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## Applications of MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) in photocatalysis: a review

Xing Li,<sup>a</sup> Yang Bai,<sup>\*a</sup> Xian Shi,<sup>b</sup> Na Su,<sup>a</sup> Gongzhe Nie,<sup>a</sup> Rumeng Zhang,<sup>c</sup>  
Hongbo Nie<sup>ad</sup> and Liqun Ye<sup>id \*ae</sup>

MXenes are two-dimensional nanomaterials, which can be constructed from different elements. The rich interlayer groups, surface groups, and the flexible layer spacing of MXenes make them ideal catalysts. Among these,  $\text{Ti}_3\text{C}_2\text{T}_x$  has gained particular attention as a photocatalyst for photocatalytic  $\text{CO}_2$  reduction reactions ( $\text{CO}_2\text{RR}$ ), hydrogen evolution reactions (HER), and photocatalytic degradation reactions. The structure of  $\text{Ti}_3\text{C}_2\text{T}_x$ , hydrophilic surface functional groups, and the Gibbs free energy for hydrogen adsorption lead to the excellent photocatalytic HER performance of this material. Numerous surface defects on  $\text{Ti}_3\text{C}_2\text{T}_x$  also provide plentiful  $\text{CO}_2$  adsorption sites for  $\text{CO}_2\text{RR}$ . It is the structure of two-dimensional nanomaterials and their high-speed electron transport channels that enable their excellent catalytic oxidation activity. However, at present, there are still challenges that limit their further application, the most significant of which is the material stability. In order to overcome this, the synthetic routes to prepare these photocatalysts need to be adapted.

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## 1 Introduction

Photocatalysis is an environment-friendly technology developed in the 20th century. When light is absorbed by some special semiconductors, namely “photocatalysts”, electrons ( $e^-$ ) originally in the valence band (VB) are excited to the conduction band (CB) and holes ( $h^+$ ) are formed in the initial position. Free electrons with strong reducibility can reduce the valence state of some elements in compounds (such as carbon in  $\text{CO}_2$  and nitrogen in  $\text{N}_2$ ) when regular methods are not useful or cost too much. Thus far, photocatalysis has shown its huge application prospects in clean energy, environmental remediation, and many other fields; currently, researchers are heading towards new photocatalyst development and reaction mechanisms. Photocatalytic hydrogen evolution reaction (HER),  $\text{CO}_2$  reduction reaction ( $\text{CO}_2\text{RR}$ ), and photocatalytic degradation reaction represent the three main aspects of photocatalysis.

Photocatalytic nanomaterials have an extensive number of potential applications. When their particle size is below a certain value, the Fermi level of the electronic energy levels morphs from continuous to discrete levels and the energy gap grows wider. These semiconductors are, therefore, more susceptible to photon excitation, which improves their photocatalytic activity.<sup>1</sup>

Nanomaterials can be divided into four categories, according to the dimensions of their structural scale: (1) zero-dimensional materials, *e.g.*, groups of nanostructure clusters; (2) one-dimensional nanomaterials, *e.g.*, fibrous nanotubes, nanowires, nanoribbons, or other related structures; (3) two-dimensional nanomaterials, *e.g.*, layered nanomaterials, quantum wells, superlattices, and other structures; (4) three-dimensional nanomaterials, *e.g.*, composite structures consisting of one or more zero-dimensional, one-dimensional, or two-dimensional nanomaterials. The first three are collectively known as low Vannami materials. In low Vannami materials, two-dimensional nanomaterials show significant changes in the surface, electron energy levels, state density, and other aspects compared with three-dimensional materials. This due to the fact that their thickness is greatly reduced compared to other two-dimensional materials; thus, these possess unique optical and electronic characteristics, which make them a hot topic in catalysis.<sup>2,3</sup>

MXenes are two-dimensional nanomaterials and have a general material formula of  $\text{M}_{n+1}\text{X}_n\text{T}_x$ . In this formula, M represents nitrogen or carbon, X is generally a transition metal element, and T represents the functional groups. MXenes typically consist of transition metal carbides, nitrides, or carbides that are several

<sup>a</sup> State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, School of Oil & Natural Gas Engineering, Southwest Petroleum University, Chengdu, 610500, China. E-mail: baiyanghyq@foxmail.com

<sup>b</sup> Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, 610054, China

<sup>c</sup> Key Laboratory of Ecological Security for Water Source Region of Mid-line Project of South-to-North Water Diversion of Henan Province, College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, 473061, China

<sup>d</sup> CNOOC (China) Co., LTD. Tianjing Branch, Tianjing, 300452, China

<sup>e</sup> College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, 443002, China. E-mail: lqye@ctgu.edu.cn



atomic layers thick. It was first reported in 2011<sup>4</sup> that MXene materials have comparable conductivity towards transition metal carbides due to the presence of hydroxy groups or terminal oxygen species on their surfaces. The most important feature of this range of materials is that, unlike conventional battery materials, they provide more channels for ions to move through, thus dramatically increasing their speed.

$\text{Ti}_3\text{C}_2\text{T}_x$  was the first discovered MXene material and is also the most widely used MXene material in the field of photocatalysis.<sup>5–7</sup> It was first obtained by etching the Al layer of  $\text{Ti}_3\text{AlC}_2$  with hydrofluoric acid. In this paper, the application of  $\text{Ti}_3\text{C}_2\text{T}_x$  as a photocatalyst and approaches to improve its catalytic performance are summarized.

## 2 MXene

**2.1 From MAX to MXene.** MXenes are a type of two-dimensional nanomaterials with covalent bonds formed between the early transition elements and nitrogen or carbon elements. This furnishes an intramolecular skeleton in which the layers are connected by hydrogen bonds. Since the first MXene,  $\text{Ti}_3\text{C}_2\text{T}_x$ , was discovered in 2011, more than 20 kinds of MXene materials including  $\text{M}_2\text{X}$ ,  $\text{M}_3\text{X}_2$ , and  $\text{M}_4\text{X}_3$  have been successively prepared.<sup>7,8</sup> Due to their unique structure and properties, MXenes have been widely favored for use in battery applications.

The preparation of MXenes can be divided into two approaches, namely, bottom-up and top-down. Presently, the top-down etching method is commonly employed. This is due to the MAX phase<sup>9,10</sup> (commonly, M means early transition metal elements such as Ti and Nb; A represents the Al or Si layer; X represents C or N elements) as M is mainly composed of metallic bonds between the atoms, which are connected to A. The chemical properties are largely dictated by A. By using certain concentrations of hydrofluoric acid or  $\text{LiF}/\text{HCl}$ <sup>11</sup> to etch the MAX phase of  $\text{Ti}_3\text{AlC}_2$ , ternary carbides within the titanium carbon layers become closer to each other. In this process, the Al layer is etched away gradually, resulting in a greater carbon–titanium interlayer spacing in the  $\text{Ti}_3\text{C}_2\text{T}_x$  product. In order to obtain  $\text{Ti}_3\text{AlC}_2$  with a graphene-like structure consisting of only

a few or single layers, mechanical or chemical intercalation dissection is required. However, when chemical intercalation is used for stripping, some organic molecules may occupy the active sites exposed on the surface, which is unfavorable for photocatalytic reactions.

Etching is a slow process, as shown in Fig. 1(a). In this process, Al layers are gradually peeled off, while the Ti–C skeleton layers are not damaged because of their strong ionic bonding.<sup>12</sup> Free groups such as –OH and some  $\text{H}_2\text{O}$  molecules enter into the framework of Ti–C and become inter-connected by hydrogen bonds, which expands the layer spacing of  $\text{Ti}_3\text{C}_2\text{T}_x$ . This permits ions with a large radius to enter the layer spacing,<sup>13</sup> providing an operating space for the ion intercalation method to peel-off few layers of  $\text{Ti}_3\text{C}_2\text{T}_x$ . The number of –OH groups and  $\text{H}_2\text{O}$  molecules within the interlayer space accounts for the large electrical capacity of  $\text{Ti}_3\text{C}_2\text{T}_x$ .

$\text{Ti}_3\text{C}_2\text{T}_x$  obtained by direct etching with hydrofluoric acid possesses a different morphology to  $\text{Ti}_3\text{C}_2\text{T}_x$  obtained by etching with  $\text{LiF}/\text{HCl}$ . Furthermore, NMR spectroscopy revealed a greater number of –OH and –F functional groups on the surface of  $\text{Ti}_3\text{C}_2\text{T}_x$  etched by hydrofluoric acid, while  $\text{LiF}/\text{HCl}$  etching furnished a material with predominantly –O functional groups.

## 2.2 Structure and properties of $\text{Ti}_3\text{C}_2\text{T}_x$

**2.2.1 Structure of  $\text{Ti}_3\text{C}_2\text{T}_x$ .** As shown in Fig. 2(a), the structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  is comprised of three parts: the intralayer skeleton region, the interlayer region, and the surface terminating groups. In the intramolecular skeleton region, Ti atoms and C atoms are stacked alternately to form ionic bonds, and the skeleton of the entire main structure is formed on this basis. In the interlayer region, it was found through neutron diffraction that the interaction between the layers is established through hydrogen bonding between either O or F atoms on the surface and van der Waals forces between these atoms. The strength of interlayer hydrogen bonding depends not only on the orientation of –OH relative to the entire sheet but also on the number and distribution of the –OH groups. When there is water between the layers, it can also participate in hydrogen bonding. In addition, a large number of terminal groups are

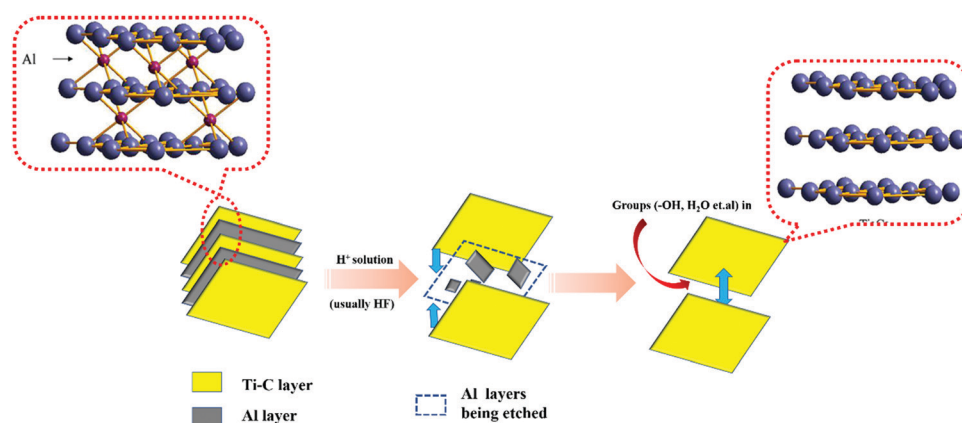


Fig. 1 The process of etching  $\text{Ti}_3\text{AlC}_2$  to yield  $\text{Ti}_3\text{C}_2$ .



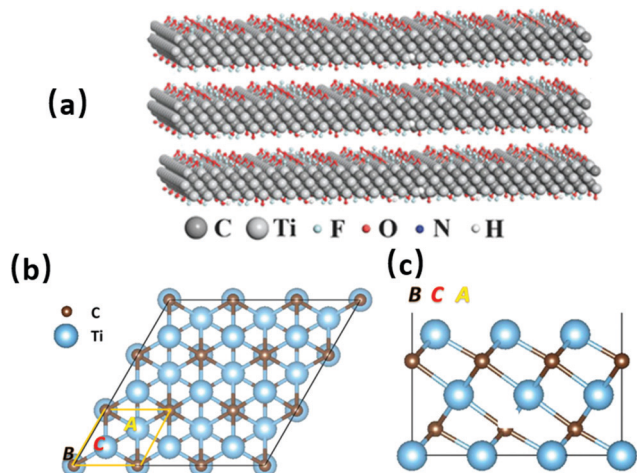


Fig. 2 Schematic diagram showing the crystal structure of  $\text{Ti}_3\text{C}_2$  (a)<sup>19</sup> and its monolayer with (b) top and (c) side view. The large blue balls represent Ti atoms and the small brown balls represent C atoms. The highlighted unit cell indicates the high symmetry A, B, and C adatom sites.<sup>20</sup>

randomly distributed on the surface of the  $\text{Ti}_3\text{C}_2\text{T}_x$  main structure. These surface groups are directly bonded to the exposed surface and  $\text{Ti}_3\text{C}_2\text{T}_x$  is obtained by top-down etching, which mainly includes surface groups such as  $-\text{O}$ ,  $-\text{OH}$ , and  $-\text{F}$ . After a period of placement, the  $-\text{F}$  groups can be replaced by  $-\text{O}$  groups. The surface groups have a great influence on the properties of the  $\text{Ti}_3\text{C}_2\text{T}_x$  formed, which can be analyzed by electron energy loss spectroscopy (TEM),<sup>14,15</sup> neutron scattering,<sup>16</sup> and NMR techniques.<sup>17,18</sup> These experiments confirm that the surface functional groups of  $\text{Ti}_3\text{C}_2\text{T}_x$  are randomly distributed with  $-\text{O}$ ,  $-\text{OH}$ , and  $-\text{F}$  all directly bonded to the surface of the exposed MXene plane. Furthermore, there are no adjacent  $-\text{OH}$  functional groups found between the layers. The presence of cations between the layers causes the MXene lamellae to slide easily relative to each other, changing their rheological properties and resulting in their clay-like properties.

