and then dried in a vacuum for 12 h at 60 °C.

Synthesis of TiO$_2$-$xF_x$/CTFs heterojunction photocatalyst

Two types of semiconductor photocatalysts were synthesised through different synthesis methods. In brief, a TiO$_2$-$xF_x$/CTFs van der Waals heterojunction was produced using an ultrasonic and mechanical method. The TiO$_2$-$xF_x$/CTFs mixture was added into a DMF aqueous dispersion (50 mL) and stirred for 2 h. Thereafter, the sample was sonicated for 1 h, washed with ethanol three times, and finally dried in a vacuum overnight at 50 °C. To optimise the photocatalytic characteristic, TiO$_2$-$xF_x$/CTFs was synthesised with three different weight ratios between TiO$_2$-$xF_x$ and CTFs (1 : 0.2, 1 : 0.5, and 1 : 1).

Characterisation

The crystal structures of the synthesised composites were examined using XRD (X’Pert Pro MPD, Panalytical, Netherlands) with a Cu Kα X-ray radiation source (60 kV and 55 mA). The morphology and textural properties of different samples were determined using SEM (SU8010, Hitachi, Japan). The Brunauer–Emmett–Teller (BET) was used to record the surface area with N$_2$ adsorption–desorption isotherms on an ASAP 2020 system (Micromeritics, USA). FTIR spectra (Thermo Scientific, USA) was measured on a Nicolet iS 10 spectrometer. XPS (Thermo Scientific K-Alpha, USA) was recorded to analyse the surface chemical environments. The excitation source was Al Kα (hv = 1486.6 eV) and the X-ray gun was operated at 72 W (12 kV, 6 mA).

Photocatalytic reaction

The photocatalytic activity of three prepared TiO$_2$-$xF_x$/CTFs catalysts and pure TiO$_2$-$xF_x$ were examined through the photodegradation of carbamazepine (CBZ) in aqueous solutions with simulated sunlight irradiation. The solution of CBZ (5 mg L$^{-1}$) was prepared and diluted with deionised water to desirable experimental concentrations. The experiments were performed using a CEL-S500/350 Xe lamp (Beijing CeauLight Co., Ltd, China) with an optical cut-off filter (λ > 420 nm). A thermostat (DFY-5L/40, Gongyi City Yuhua Instrument Co., Ltd, China) was applied to preserve the invariable temperature at 25 °C.
Before mixing with the four different photocatalysts, PMS (40 mg) was added to a CBZ aqueous solution (100 mL, 5 mg L$^{-1}$) in a photo-reactor. The suspension was continuously stirred under dark conditions for 30 min at 25 °C to establish an adsorption–desorption equilibrium. Thereafter, the Xe lamp was turned on to start the photocatalytic reaction, and then during the

Fig. 2 Transmission electron spectroscopy images of (a) TiO$_2$-xF$_x$ (b) CTFs and (c) TiO$_2$-xF$_x$/CTFs (1 : 1), (d and e) inverse fast Fourier transform images (the insets) (f) energy-dispersive X-ray spectroscopy and (g) element mapping images of TiO$_2$-xF$_x$/CTFs (1 : 1).
In the photocatalytic reaction, aliquots (1.0 mL) were taken and filtered at certain intervals using a syringe filter (0.22 μm). The concentration of the filtered solution was detected using mass spectrometry (Agilent HPLC-1260 with a C18 column (4.6 mm × 150 mm, 4 μm) and a UV detector). The mobile phase was methanol (80%) in ultrapure water (flow rate of 1.0 mL min⁻¹), the column temperature was 40 °C, and the detection wavelength was 285 nm.

Result and discussion

Fig. 1 showed SEM images of pure TiO₂xFx, pure CTFs and the combination of two catalysts. In Fig. 1a, TiO₂xFx demonstrated a uniform octahedral sheet structure¹ and CTFs displayed a structure with a rough surface (Fig. 1b). SEM images of TiO₂xFx/CTFs heterojunctions were shown in Fig. 1c, in which the agglomerate structure of TiO₂xFx was exhibited.

TEM

Transmission electron microscopy (TEM) was performed to reveal the crystallographic properties of pristine TiO₂xFx, pristine CTFs, and the synthesised TiO₂xFx/CTFs with a weight ratio 1 : 1 at an atomic scale (Fig. 2a–c). TEM images indicated that TiO₂xFx possesses the regular octahedral shape (Fig. 2a), the CTFs edge showed a layered structure (Fig. 2b), and the TiO₂xFx/CTFs (1 : 1) catalyst demonstrated a combination of the two substances (Fig. 2c). As shown in Fig. 2d and e, to further investigate the structure of TiO₂xFx/CTFs (1 : 1), we enlarged the selected regions (red box) with the inverse fast Fourier transform (IFFT) images (Fig. 2d and e). The IFFT image revealed regular lattice fringes with a d-spacing of 0.23 and 0.35 nm, corresponding to the (004) plane and (101) plane of anatase.⁴ The IFFT image also displayed the CTFs layer extending to the border in Fig. 2e.