**2.2.2 Properties of  $\text{Ti}_3\text{C}_2\text{T}_x$ .** The structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  determines the electric storage performance. As  $\text{Ti}_3\text{C}_2\text{T}_x$  has a wide spacing between the layers, the ions can travel through the layers at a high speed, whilst the hydroxyl or terminal oxygen groups on the surface furnish a material with excellent conductivity. Both factors are important for the use of these MXene materials in batteries.<sup>20–25</sup>

Various surface groups (such as  $-\text{O}$ ,  $-\text{F}$ , and  $-\text{OH}$ ) have supplied abundant anchored sites for the base photocatalyst to form efficient heterojunction structures, which are ideal for photocatalytic activities.<sup>26</sup> There is also a large number of exposed metal sites on the surface, which can be used as active sites for reactions.

The surface chemical state of MXene materials has a large influence on the regulation of its physical properties. When  $-\text{F}$  on the surface is replaced by an  $-\text{O}$  group, the electrochemical performance is improved. For example, when  $\text{Ti}_3\text{C}_2\text{T}_x$  is treated with a KOH and  $\text{CH}_3\text{OOK}$  solution, the  $-\text{O}$  groups on the surface increase, along with the electric capacity. Under an

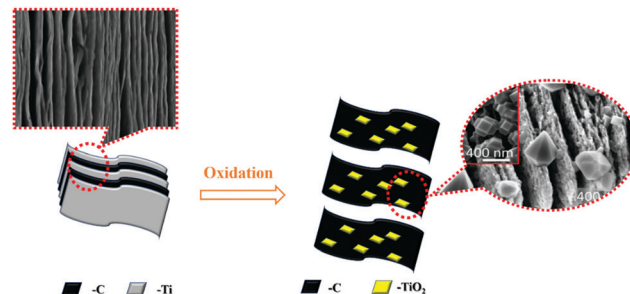


Fig. 3 Oxidation process of  $\text{Ti}_3\text{C}_2\text{T}_x$ .

atmosphere of  $\text{N}_2$ , Ar, or other inert gases, the number of  $-\text{F}$  groups on the surface of  $\text{Ti}_3\text{C}_2\text{T}_x$  is reduced, after which the electrical capacity is greatly increased.

$\text{Ti}_3\text{C}_2\text{T}_x$  shows an excellent absorption of light between 300 nm and 500 nm.<sup>27</sup> Recently, researchers have even found that the absorption can be broadened to the near-infrared (NIR) region. According to a further study, this may be related to its surface plasmon resonance (SPR), and the thinner the material, the stronger the SPR.<sup>28</sup> Such a peculiarity makes  $\text{Ti}_3\text{C}_2\text{T}_x$  an ideal photothermal co-catalyst.

**2.2.3 Instability of  $\text{Ti}_3\text{C}_2\text{T}_x$ .** MXenes typically have poor stability.  $\text{Ti}_3\text{C}_2\text{T}_x$  is rapidly oxidized when heated under  $\text{CO}_2$ , air, and other environments, and when the surface groups are all  $-\text{O}$ ,  $\text{Ti}_3\text{C}_2\text{O}_2$  exhibits metallic properties.<sup>29,30</sup>  $\text{Ti}_3\text{C}_2\text{T}_x$  is also slowly oxidized when exposed to air under atmospheric conditions. After oxidation,  $\text{Ti}_3\text{C}_2\text{T}_x$  is called oxidized MXene (denoted as MO).

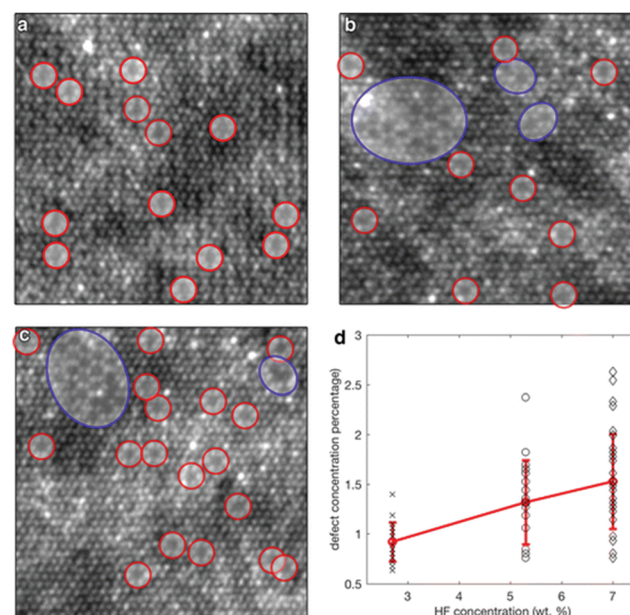


Fig. 4 HAADF-STEM images from single-layer  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene flakes prepared using etchants with different HF concentrations: (a) 2.7 wt% HF, (b) 5.3 wt% HF, and (c) 7 wt% HF. Single  $\text{V}_{\text{Ti}}$  vacancies are indicated by the red circles, while vacancy clusters  $\text{V}_{\text{Ti}}^n$  are shown by the blue circles. (d) Scatter plot of the defect concentration from the images acquired from samples produced using different HF concentrations. The red line shows the error plot with the average and standard deviation for different HF concentrations.<sup>33</sup>



Table 1 Comparison of photocatalysts including  $\text{Ti}_3\text{C}_2\text{T}_x$  in HER

Name	$\text{H}_2$ production ( $\mu\text{mol h}^{-1}$ $\text{g}_{\text{catalyst}}^{-1}$ )	AQY (%)	Activity improvement factor	Sacrificial reagent	Preparation methods	Monolayer or multilayer	Light source	Morphology	Year	Ref.
$\text{CdS}/\text{Ti}_3\text{C}_2\text{T}_x$	14 342	40.1% (420 nm)	135.59 times	Lactic acid (17.6%)	One-step hydrothermal method	$\text{Ti}_3\text{C}_2\text{T}_x$ NPs	300 W Xe lamp ( $\lambda > 420$ nm)	Cauliflower- structure by self-assembly of many NPs	2017	30
2D-Layered Carbon/ $\text{TiO}_2$	480.8	1.98% (400 nm)		TEOA (10%)	$\text{Ti}_3\text{C}_2\text{T}_x$ oxidation	Multilayer	300 W Xe lamp ( $\lambda > 400$ nm)	Nanosheets	2017	44
$\text{Ti}_3\text{C}_2\text{T}_x/\text{rutile TiO}_2$	17.8	0.3%	Approximately 4 times	Methanol (25%)	Hydrothermal method	Monolayer	200 W Hg lamp ( $\lambda > 400$ nm)	2D sheets with $\text{TiO}_2$ attached on the surfaces and between the sheets	2016	45
$\text{Ti}_3\text{C}_2/\text{Pt}/\text{g-C}_3\text{N}_4$	5000	3.1% (420 nm)	15 times than pristine $\text{g-C}_3\text{N}_4$	TEOA (10%)	Hydrothermal and photodeposition method	Monolayer	300 W Xe lamp	Nanosheets with porous nanoparticles	2018	46
Sulfur-doped Carbon/ $\text{TiO}_2$	333	7.36%		Methanol (10%)	$\text{Ti}_3\text{C}_2\text{T}_x$ oxidation	Multilayer	300 W Xe lamp ( $\lambda > 400$ nm)	Nanosheets	2018	47
$\text{Ti}_3\text{C}_2\text{T}_x/\text{TiO}_2$	783.11	5.86 (350 nm)	6 times	Methanol (20%)	Hydrothermal and calcination	Multilayer	300 W Xe lamp	Nanoflowers	2018	48
$\text{Zn}_2\text{In}_2\text{S}_5/\text{Ti}_3\text{C}_2\text{T}_x$	2596.76	8.96% (420 nm)	1.97 times	0.25 M $\text{Na}_2\text{SO}_3$ / 0.35 M $\text{Na}_2\text{S}$ / $\text{H}_2\text{PtCl}_6$	Hydrothermal	Multilayer	300 W Xe lamp ( $\lambda > 420$ nm)	Flower-like microspheres	2018	49
d- $\text{Ti}_3\text{C}_2/\text{TiO}_2/\text{g-C}_3\text{N}_4$	1620	4.16% (420 nm)	12.15 times than pure $\text{g-C}_3\text{N}_4$	TEOA (10%)	Calcination	Monolayer	300 W Xe lamp ( $\lambda > 420$ nm)	2D-2D heterostructure	2018	50
$\text{ZnS}/\text{Ti}_3\text{C}_2$	502.6		4 times	Lactic acid (20%)	Hydrothermal	Multilayer	300 W Xe lamp	Sphere-like structure	2019	51
1D $\text{CdS}$ nanorod/2D $\text{Ti}_3\text{C}_2$ MXene nanosheet	2407	35.6% (429 nm)	6.68 times	Lactic acid (10%)	Electrostatic self-assembly	Monolayer	300 W Xe lamp ( $\lambda > 420$ nm)	1D/2D nanosheets	2019	52
$\text{TiO}_2$ nanofibers/MXene $\text{Ti}_3\text{C}_2$	6979		3.8 times than $\text{TiO}_2$ nanofibers	Methanol (10%)	Electrostatic self-assembly technique	Monolayer	300 W Xe lamp	Nanofibers/ nanosheets	2019	53
$\text{TiO}_2$ nanoparticle/ monolayer $\text{Ti}_3\text{C}_2$	2650	15.8% (305 nm)	2.88 times than $\text{TiO}_2$ nanoparticles/multilayer $\text{Ti}_3\text{C}_2$	Methanol (25%)	Electrostatic self-assembly technique	Monolayer	200 W Hg lamp (285–325 nm)	Nanosheets	2019	54
$\text{MoS}_2/\text{Ti}_3\text{C}_2$	6144.7		2.33 times	Methanol (30%)	Hydrothermal	Multilayer	300 W Xe lamp ( $\lambda > 400$ nm)	Spheres-like structure	2019	55
$\text{Ti}_3\text{C}_2$ MXene/O-doped $\text{C}_3\text{N}_4$	25124	17.59% (405 nm)	1.8 times than O-doped $\text{g-C}_3\text{N}_4$	TEOA	Electrostatic self-assembly technique	Multilayer	300 W Xe lamp ( $\lambda > 400$ nm)	2D nanosheets structure	2019	56
$\text{CdLa}_2\text{S}_4/\text{Ti}_3\text{C}_2$	11182.4	15.60% (420 nm)	13.4 times	0.25 M $\text{Na}_2\text{SO}_3$ and 0.35 M $\text{Na}_2\text{S}$	Hydrothermal	Monolayer	300 W Xe lamp ( $\lambda > 420$ nm)	Particle-like	2019	57
$\text{Ti}_3\text{C}_2$ MXene quantum dots/ $\text{g-C}_3\text{N}_4$	5111.8	3.654%	25.97 times	TEOA (15%)	Deposition	$\text{Ti}_3\text{C}_2$ MXene quantum dots Multilayer	300 W Xe lamp	Nanosheets	2019	58
$\text{Mo}_2\text{S}_3/\text{TiO}_2/\text{Ti}_3\text{C}_2$	10505.8	7.535%	5.99 times than $\text{Mo}_2\text{S}_3/\text{TiO}_2/\text{Ti}_3\text{C}_2$	TEOA	<i>In situ</i> growth and hydrothermal	Multilayer	300 W Xe lamp	Nanosheets	2019	59
$\text{Ti}_3\text{C}_2$ /porous MOFs ( $\text{UiO-66-NH}_2$ )	204		Approximately 8 times	0.1 M $\text{Na}_2\text{S}$ and 0.1 M $\text{Na}_2\text{SO}_3$	Hydrothermal	Monolayer	350 W Xe lamp	3D structure	2019	60
C- $\text{TiO}_2/\text{g-C}_3\text{N}_4$	1409		8 times than C- $\text{TiO}_2$	TEOA (10%)	Calcination	Multilayer	300 W Xe lamp ( $\lambda > 420$ nm)	Smooth sheet-like structure	2019	32





Table 1 (continued)

Name	H <sub>2</sub> production ( $\mu\text{mol h}^{-1}$ $\text{g}_{\text{catalyst}}^{-1}$ )	AQY (%)	Activity improvement factor	Sacrificial reagent	Preparation methods	Monolayer or multilayer	Light source	Morphology	Year	Ref.
CdS@Ti <sub>3</sub> C <sub>2</sub> @CoO	134.46		1.75 times than CdS@CoO		Calcination	Monolayer	300 W Xe lamp ( $\lambda > 420$ nm)	Spheres-like structure	2019	61
TiO <sub>2</sub> -Ti <sub>3</sub> C <sub>2</sub> -CoS <sub>x</sub>	950		5.8 times than TiO <sub>2</sub>	Methanol (20%)	Hydrothermal	Multilayer	300 W Xe lamp	Smooth round block morphology	2019	62
Ti <sub>3</sub> C <sub>2</sub> (TiO <sub>2</sub> )@CdS/MoS <sub>2</sub>	8470		3.76 times than CdS/MoS <sub>2</sub>	lactic acid (20%)	Hydrothermal	Multilayer	300 W Xe lamp ( $\lambda > 420$ nm)	Nanospheres	2019	63
Ti <sub>3</sub> C <sub>2</sub> MXene/MoS <sub>2</sub> nanosheets/TiO <sub>2</sub>	6425.297	4.61%	7.15 times than TiO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub>	TEOA	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> oxidation	Multilayer	300 W Xe lamp	Ti <sub>3</sub> C <sub>2</sub> nanosheets with MoS <sub>2</sub>	2019	64
2D/3D g-C <sub>3</sub> N <sub>4</sub> /Ti <sub>3</sub> C <sub>2</sub> (MXene) heterojunction	116.2		6.64 times	TEOA (10%)	Calcination	Multilayer	300 W Xe lamp ( $\lambda > 420$ nm)	Nanoparticles Nanosheets	2020	65
Au/MoS <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub>	12000			Methanol (30%)	Electrostatic self- assembly technique	Multilayer		Nanosphere-like	2020	66
2D/2D Ti <sub>3</sub> C <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	72.3	0.81% (400 nm)	10.18 times than pure g-C <sub>3</sub> N <sub>4</sub>	TEOA (10%)	Electrostatic self- assembly approach	Monolayer	200 W Hg lamp	Flat irregularly shaped nanosheets of 2D/2D structures	2019	67
MXene@Au@CdS	17070.43		1.85 times than pure CdS	0.35 mol L <sup>-1</sup> Na <sub>2</sub> S and 0.25 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>3</sub> solution	Hydrothermal	Monolayer	300 W Xe lamp ( $\lambda > 420$ nm)	Nanosheets	2020	68
Black phosphorus quantum dots/ Ti <sub>3</sub> C <sub>2</sub> @TiO <sub>2</sub>	684.5		11.35 times	TEOA (25%)	Solvent-heat method	Multilayer	300 W Xe lamp ( $\lambda > 420$ nm)	Nanosheets	2020	69

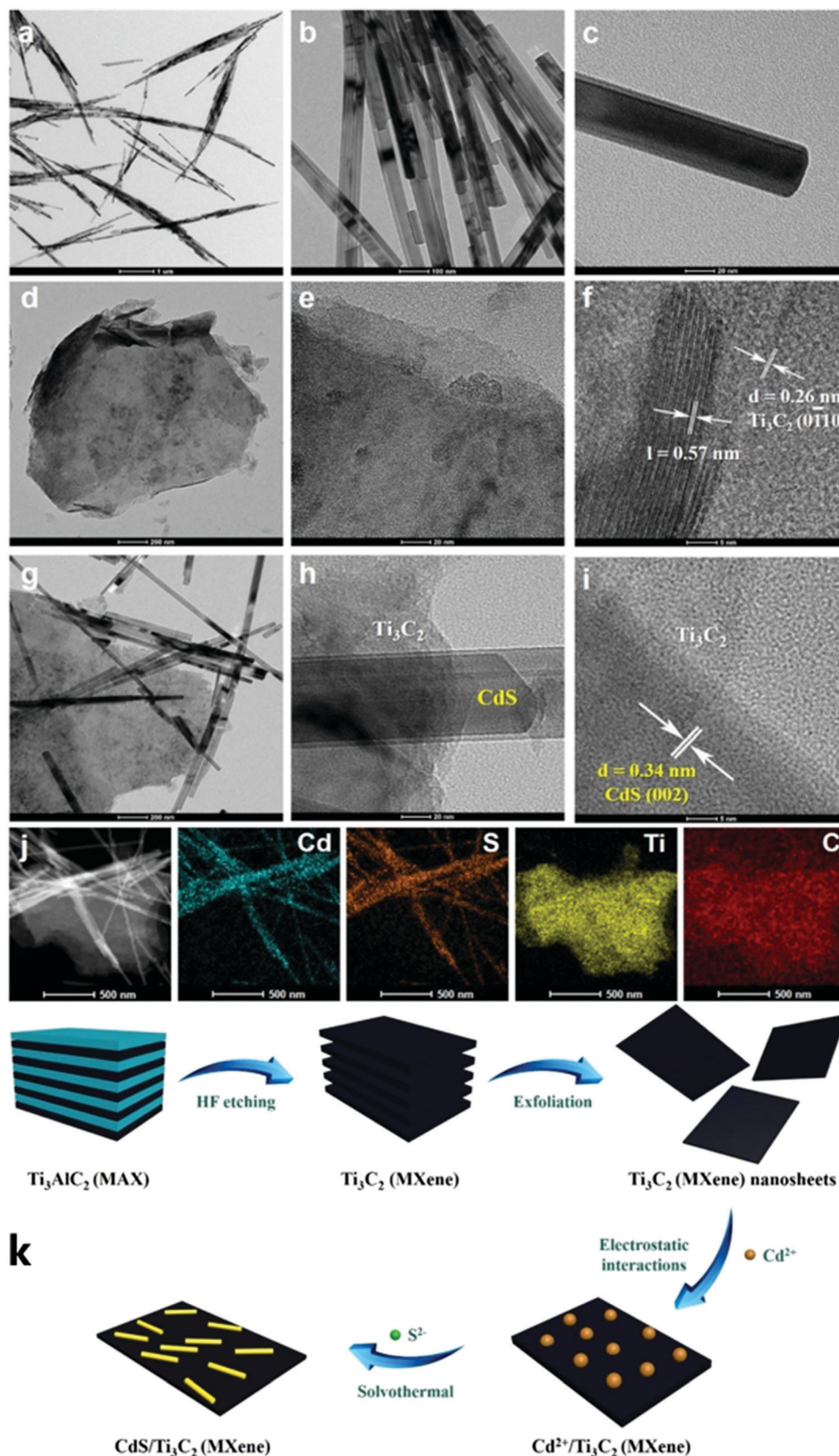


Fig. 5 TEM images of (a–c) CdS, (d–f) exfoliated Ti<sub>3</sub>C<sub>2</sub> MXene nanosheets, (g–i) the composite CM-20, (j) the corresponding elemental mapping results of CM-20, and (k) the oxidation process of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.<sup>52</sup>



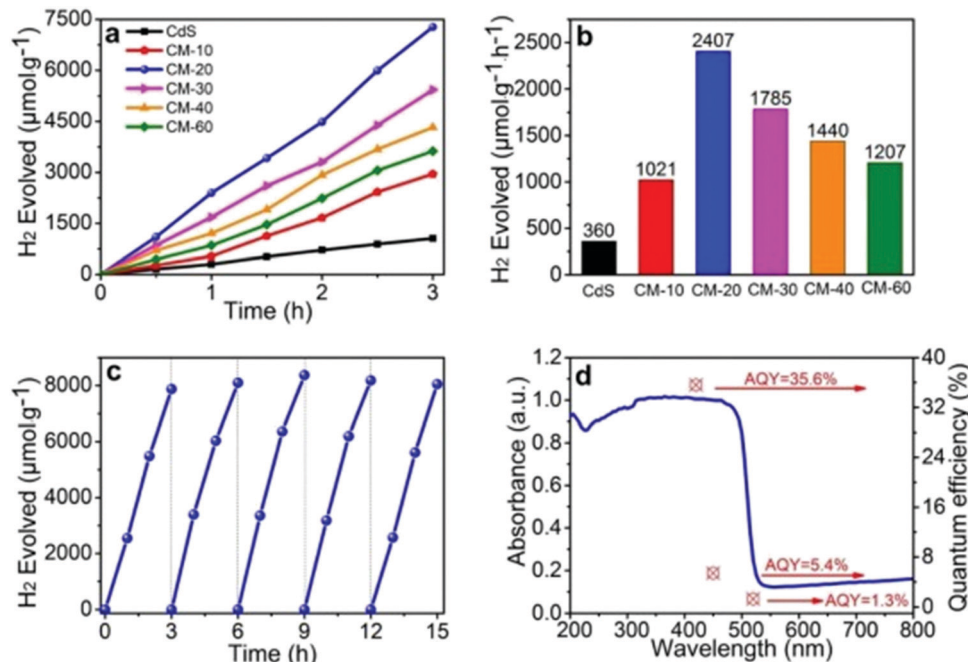


Fig. 6 (a and b) Photocatalytic H<sub>2</sub> evolution performance of different samples, (c) the recycled photocatalytic H<sub>2</sub> evolution experiments of CM-20, (d) AQY values and the wavelength dependence of photocatalytic H<sub>2</sub> evolution in the composite CM-20.<sup>52</sup>

When Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is oxidized, it is only the Ti atoms that are oxidized into the corresponding oxide (TiO<sub>2</sub>), while the C atoms remain unchanged. In other words, MO comprises a sandwich structure of layered carbon layers and titanium oxide.<sup>31</sup> Fig. 3 shows the structural evolution of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> oxidation to MXene (MO). As can be seen from Fig. 3, MO maintains a layered structure, whilst the TiO<sub>2</sub> nanoparticles formed by oxidation are coated within the carbon layer structure. Due to the photoresponse capacity of TiO<sub>2</sub>, this resulting structure is photocatalytically active. An example of this is MO/g-C<sub>3</sub>N<sub>4</sub>, which can photocatalytically split water with a relatively high efficiency.<sup>32</sup>

The crystal structure of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> contains Ti defects, which appear to contribute significantly to the instability of this material.<sup>14,33</sup> High angle annular dark field (HAADF)-STEM imaging is an important tool in 2D materials' characterization and is used to unambiguously resolve the crystal structure and

defect configurations.<sup>34,35</sup> As shown in Fig. 4, widespread Ti defects were directly detected through the HAADF-STEM imaging of the single-layer Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> flakes. Single-layered Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> obtained by HF etching was observed through HAADF-STEM images in Fig. 4(a)–(c). Fig. 4(d) was obtained by calculating tens of such images, and it reveals that the relationship between HF concentration and defect formation. It was found that vacancy clusters are rarely observed after etching with 2.7 wt% HF concentration but are relatively common after etching with 7 wt% HF.<sup>33</sup> Generally speaking, the average concentration of V<sub>Ti</sub> (Ti vacancies) is positively related to that of HF.