Furthermore, energy-dispersive X-ray spectroscopy (EDS) (Fig. 2f) revealed that TiO₂xFx/CTFs mainly consists of C, N, O, Ti, and F. The element mapping images of TiO₂xFx/CTFs (1 : 1) (Fig. 2g) showed that C (deep red), N (green), O (yellow), and Ti (deep blue) were evenly dispersed, which confirmed that TiO₂xFx and CTFs were well combined. These results were further demonstrated by XRD and XPS analyses.

BET

N₂ adsorption–desorption measurements shown in Fig. 3 indicated the porosity of the four photocatalysts. The samples exhibited a type IV isotherm and H3 hysteresis loop.⁷ The plunge in the desorption curve and the hysteresis loop at high relative pressure indicated the mesoporosity of the samples (Fig. 3a). The pore size distributions (Fig. 3b), which were acquired using the BJH (Barret–Joyner–Halenda) method, indicated that the samples have a wide pore distribution range (10–130 nm).

The BET specific surface area, total pore volume, and average pore diameter of the four catalysts were shown in Table 1. With an increase in CTF concentration, a slight decrease in BET surface area and pore volume was seen. This indicated that the addition of CTFs might result in a relatively dense organic framework through agglomeration, which was indicated by SEM images, and led to smaller mesopore size and lower surface area.

![Fig. 4 (a) X-ray diffraction patterns of different photocatalysts and (b) enlarged XRD patterns of the TiO₂xFx/CTFs photocatalysts with different weight ratios.](image)

![Table 1](table)

| TiO₂xFx/CTFs | BET surface areas (m² g⁻¹) | Total pore volume (cc g⁻¹) | Average pore diameter (nm) |
|-------------|-----------------------------|-----------------------------|---------------------------|
| 1 : 0       | 23.283                      | 0.212                       | 36.42                     |
| 1 : 0.2     | 18.785                      | 0.1811                      | 38.56                     |
| 1 : 0.5     | 13.323                      | 0.08727                     | 25.81                     |
| 1 : 1       | 9.357                       | 0.057                       | 24.37                     |
XRD

Three TiO$_2$–xF$_x$/CTFs photocatalysts with different weight ratios and a pure TiO$_2$–xF$_x$ catalyst were analysed using XRD. Fig. 4a showed the diffraction peaks which corresponded to the TiO$_2$ crystalline phase of anatase. The diffraction peaks at approximately 25.3°, 37.8°, 48.1°, 53.9°, 55.1°, 62.7°, 68.7°, 70.3°, and 75.1° correspond to the crystal planes of (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively. An increase in the characteristic peak for CTFs was observed in the XRD patterns (Fig. 4b). The main increased intensity was observed at around 27.0°, which indicated the crystal plane of the π-conjugated bond rings. These results indicated the presence of both photocatalysts. With decreasing weight ratio of TiO$_2$–xF$_x$/CTFs from 1:0.2 to 1:1, the intensity of anatase decreased. Meanwhile, the intensity of CTFs was improved.

FTIR

To investigate the impact of exfoliation on bulk CTFs through sonication, FTIR was measured. As shown in Fig. 5a, the characteristic bands for triazine (1560–1350 cm$^{-1}$) were seen for bulk CTFs and nanosheet CTFs. Compared with bulk CTFs, an increased intensity for the adsorption peak corresponding to triazine in the nanosheet CTFs was observed, which indicated that by exfoliating bulk CTFs to form nanosheet CTFs, triazine was exposed on the surface of CTFs. FTIR analysis of the photocatalysts indicated the successful formation of triazine (Fig. 5b). All samples showed a strong adsorption band at approximately 1560–1350 cm$^{-1}$, which corresponded to the triazine unit. A strong adsorption band at approximately 520 cm$^{-1}$, which corresponded to the Ti–O stretching band, was demonstrated when the TiO$_2$–xF$_x$/CTFs weight ratio is at 1:0.2. However, for the weight ratios 1:0.5 and 1:1, the Ti–O stretching band was hardly visible.

XPS

The XPS survey spectra of the photocatalysts indicated that they contained C, N, Ti, O, and F. For the TiO$_2$–xF$_x$/CTFs photocatalysts with weight ratios 1:0.2 (black), 1:0.5 (red), and 1:1 (blue).
Fig. 6  (a) X-ray survey and high-resolution spectrum for (b) C 1s, (c) N 1s, (d) O 1s, and (e) Ti 2p.
The effect of TiO$_2$/C0X/CTFs on CBZ photocatalytic degradation

To investigate the photocatalytic activity of the catalysts, the degradation of CBZ in the presence of PMS irradiated under visible light was performed. It is well-known that PMS cannot degrade CBZ effectively without a catalyst. The results of these measurements were shown in Fig. 7a.