### 3. Application in photocatalysis

Due to the excellent structural properties of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, there are many cases in which Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is used as a co-catalyst in

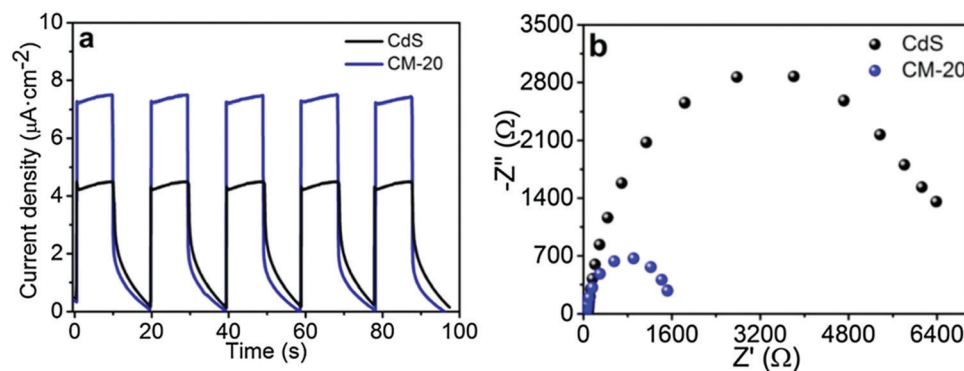


Fig. 7 (a) Photocurrent density curves and (b) EIS Nyquist plots of CdS and CM-20.<sup>52</sup>





photocatalytic systems or is directly involved in photocatalytic reaction systems. This paper summarizes the application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in the field of photocatalysis from three aspects: photocatalytic hydrogen evolution reactions (HER), photocatalytic  $\text{CO}_2$  reduction reactions ( $\text{CO}_2\text{RR}$ ), and photocatalytic degradation reactions.

### 3.1 Application in HER

$\text{Ti}_3\text{C}_2\text{T}_x$  is the most widely used photocatalytic agent in hydrogen evolution reactions<sup>36–39</sup> (HER).  $\text{Ti}_3\text{C}_2\text{T}_x$  has the following advantages that make it ideal for use in photolysis: (a) hydrophilic surface functional groups are conducive for the adsorption of water molecules and promote the reaction; and (b) the Gibbs free energy of  $\text{Ti}_3\text{C}_2\text{T}_x$  adsorption on hydrogen approaches zero infinitely, which is conducive for the reduction of  $\text{H}^+$ .

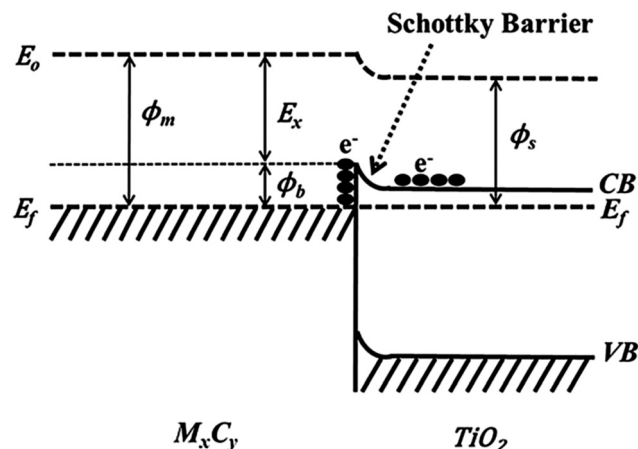
There are three important steps in the HER process, which are:<sup>30,40,41</sup> (a) initial  $\text{h}^+ + \text{e}^-$  formation; (b) generation of  $\text{H}^*$  (the intermediate adsorption state); and (c) formation of the  $1/2 \text{H}_2$  product. The adsorption state of  $\text{H}^*$  in process (b) directly affects the final hydrogen evolution efficiency and is an extremely important factor, which can be represented by the Gibbs adsorption free energy  $|\Delta G_{\text{H}^*}|$ . Through simulation calculations, it was found that when all the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface groups are  $-\text{F}$ ,  $\Delta G_{\text{H}^*} = -0.927 \text{ eV}$ , and the adsorption is too strong. When all the surface groups are  $-\text{O}$ ,  $|\Delta G_{\text{H}^*}|$  is  $0.003 \text{ eV}$ , which is even better than the commonly used catalyst Pt ( $\Delta G_{\text{H}^*} \approx -0.090 \text{ eV}$ ).<sup>42,43</sup> Therefore,  $\text{Ti}_3\text{C}_2\text{T}_x$  is a good HER co-catalyst. Examples of  $\text{Ti}_3\text{C}_2\text{T}_x$  used for photolysis in recent years are summarized below (Table 1).

$\text{Ti}_3\text{C}_2\text{T}_x$  plays a significant role in HER, whether as a co-catalyst or as a part of the overall catalyst, as it greatly improves the performance of the base catalyst. As shown in Table 1, the presence of  $\text{Ti}_3\text{C}_2\text{T}_x$  increases the yield of  $\text{H}_2$  compared to solely the base catalyst by more than 2 times. The quantum efficiency is also significantly improved to 40.1%, whilst the maximum value of hydrogen production is  $14.34 \text{ mmol g}^{-1} \text{ h}^{-1}$ .

Monolayer  $\text{Ti}_3\text{C}_2\text{T}_x$  or quantum dot  $\text{Ti}_3\text{C}_2\text{T}_x$  displays better activity in HER. However, the use of monolayer  $\text{Ti}_3\text{C}_2\text{T}_x$  as a photocatalyst has several disadvantages: (a) the preparation of monolayer  $\text{Ti}_3\text{C}_2\text{T}_x$  is complex; (b) the structural stability is low and the catalyst is easily oxidized in water; (c) manipulation of the mono-layer or few-layer structures is not easy to carry out. Few-layer structures are presently prepared by electrostatic self-assembly or by *in situ* growth. The stability of the composite catalyst obtained by *in situ* growth is significantly greater than that obtained by electrostatic self-assembly.

Due to the surface hydrophilic groups,<sup>70</sup> suitable Gibbs adsorption free energies  $|\Delta G_{\text{H}^*}|$ , and excellent electron transfer efficiency,  $\text{Ti}_3\text{C}_2\text{T}_x$  not only plays an important role in the three-step process of HER but can participate in electron hole separation.

Xiao *et al.* successfully synthesized the Schottky junction of 1D CdS nanorod/2D  $\text{Ti}_3\text{C}_2$  MXene nanosheet in 2019.<sup>52</sup> As shown in Fig. 5, Xiao *et al.* anchored  $\text{Cd}^{2+}$  using the deficiency of Ti on the  $\text{Ti}_3\text{C}_2$  surface and the electrostatic interaction of free  $\text{Cd}^{2+}$  to prepare the 1D CdS nanorods. The composite material demonstrated excellent hydrogen production performance



Scheme 1 Formation of Schottky barrier at the MXene/ $\text{TiO}_2$  interface.<sup>45</sup>

( $2407 \mu\text{mol h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$ ), producing 6.68 times as much  $\text{H}_2$  as pure CdS (Fig. 6).

Theoretically, the surface negative value (zeta potential value:  $\sim 18 \text{ mV}$ ) of  $\text{Ti}_3\text{C}_2\text{T}_x$  is sufficient to adsorb positively charged  $\text{Cd}^{2+}$ .  $\text{Ti}_3\text{C}_2\text{T}_x$  treated with DMSO forms a low-layered structure, on which  $\text{Cd}^{2+}$  can be anchored and one-dimensional CdS nanorods can be grown. As shown in Fig. 5, due to the constraint effect of  $\text{Ti}_3\text{C}_2\text{T}_x$ , the length of 1D CdS nanorods in the 1D CdS nanorods/2D  $\text{Ti}_3\text{C}_2\text{T}_x$  heterojunctions is smaller than that of the 1D CdS nanorods alone.

CdS equipped with  $\text{Ti}_3\text{C}_2\text{T}_x$  displays excellent electrochemical properties. As shown in Fig. 7, the photocurrent of 1D CdS nanorods/2D  $\text{Ti}_3\text{C}_2\text{T}_x$  was significantly better than that of one-dimensional CdS nanorods and the optical resistance was significantly lower than that of one-dimensional CdS nanorods. ESR tests show that the hydroxyl radical and superoxide radical signals of 1D CdS nanorods/2D  $\text{Ti}_3\text{C}_2\text{T}_x$  were significantly enhanced after the addition of  $\text{Ti}_3\text{C}_2\text{T}_x$ . In conclusion, under the same illumination conditions, 1D CdS nanorods/2D  $\text{Ti}_3\text{C}_2\text{T}_x$  generate more photogenic carriers. These produce oxygen-containing

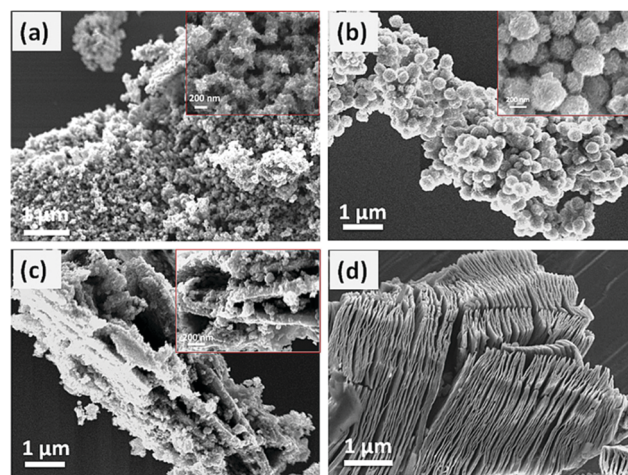


Fig. 8 SEM images of (a)  $\text{TiO}_2$  (50 wt%), (d)  $\text{Ti}_3\text{C}_2\text{T}_x$ , (b)  $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$  (5 wt%), and (c)  $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ .<sup>45</sup>





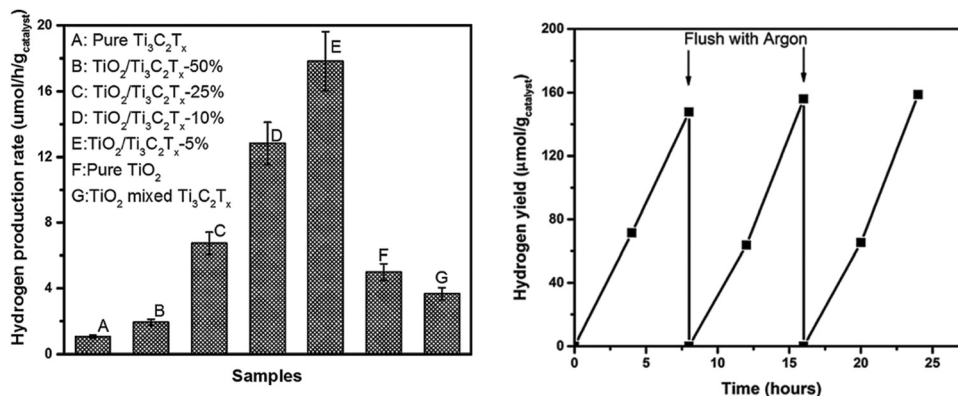


Fig. 9 (a) Photocatalytic hydrogen production rates and (b) recycling studies over the TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (5 wt%) sample.<sup>45</sup>

groups with oxidizing reductivity, which can participate in photocatalytic hydrogenation reactions.

1D CdS nanorods/2D Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> typically exhibit better visible light response, electron hole separation efficiency, and more effective carrier transport efficiency after the formation of multi-dimensional heterojunctions. This accounts for their excellent photocatalytic hydrogen evolution capability.

Using Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> as the co-catalyst, Wang *et al.* synthesized a TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> complex photocatalyst,<sup>45</sup> which was 4 times more efficient than pure phase TiO<sub>2</sub> in photohydrolyzing aquatic hydrogen. This is attributed to the Schottky barrier formed between TiO<sub>2</sub> and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, which effectively improves the separation efficiency of the electron holes. As shown in Scheme 1, excited electrons can be wired to Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> from the conduction band of TiO<sub>2</sub> owing to the close contact between Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and TiO<sub>2</sub>; thus, negative charge is accumulated in Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and a depletion layer formed at the metal-semiconductor interface, which is the Schottky barrier.<sup>45</sup>

In this work, Wang *et al.* treated Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> with DMSO to form low-layer structures. Amorphous TiO<sub>2</sub> was formed from TiCl<sub>4</sub> hydrolysis and then on the surface of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, amorphous TiO<sub>2</sub> was coated. After hydrothermal treatment, anatase TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> material was formed, as shown in Fig. 8. Amorphous TiO<sub>2</sub> is micro-spherical and is coated on the surface of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, displaying

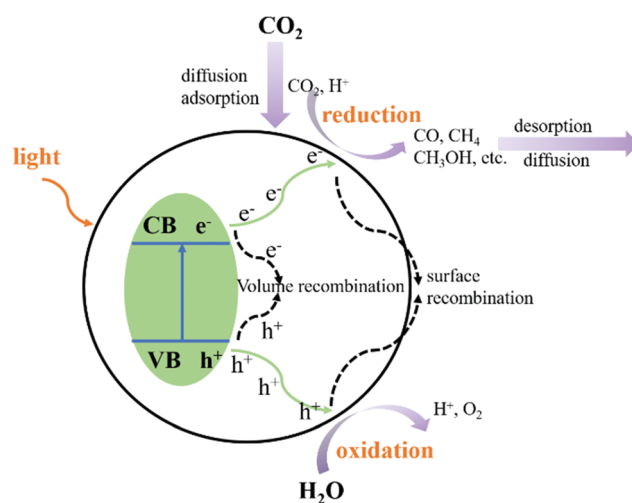


Fig. 11 CO<sub>2</sub>RR process.

a low-layered structure (Fig. 8). After water heat treatment, the whole structure forms into a brittle cake structure (Fig. 9).

The TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> material displays excellent photocatalytic hydrogen evolution capability with good cycling stability. The hydrogen production efficiency of TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-5% is about 4 times as high as

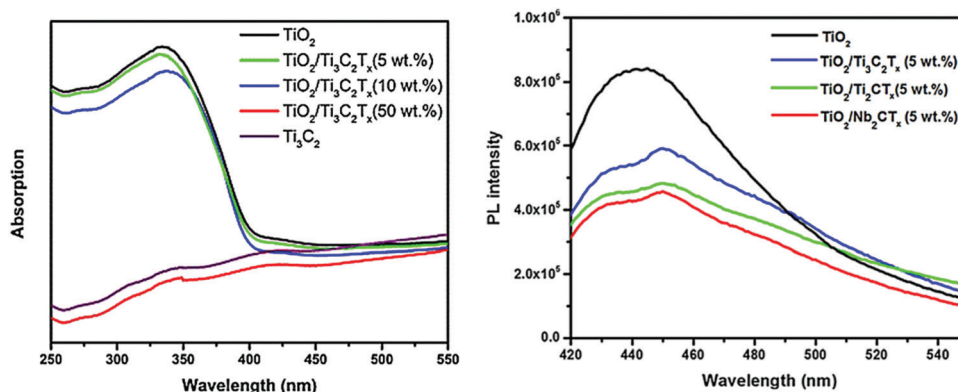
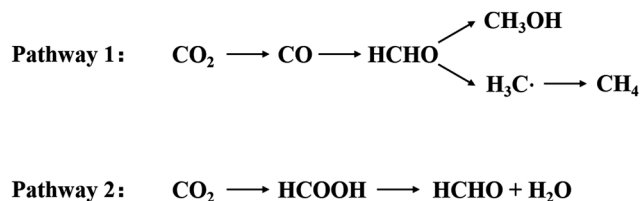


Fig. 10 (a) PL spectra and (b) DRS spectra of TiO<sub>2</sub>, TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (5 wt%), TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (10 wt%), and TiO<sub>2</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (50 wt%).<sup>45</sup>

Fig. 12 Two pathways in  $\text{CO}_2\text{RR}$ .

that of pure phase  $\text{TiO}_2$ , reaching  $17.8 \mu\text{mol h}^{-1} \text{g}_{\text{catalyst}}^{-1}$ . The hydrogen production efficiency of the 10% and 50% samples decreased slightly, which may be related to light energy absorption, as shown in Fig. 10(a). With the increase in  $\text{Ti}_3\text{C}_2\text{T}_x$  addition, the light absorption capacity of the samples in the 250–380 nm region is gradually decreased. This significant improvement in the hydrogen production efficiency is closely related to the smooth carriage of  $\text{Ti}_3\text{C}_2\text{T}_x$ . As shown in Fig. 10(b), after the formation of the Schottky barrier, the carrier separation efficiency is improved, thus improving its photocatalytic capacity.

Thus, in conclusion, after loading with  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{H}_2$  production increased at least twice. Such an amazing promotion is mainly related with 3 aspects of  $\text{Ti}_3\text{C}_2\text{T}_x$ : (a) it supplies a high throughput channel as a co-catalyst for the excited electrons while the holes cannot pass the boundaries; (b) its hydrophilicity; and (c) the Gibbs free energy of  $\text{Ti}_3\text{C}_2\text{T}_x$  adsorption on hydrogen approaches zero infinitely.

### 3.2 Application in $\text{CO}_2\text{RR}$

The photocatalytic  $\text{CO}_2$  reduction reaction ( $\text{CO}_2\text{RR}$ ) consists of five steps:<sup>71–74</sup> light absorption, charge separation,  $\text{CO}_2$  adsorption, surface redox reaction, and product desorption. As shown in Fig. 11, when the CB of the photocatalyst is greater than the redox potential of  $\text{CO}_2$ , and charge separation occurs whilst the electrons and holes recombine. Several complex factors dictate which of these two competing processes predominantly occurs. After the adsorption of  $\text{CO}_2$  and the migration of photogenerated electrons and holes from the inside of the crystal structure to the

surface, the redox reaction is carried out on the surface of the catalyst. The product then de-attaches, which completes the entire photocatalytic  $\text{CO}_2$  reduction reaction.

$\text{Ti}_3\text{C}_2\text{T}_x$  is also widely used in the photocatalytic  $\text{CO}_2$  reduction reaction. However, due to its own carbon source and instability, further research is needed to understand the mechanism of photocatalytic  $\text{CO}_2$  reduction of  $\text{Ti}_3\text{C}_2\text{T}_x$ .

In 2017, Zhang *et al.* summarized the  $\text{CO}_2$  reduction capacity of three MXene materials with surface groups, which terminate with  $-\text{O}$  through theoretical calculations.<sup>75</sup> Among the three materials,  $\text{Ti}_2\text{CO}_2$ ,  $\text{V}_2\text{CO}_2$ , and  $\text{Ti}_3\text{C}_2\text{O}_2$ ,  $\text{Ti}_2\text{CO}_2$  showed the best photocatalytic  $\text{CO}_2$  reduction capacity. Of the two reduction paths<sup>76–78</sup> shown in Fig. 12, the pathway of “ $\text{CO}_2\text{--HCOO--HCOOH}$ ” has a favorable energy barrier of about 0.53 eV.

Through DFT calculations, it was revealed that in the first step reaction of  $\text{CO}_2$  adsorption in  $\text{CO}_2\text{RR}$ , the O atom of the  $\text{CO}_2$  molecule occupies an O defect position on the MXene. This mode in adsorption requires the lowest energy. The adsorption energies of the three materials were  $\text{Ti}_3\text{C}_2\text{O}_2$  (−0.73 eV),  $\text{Ti}_2\text{CO}_2$  (−0.67 eV), and  $\text{V}_2\text{CO}_2$  (−0.35 eV).  $\text{Ti}_2\text{CO}_2$  has a lower adsorption energy compared to  $\text{V}_2\text{CO}_2$  as the Ti atoms are more likely to lose electrons than the V atoms.

If the reaction proceeds *via* pathway 1 (Fig. 11), one of the oxygen atoms of the  $\text{CO}_2$  molecule is captured by the oxygen defect. This results in the breaking of the C–O bond, while CO is produced. In this step,  $\text{Ti}_3\text{C}_2\text{O}_2$  would lower the energy barrier of the C–O bond to about 0.86 eV. Pathway 2 (Fig. 11) has an energy barrier greater than 1 eV. In this pathway, the  $\text{CO}_2$  molecules are captured by an oxygen defect on the surface of MXene and are hydrogenated to form COOH. This is further hydrogenated and converted into the products CO and  $\text{H}_2\text{O}$ . CO, which is produced, can further react to form HCOOH, HCOH,  $\text{CH}_2\text{OH}$ ,  $\text{CH}_4$ , and other products.

Studies into the application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in  $\text{CO}_2\text{RR}$  is summarized in Table 2.

In 2018, Cao *et al.* prepared a 2D/2D heterogeneous junction of  $\text{Ti}_3\text{C}_2\text{T}_x/\text{Bi}_2\text{WO}_6$  and the composite showed excellent photocatalytic  $\text{CO}_2$  reduction performance.<sup>82</sup> As shown in Fig. 13,

Table 2 Comparison of photocatalysts including  $\text{Ti}_3\text{C}_2\text{T}_x$  in  $\text{CO}_2\text{RR}$ 

Photocatalyst	Products and yield ( $\mu\text{mol g}^{-1} \text{h}^{-1}$ )	Activity improvement factor	Reaction conditions	Light source	Preparation method	Morphology	Monolayer or Multilayer	Year	Ref.
2D/2D $\text{Ti}_3\text{C}_2$ MXene/ $\text{g-C}_3\text{N}_4$ nanosheet	CO (5.19) CH <sub>4</sub> (0.044)	8.37 (CO) 2.09 (CH <sub>4</sub> )	20 mg catalyst gas-solid	300 W Xe lamp ( $\lambda > 420 \text{ nm}$ )	Calcination under N <sub>2</sub> atmosphere	2D/2D nanosheets	Monolayer	2020	79
Alkalinized $\text{Ti}_3\text{C}_2$ /decorating $\text{g-C}_3\text{N}_4$	CO (11.21 $\mu\text{mol g}^{-1}$ ) CH <sub>4</sub> (0.044 $\mu\text{mol g}^{-1}$ )	5.96 (CO) 5.6 (CH <sub>4</sub> )	40 mg catalyst gas-solid	300 W Xe lamp ( $\lambda > 420 \text{ nm}$ )	Alkali etching	3D	Multilayer	2019	80
$\text{TiO}_2/\text{Ti}_3\text{C}_2$	CO CH <sub>4</sub> (0.22)	—	50 mg catalyst liquid-solid	300 W Xe lamp	Calcination	Nanoparticles	Multilayer	2018	81
2D/2D ultrathin $\text{Ti}_3\text{C}_2/\text{Bi}_2\text{WO}_6$	CO CH <sub>4</sub> (1.78)	4.34 (CH <sub>4</sub> ) 6.28 (CH <sub>3</sub> OH)	100 mg catalyst liquid-solid	Xe lamp	Hydrothermal	Flat shape 2D structure	Monolayer	2018	82
2D/2D/0D $\text{TiO}_2/\text{C}_3\text{N}_4/\text{Ti}_3\text{C}_2$	CH <sub>3</sub> OH (0.44) CO (4.39) CH <sub>4</sub> (1.20)	1.39 (CO) (than $\text{TiO}_2/\text{C}_3\text{N}_4$ )	30 mg catalyst liquid-solid	300 W Xe lamp	Electrostatic self-assembly	2D/2D structure	$\text{Ti}_3\text{C}_2$ quantum dots	2020	83