After treatment under dark conditions for 30 min, the TiO$_2$-xF$_x$/CTFs catalysts had a higher CBZ adsorption than pure TiO$_2$-xF$_x$ catalyst (approximately 4.7%). Notably, for the catalyst with 50% CTF, the degradation efficiency was 46.7%, which is almost 10 times higher than pure TiO$_2$-xF$_x$. In this study, the degradation efficiency of the TiO$_2$-xF$_x$/CTFs catalyst was enhanced owing to the presence of Ti$^{3+}$ and triazine units, which provide a large number of active sites, thus improving CBZ absorption.

Under visible light, the degradation efficiency of the TiO$_2$-xF$_x$ and CTFs catalysts with weight ratios 1:0, 1:0.2, 1:0.5, 1:1, and 0:1 was 13.3%, 29.2%, 50.5%, 72.8%, and 82.7%, respectively, within 100 min of irradiation. These results showed that there was an increase in CBZ degradation with an increase in the weight ratio of CTFs. In addition, the trend of CBZ degradation efficiency of the pure CTFs was similar to that of the pure TiO$_2$-xF$_x$, there was no significant degradation trend when compared to the TiO$_2$-xF$_x$/CTFs heterojunction catalyst in the visible light region, which indicated that the synthesis of heterostructures could decrease the recombination of the electron-hole pairs, thus improving photocatalytic performance.

The bandgaps of TiO$_2$-xF$_x$ and CTFs are 3.13 eV$^1$ and 1.85–1.50 eV,$^{54}$ respectively. The shift of the O 1s and Ti 2p XPS peaks to lower binding energy demonstrated that the presence of CTFs could decrease the bandgap. As mentioned above, the cooperative effect of CTFs not only exposes a large number of active sites, but also significantly narrows the bandgap, decreasing the photo-generated charge transfer distance, and increasing visible light adsorption, so that the recombination of the electrons and holes is impeded, which improves the photocatalytic activity.

To further evaluate the stability of the TiO$_2$-xF$_x$/CTFs heterojunction photocatalyst, recyclability tests for CBZ photodegradation were performed on a representative TiO$_2$-xF$_x$/CTFs catalyst (1:1). As shown in Fig. 7b, no obvious decrease in the removal efficiency of CBZ could be observed for 650 min under visible-light irradiation over five continuous runs. The results exhibited the recyclability and stability of the TiO$_2$-xF$_x$/CTFs photocatalyst.

Mechanism for CBZ photocatalytic degradation on TiO$_2$-xF$_x$/CTFs

A possible mechanism for CBZ photocatalytic degradation on TiO$_2$-xF$_x$/CTFs is presented in Fig. 8. After exposure to the Xe lamp, photogenerated carriers are excited from the valence band into the conduction band of catalysts. PMS quickly captures the photo-generated electrons on the surface of the...
catalysts, and transfers into $\text{O}_2^{-\text{aq}}$ and $\text{SO}_4^{2-}$ radicals form. Intermediate $\text{O}_2^{-\text{aq}}$ could further react with PMS to produce ‘OH and $\text{SO}_4^{2-}$ radicals. As for $\text{SO}_4^{2-}$, it may oxidise $\text{H}_2\text{O}$ to form a ‘OH radical. After a series of reactions, PMS is oxidised to generate chiefly ‘OH and $\text{SO}_4^{2-}$ radicals.\textsuperscript{54} In addition, CBZ may be oxidised by photogenerated h$^+$ directly. So CBZ could be degraded in the presence of ‘OH, $\text{SO}_4^{2-}$ and h$^+$ oxidative species to finally transform into $\text{CO}_2$ and $\text{H}_2\text{O}$ via a chain of reactions.

As is shown in Fig. 8, the conduction band of CTFs (0.2 eV)\textsuperscript{54} is more positive than TiO$_2$-xF$_x$ (–0.5 eV),\textsuperscript{44} whereas the valence band of CTFs (1.48–1.83 eV)\textsuperscript{54} is more negative than TiO$_2$-xF$_x$ (2.63 eV). Therefore, the photogenerated electrons and holes could transfer easily from the surface of TiO$_2$-xF$_x$ to the surface of CTFs. In this case, the migration of e$^-$ and h$^+$ between the two photocatalysts could effectively separate photo-charged carriers and further favour visible light absorption.

Conclusions

In summary, TiO$_2$-xF$_x$/CTFs van der Waals heterojunction photocatalysts were successfully synthesised using a stirring and sonication method. A synergetic effect of heterostructure catalysts was observed through the photocatalytic degradation of CBZ. The removal efficiency of CBZ was influenced by the TiO$_2$-xF$_x$/CTFs weight ratio and reaction time. The XPS results suggested a strong interaction between TiO$_2$-xF$_x$ and CTFs and electron transfer between the two photocatalysts. The synergetic effect results in a smaller bandgap, improved light adsorption, and the separation of electrons and holes. In addition, CBZ adsorption under dark conditions was enhanced compared to TiO$_2$-xF$_x$ owing to the increased number of active sites, which could be observed using FTIR and XPS. Furthermore, this highly efficient, low toxic, cheap, and high-performing photocatalyst provides a novel, green, and facile method for organic pollutant treatment.

Conflicts of interest

There are no conflicts to declare.

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