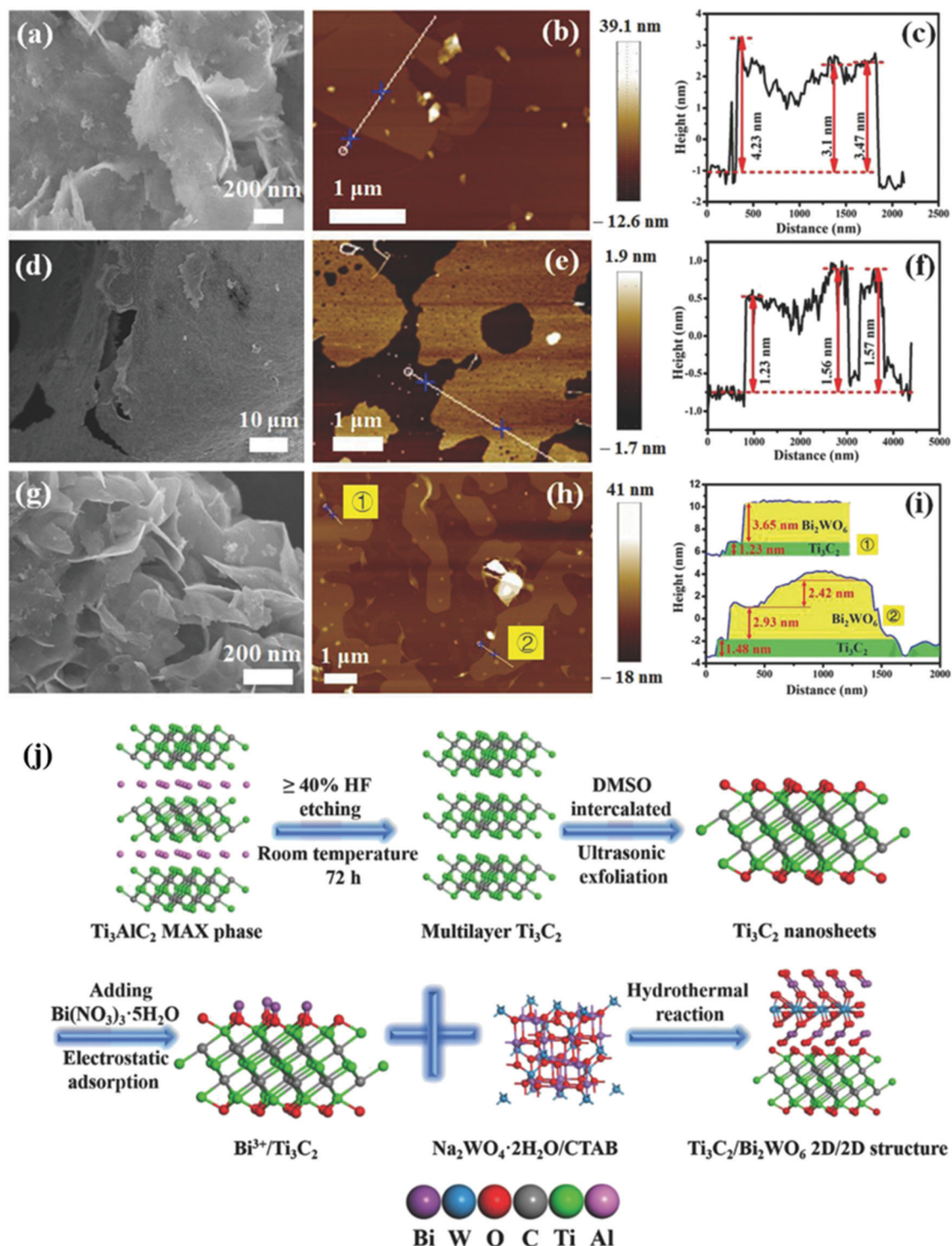


Fig. 13 (a–c) Typical FESEM, AFM images, and height cutaway view of  $\text{Bi}_2\text{WO}_6$ , (d–f)  $\text{Ti}_3\text{C}_2$  nanosheets, (g–i) TB2 ( $\text{Ti}_3\text{C}_2\text{T}_x/\text{Bi}_2\text{WO}_6$ ), and (j) schematic illustration of the synthetic process.<sup>82</sup>

multi-layer structure  $\text{Ti}_3\text{C}_2\text{T}_x$  was tested with DMSO. After the formation of low-layer structure  $\text{Ti}_3\text{C}_2\text{T}_x$ , the oxygen-rich surface was negatively charged, which permitted  $\text{Bi}^{3+}$  to be adsorbed from hydrolyzed  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ .<sup>84</sup> After the addition of a tungsten source, a 2D/2D  $\text{Ti}_3\text{C}_2\text{T}_x/\text{Bi}_2\text{WO}_6$  heterojunction was

formed. The concurrent addition of CTAB furthermore ensures the ultrathin structure of both  $\text{Bi}_2\text{WO}_6$ <sup>85</sup> and  $\text{Ti}_3\text{C}_2\text{T}_x$ .<sup>86</sup>

The successful preparation of heterojunctions greatly enhances the ability of  $\text{Bi}_2\text{WO}_6$  to reduce  $\text{CO}_2$ . The  $\text{CH}_4$  production of the sample TB2 reached  $1.78 \mu\text{mol h}^{-1} \text{g}^{-1}$ , while



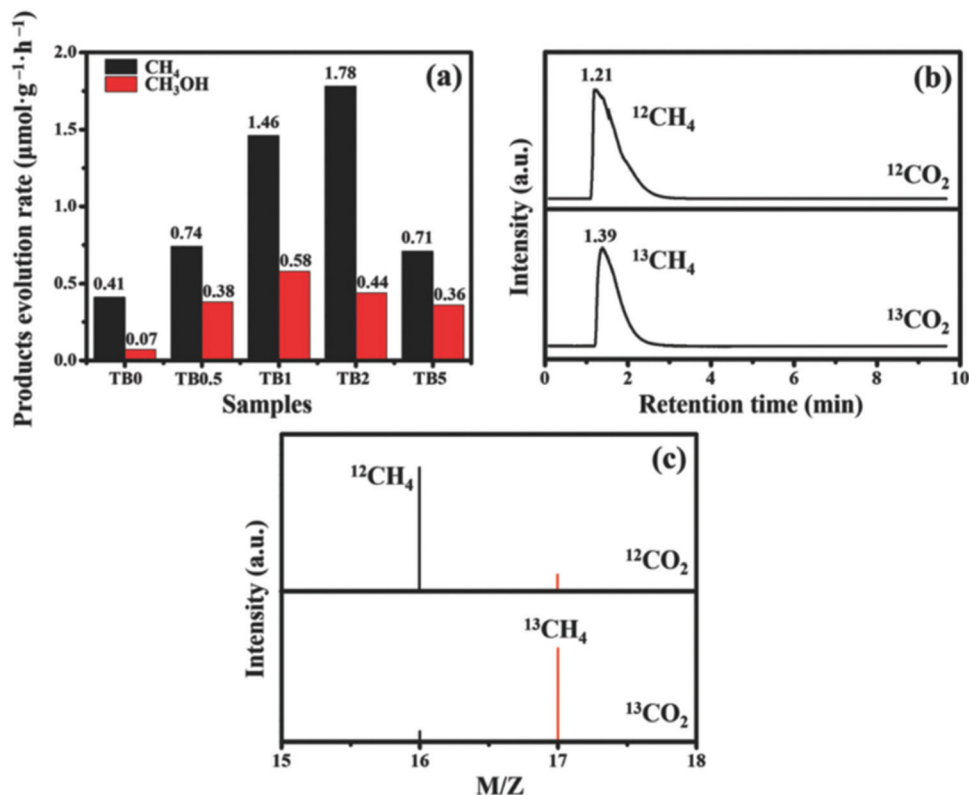


Fig. 14 (a) Photocatalytic activity of TB0 to TB5; (b) GC-MS spectra over TB2 after irradiation for several hours with different carbon sources; (c) GC-MS analysis of the reaction products with  $^{12}\text{C}$  and  $^{13}\text{C}$  as carbon sources.<sup>82</sup>

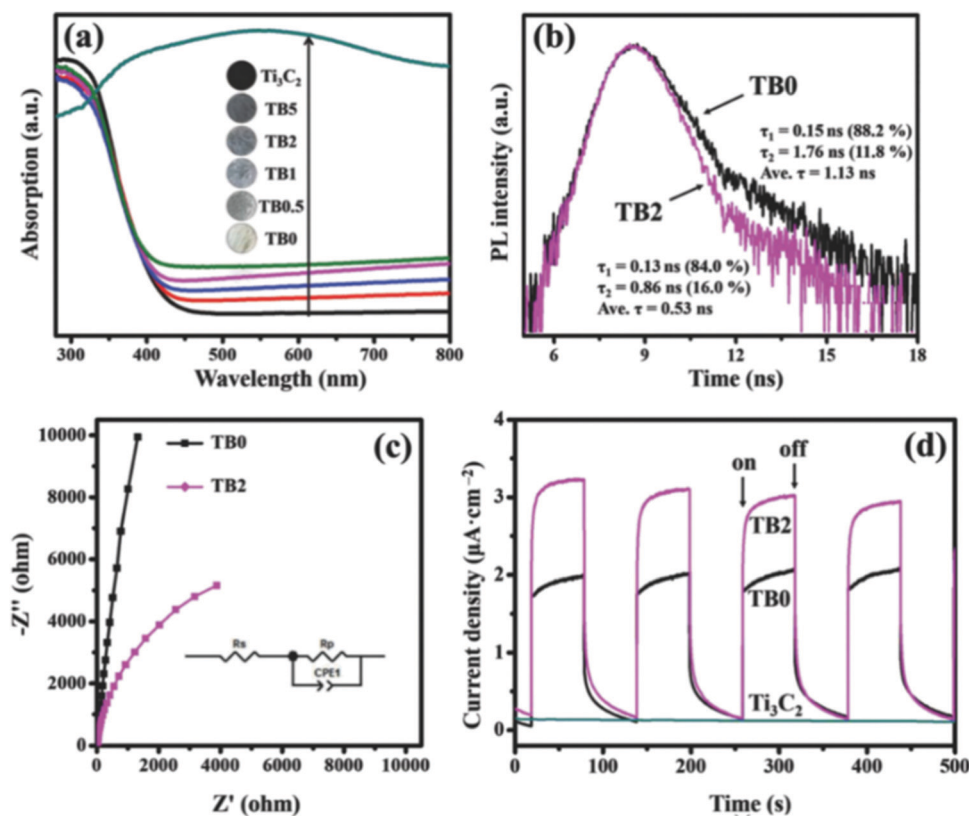


Fig. 15 (a) UV-Vis DRS of all the as-prepared samples; (b) TRPL spectra of TB0 and TB2; (c) EIS plots and (d) transient photocurrent of the prepared samples.<sup>82</sup>





the yield of  $\text{CH}_3\text{OH}$  reached  $0.44 \mu\text{mol h}^{-1} \text{g}^{-1}$ . The isotopic spectra of Fig. 14(b) and (c) indicates that the produced  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  are formed from the photocatalytic reduction of  $\text{CO}_2$ .

As shown in Fig. 15(a),  $\text{Ti}_3\text{C}_2\text{T}_x$  exhibits excellent light absorption performance between 200–800 nm. The light absorption capacity of  $\text{Bi}_2\text{WO}_6$  was also significantly improved by carrying  $\text{Ti}_3\text{C}_2\text{T}_x$ . To be noted, as shown in Fig. 14(b), the fluorescence lifetime decreased after loading with  $\text{Ti}_3\text{C}_2\text{T}_x$ . This is because TC supplies a more efficient non-radiative decay pathway. In electrochemical tests, the photocurrent photoelectric impedance spectrum further revealed that the carriage of  $\text{Ti}_3\text{C}_2\text{T}_x$  greatly promoted the carrier strength of  $\text{Bi}_2\text{WO}_6$ . This further confirmed the successful construction of the  $\text{Ti}_3\text{C}_2\text{T}_x/\text{Bi}_2\text{WO}_6$  heterojunction.

Yang *et al.* prepared 2D/2D  $\text{Ti}_3\text{C}_2$  MXene/ $\text{g-C}_3\text{N}_4$  heterojunctions in 2020.<sup>79</sup> As shown in Fig. 16(g),  $\text{Ti}_3\text{AlC}_2$  was successfully etched to form  $\text{Ti}_3\text{C}_2$ , as indicated by the XRD patterns.<sup>87,88</sup> 2D  $\text{g-C}_3\text{N}_4$  was found to grow on the surface of  $\text{Ti}_3\text{C}_2$  under an atmosphere of  $\text{N}_2$ . The formed 2D/2D  $\text{Ti}_3\text{C}_2$  MXene/ $\text{g-C}_3\text{N}_4$  demonstrated excellent photocatalytic  $\text{CO}_2$  reduction capability. As shown in Fig. 17, the photocatalytic performance of pure phase  $\text{g-C}_3\text{N}_4$  for the production of  $\text{CO}$  and  $\text{CH}_4$  is only  $0.62 \mu\text{mol h}^{-1} \text{g}^{-1}$  and  $0.021 \mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively, in contrast to  $\text{Ti}_3\text{C}_2$ , wherein the production of  $\text{CO}$  and  $\text{CH}_4$  is  $5.19 \mu\text{mol h}^{-1} \text{g}^{-1}$ ,  $0.044 \mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively. The isotopic experiments confirm that the product is produced by the photocatalytic reduction of  $\text{CO}_2$ .

The tests of PL and TRPL showed that the composite rate of electron holes<sup>45,89</sup> decreased significantly after carrying  $\text{Ti}_3\text{C}_2$ . As shown in Fig. 18(b), the fitted pure phase  $\text{C}_3\text{N}_4$  had a lifetime of only 4.14 ns, while 10TC had a lifetime of 4.51 ns, which represents a significant increase in the lifetime of the carriers. This is closely related to the smooth carrying of  $\text{Ti}_3\text{C}_2$ . An excellent “storage capacitor” is produced when  $\text{Ti}_3\text{C}_2$  forms a heterojunction with  $\text{g-C}_3\text{N}_4$ . When the electrons are transmitted to the semiconductor surface, they transfer to  $\text{Ti}_3\text{C}_2$  quickly while the holes cannot. This greatly reduces the electron hole composite and improves the photocatalytic performance of the material. On the other hand, abundant defects on the  $\text{Ti}_3\text{C}_2$  surface provide excellent sites for  $\text{CO}_2$  adsorption.

In conclusion, the application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in  $\text{CO}_2\text{RR}$  is relatively less than that of photocatalytic water splitting. This is because of its instability and its own carbon resources, which can cause interferences during the photocatalytic  $\text{CO}_2$  reduction reaction. As shown in Table 2, among limited reports,  $\text{Ti}_3\text{C}_2\text{T}_x$  with both single-layered structures and multi-layered structures shows an obvious production promotion. It is to be noted that there are no new products (such as  $\text{C}_2$  products, formaldehyde, and methyl ether) after loading with  $\text{Ti}_3\text{C}_2\text{T}_x$  compared to the base photocatalyst. This phenomenon confirms that  $\text{Ti}_3\text{C}_2\text{T}_x$  cannot change the energy barrier of the base photocatalyst for  $\text{CO}_2$  reduction. Thus, in general, the obvious promotion during  $\text{CO}_2\text{RR}$  may be related to the two features of  $\text{Ti}_3\text{C}_2\text{T}_x$ : (a) abundant surface vacancies for  $\text{CO}_2$  adsorption and (b) promoting the separation of carriers.

### 3.3 Applications in degradation

The main principle of photocatalytic degradation by photocatalytic semiconductor materials is that light stimulates the generation of oxidizing holes.<sup>90–93</sup> These can oxidize dissolved oxygen into efficient oxygen-active species such as superoxide radicals ( $\cdot\text{O}_2^-$ ), singlet oxygen ( $\cdot\text{O}$ ), and hydroxyl radicals ( $\cdot\text{OH}$ ). These species can directly oxidize the substrate.<sup>94–96</sup>  $\text{Ti}_3\text{C}_2$  has a wealth of surface groups and active sites, which are conducive for the adsorption of substrates. Accordingly,  $\text{Ti}_3\text{C}_2$  has been of particular interest as a photoactive degradation catalyst. A summary of the previous studies investigating the application of  $\text{Ti}_3\text{C}_2$  in photocatalytic degradation reactions is shown in Table 3.

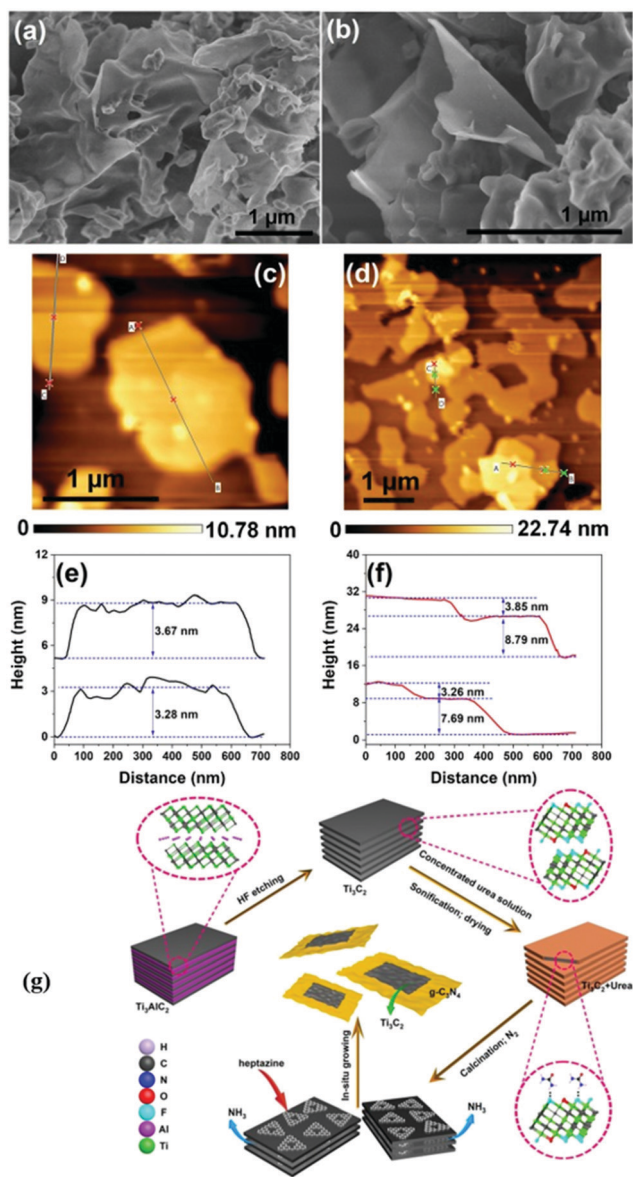


Fig. 16 FESEM images of UCN (a) and 10TC (b) samples, AFM images and the corresponding height profiles of UCN (c and e), 10TC (d and f) samples, and (g) schematic illustration for the fabrication process.<sup>79</sup>



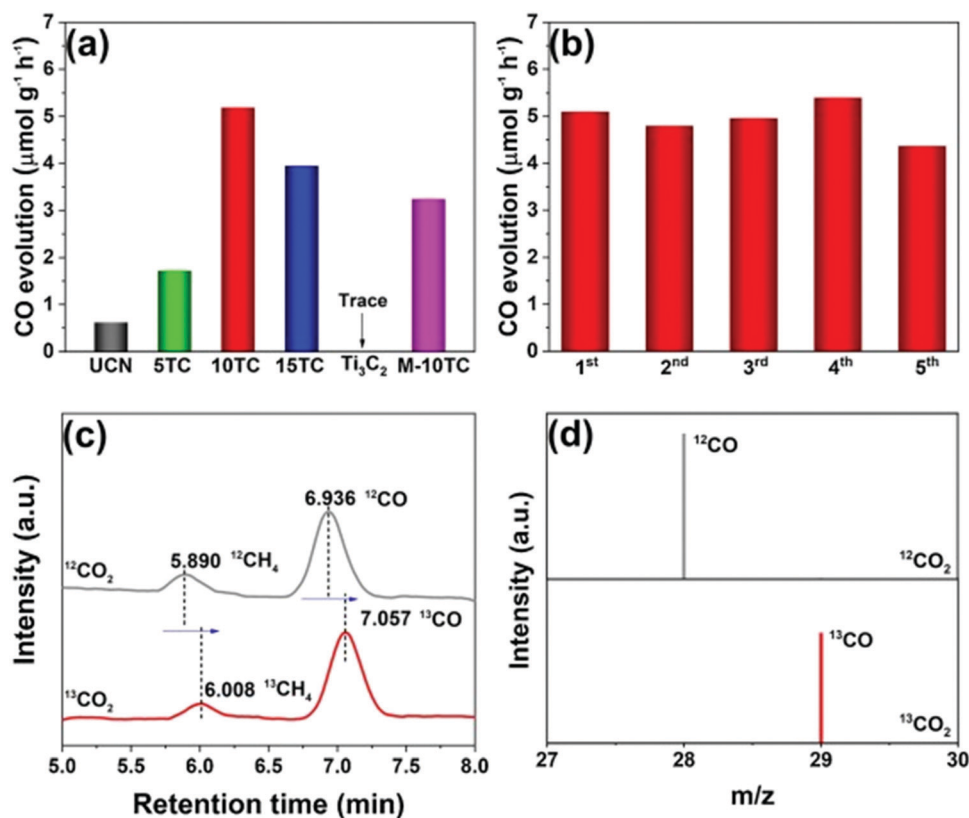


Fig. 17 Photocatalytic  $\text{CO}_2$  reduction performance of the as-prepared samples (a); cycling tests over the 10TC sample (b); GC-MS analysis of the products from the photoreduction of  $\text{CO}_2$  over 10TC using labelled  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  as the carbon sources (c and d).<sup>79</sup>

In 2018, Cai *et al.* produced a  $\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$  composite photocatalyst, which possessed excellent photocatalytic degradation performance.<sup>87</sup>

As shown in Fig. 19, after DMSO and sonication treatment,  $\text{Ti}_3\text{C}_2$  with a low-layer structure was formed. After the addition of silver nitrate,  $\text{Ag}^+$  was adsorbed due to the negative charge on the surface of  $\text{Ti}_3\text{C}_2$ .  $\text{Ag}_3\text{PO}_4$  nanoparticles were grown *in situ*, forming a heterojunction between the  $\text{Ag}_3\text{PO}_4$  nanoparticles and the  $\text{Ti}_3\text{C}_2$  nanosheets.

As shown in Fig. 20, the heterojunction of the  $\text{Ag}_3\text{PO}_4$  nanoparticles/ $\text{Ti}_3\text{C}_2$  nanosheets shows a photocatalytic degradation stage rate  $K$  of 0.094, 0.005, 0.32, and 0.0042  $\text{min}^{-1}$  for methyl orange (MO), 2,4-dinitrophenol (2,4-DNP), tetracycline (TC-H), thiamphenicol (TPL), and chloramphenicol (CPL), respectively. According to EPR analysis, the hydroxyl radical ( $\cdot\text{OH}$ ) plays an important role in the oxidation system, as shown in Fig. 20(f). This may be related to abundant Ti defects on the  $\text{Ti}_3\text{C}_2$  surface. Ti sites exposed on the surface of  $\text{Ti}_3\text{C}_2$  have strong redox reactivity, which promotes multiple electron reduction reactions ( $\text{O}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH}$ ).

As shown in Fig. 21, PL, TRPL, and the electrochemical characterization spectra indicate that the carrier separation efficiency of the material is significantly improved after carrying  $\text{Ti}_3\text{C}_2$ . This may be attributed to (i) the abundant surface hydrophilic functional groups of the  $\text{Ti}_3\text{C}_2$  construct, which have strong interfacial contact with  $\text{Ag}_3\text{PO}_4$ , facilitating the separation

of carriers; (ii) the strong redox reactivity of the surface Ti sites, which promote multiple electron reduction reactions to induce more  $\cdot\text{OH}$  production; and (iii) a Schottky junction formed at the  $\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$  interface enabling efficient transfer electrons to the  $\text{Ti}_3\text{C}_2$  surface. This inhibits the photocorrosion of  $\text{Ag}_3\text{PO}_4$  caused by photogenerated electrons.

Under high temperature conditions, Ti in the  $\text{Ti}_3\text{C}_2$  skeleton layer is oxidized into  $\text{TiO}_2$ , while C still exists in the form of a graphene-like layer. Therefore, under high temperature conditions,  $\text{Ti}_3\text{C}_2$  can be converted into amorphous  $\text{TiO}_2$  anchored within the graphene-like layer. In 2020, Wu *et al.* took advantage of this material, which displayed excellent photocatalytic degradation performance.<sup>105</sup>

As shown in Fig. 22(e) and (f), high temperature treated  $\text{Ti}_3\text{C}_2$  still retains its morphology and a 3D block-shaped morphology is formed after carrying g- $\text{C}_3\text{N}_4$  (Fig. 23).

Graphene layers anchored to  $\text{TiO}_2/\text{g-}\text{C}_3\text{N}_4$  show first-order kinetic constants for the degradation of rhodamine B (RhB), tetracycline (TC), ciprofloxacin (CIP), and bisphenol A (BPA) of 0.0559, 0.0244, 0.0168, and 0.0194  $\text{min}^{-1}$ , respectively. According to the EPR test results (Fig. 24(a)–(d)), the oxygen active species that play a role in the oxidation process mainly include  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ . Furthermore, signals corresponding to the holes ( $\text{h}^+$ ) were also detected. The contribution to the degradation of these test molecules appears to be in the order of  $\cdot\text{O}_2^- > \text{h}^+ > \cdot\text{OH}$ .



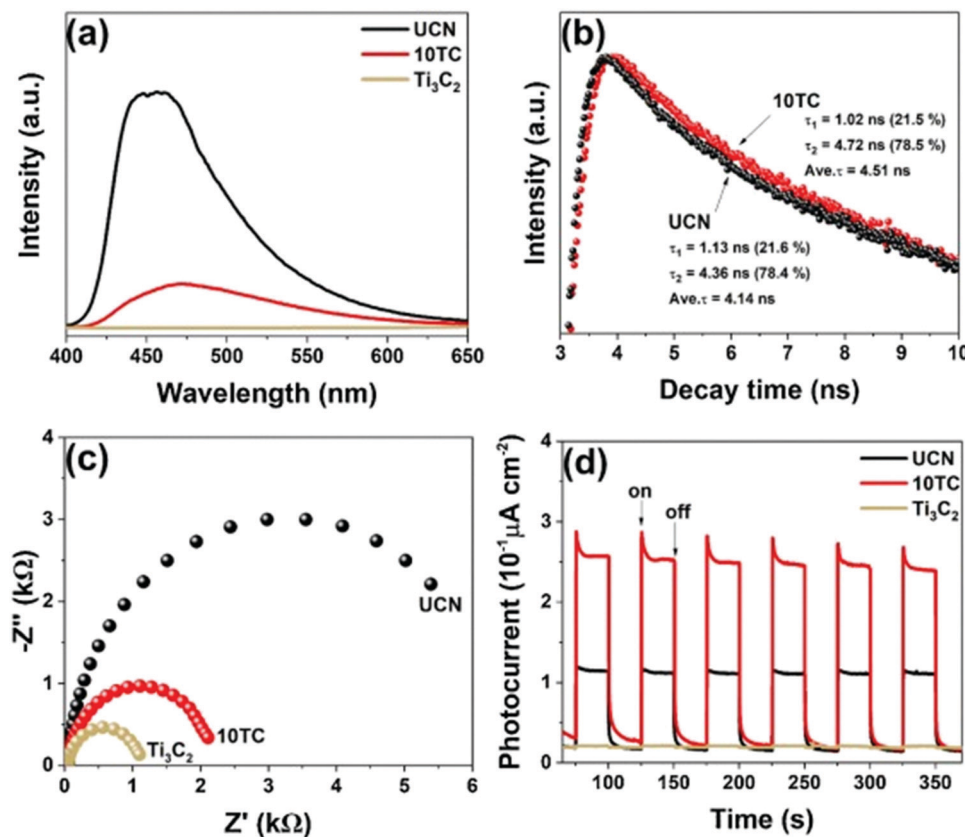


Fig. 18 PL spectra, EIS, and TPR plots of UCN,  $\text{Ti}_3\text{C}_2$ , and 10TC samples (a, c, and d); TR-PL spectra of UCN and 10TC (b).<sup>79</sup>

High-temperature treated  $\text{Ti}_3\text{C}_2$  has a greatly enhanced light absorption capacity, whilst the carrier separation efficiency and transmission efficiency are also improved. The improvement of the photocurrent (Fig. 24(e) and (f)) also verified that the graphene layers anchoring  $\text{TiO}_2$  lead to the formation of a heterogeneous junction. This is due to the change in the electric field between  $\text{g-C}_3\text{N}_4$ .

In conclusion, as a co-catalyst, the application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in photocatalytic degradation is mainly due to its three characteristics: (a) in a liquid–solid phase reaction, its hydrophilicity makes it easy for the adsorption or contact between the pollutants and photocatalysts; (b) high throughput electron transfer makes it easier to generate concentrated holes ( $\text{h}^+$ ); and (c) Ti sites exposed on the surface of  $\text{Ti}_3\text{C}_2$  have strong redox reactivity, which promotes multiple electron reduction reactions, such as the reaction of activating molecular oxygen ( $\text{O}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH}$ ).

#### 4. Challenges

The application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in photocatalysis is worthy of further investigation, despite the many problems that need to be solved. The main issue lies in the instability of the composite material, resulting in unstable photocatalytic performance. This contributes to the difficulty in determining the photocatalytic process mechanisms of  $\text{Ti}_3\text{C}_2\text{T}_x$ -based photocatalysts. Many of the existing solutions use either few- or single-layer structured materials. However, the preparation process of these

is complex. Despite this,  $\text{Ti}_3\text{C}_2\text{T}_x$  has an excellent optical response ability and displays broad catalytic activity.

## 5. Summary and outlook

### 5.1 Summary

In recent years,  $\text{Ti}_3\text{C}_2\text{T}_x$  has attracted wide interest as a photocatalytic material due to its rich surface space and surface defects, hydrophilic properties, large interlayer spacing, and excellent microwave absorbing properties.  $\text{Ti}_3\text{C}_2\text{T}_x$ -based photocatalysts are widely used in hydrogen evolution reactions (HER),  $\text{CO}_2$  reduction reactions ( $\text{CO}_2\text{RR}$ ), photocatalytic degradation reactions, and show excellent catalytic performance. The application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in photocatalysis still warrants further investigation.

The further application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in photocatalysis depends on the development of the material itself. Methods to improve the stability of the  $\text{Ti}_3\text{C}_2\text{T}_x$  structure need to be explored, starting from synthetic methods. In addition, the rich groups on the surface of  $\text{Ti}_3\text{C}_2\text{T}_x$  and its hydrophilicity should be further explored, particularly in photocatalytic liquid phase reactions.

### 5.2 Outlook

**5.2.1 Mechanism.** During the photocatalytic reaction, especially the reaction including liquid phase, the mechanism



**Table 3** Application of  $\text{Ti}_3\text{C}_2\text{T}_x$  in photocatalytic degradation reactions

Photocatalyst	Substrate of degradation	Removal rate (%) / rate constants ( $\text{min}^{-1}$ )	Reaction conditions	Light source	Oxygenic species	Morphology	Monolayer or multilayer	Year	Ref.
$\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$	Methyl orange (MO)	(rate constants) 0.094 (MO)	20 mg catalyst + 50 mL 20 $\text{mg L}^{-1}$ substrate, 30 min dark adsorption	300 W Xe lamp ( $\lambda > 420 \text{ nm}$ )	$\text{h}^+$	2D $\text{Ti}_3\text{C}_2/\text{Ag}_3\text{PO}_4$ particles	Monolayer	2018	87
$\text{Ti}_3\text{C}_2/\text{SrTiO}_3$ composites	2,4-Dinitrophenol (2,4-DNP)	2,4-DNP (0.005) TC-H (0.32)	20 mg catalyst + 60 mL 50 ppm substrate, 8 hours dark adsorption	300 W Xe lamp ( $\lambda = 320\text{--}2500 \text{ nm}$ )	$\bullet\text{OH}$	2D $\text{Ti}_3\text{C}_2/\text{SrTiO}_3$ particles	Multilayer	2019	97
	Tetracycline hydrochloride (TC-H)								
	Thiamphenicol (TPL)	TPL (0.0042) CPL (0.025)							
	Chloramphenicol (CPL)	(Removal rate)							
$\text{Ti}_3\text{C}_2/\text{OH}/\text{Bi}_2\text{WO}_6$ composites	$\text{UO}_2^{2+}$								
	Rhodamine B	77% in 180 min (Rate constants) 0.0596	10 mg catalyst + 50 mL $2 \times 10^{-5}$ mol $\text{L}^{-1}$ substrate, 30 min dark adsorption	300 W Xe lamp ( $\lambda = 400\text{--}2500 \text{ nm}$ )	$\text{h}^+$	Porous spherical structure	$\text{Ti}_3\text{C}_2\text{--OH}$	2019	98
$\text{MoS}_2/\text{Ti}_3\text{C}_2$ Nanohybrid	Liquid paraffin (LP)	(Rate constants) 0.0476	A certain amount of sample + 2.0 g of deionized water and 1.0 g of LP + 10 mL dichloromethane as the sacrifice reagent, 30 min dark adsorption	1000 W high-pressure mercury lamp		$\text{MoS}_2$ nanosheets/ $\text{Ti}_3\text{C}_2$ sheets	Multilayer	2019	99
0D/2D $\text{Bi}_3\text{TaO}_7/\text{Ti}_3\text{C}_2$	Methylene blue	(Rate constants) 0.032	50 mg catalyst + 100 mL 10 $\text{mg L}^{-1}$ substrate, 60 min dark adsorption	300 W Xe lamp ( $\lambda > 420 \text{ nm}$ )	$\bullet\text{OH}$	$\text{Bi}_3\text{TaO}_7$ nanoparticles/ $\text{Ti}_3\text{C}_2$ nanosheets	Multilayer	2020	100
2D/2D $\text{Ti}_3\text{C}_2/\text{Porous g-C}_3\text{N}_4$	Phenol	(Rate constants) 0.022	20 mg catalyst + 50 mL 10 $\text{mg L}^{-1}$ substrate, 30 min dark adsorption	500 W Xe lamp ( $\lambda > 400 \text{ nm}$ )		2D/2D $\text{Ti}_3\text{C}_2/\text{PCN}$ nanocomposite	Multilayer with ultrasonication	2020	101
$\text{CdS}/\text{Ti}_3\text{C}_2/\text{TiO}_2$	Sulfachloropyridazine (SCP)	(Removal rate) SCP (about 95% in 60 min)	50 mg catalyst + 200 mL 20 $\text{mg L}^{-1}$ substrate, 30 min dark adsorption	Light intensity 300 $\text{mW cm}^{-2}$ ( $\lambda = 400\text{--}1050 \text{ nm}$ )	$\bullet\text{O}_2^-$	$\text{CdS}$ nanoparticles/ $\text{Ti}_3\text{C}_2/\text{TiO}_2$ bulk	Bulk $\text{Ti}_3\text{C}_2/\text{TiO}_2$	2019	102
(111) $\text{TiO}_2/\text{Ti}_3\text{C}_2$	Methylene blue (MB)	MB (about 80% in 60 min)	10 mg catalyst + 200 mL 20 $\text{mg L}^{-1}$ substrate, 30 min dark adsorption	500 W Xe lamp ( $\lambda > 400 \text{ nm}$ )	$\bullet\text{OH}$ (main)	$\text{TiO}_2$ nanoparticles/ $\text{Ti}_3\text{C}_2$ nanosheets	Multilayer	2017	103
	Rhodamine B (RhB)	RhB (about 99% in 60 min)							
	Phenol	Phenol (about 50% in 60 min)							
	Methylene blue (MB)	(Removal rate) MB (75% in 150 min)							
(001) $\text{TiO}_2/\text{Ti}_3\text{C}_2$	Methyl orange (MO)	(Rate constants) 0.018	10 mg catalyst + 200 mL 20 $\text{mg L}^{-1}$ substrate, 60 min dark adsorption	300 W Xe lamp	$\bullet\text{OH}$ (main)	$\text{TiO}_2$ square nanosheets/ $\text{Ti}_3\text{C}_2$ nanosheets	Multilayer	2016	104



Table 3 (continued)

Photocatalyst	Substrate of degradation	Removal rate (%) / rate constants (min <sup>-1</sup> )	Reaction conditions	Light source	Oxygenic species	Morphology	Monolayer or multilayer	Year	Ref.
Graphene layers anchored TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Rhodamine B (RhB)	(Rate constants) 0.0559 (RhB)	10 mg catalyst + 200 mL (RhB 20 mg L <sup>-1</sup> , TC 10 mg L <sup>-1</sup> , CIP 3 mg L <sup>-1</sup> , BPA 5 mg L <sup>-1</sup> ), 60 min dark adsorption	300 W Xe lamp ( $\lambda > 400$ nm)	•OH	3D bulk	Bulk Ti <sub>3</sub> C <sub>2</sub> @TiO <sub>2</sub>	2020	105
	Tetracycline (TC)	0.0244 (TC)	50 mg catalyst + 50 mL 20, 30, 50 mg L <sup>-1</sup> substrate, 30 min dark adsorption, 60 min dark adsorption	400 W metal halide lamp	h <sup>+</sup>	Flower-like nanosphere	Multilayer	2020	106
	Ciprofloxacin (CIP)	0.0168 (CIP)							
	Bisphenol A (BPA)	0.0194 (BPA)							
2D/2D Ti <sub>3</sub> C <sub>2</sub> /MoS <sub>2</sub>	Methylene orange (MO)	(Rate constants) 0.00836							
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /ZnFe <sub>2</sub> O <sub>4</sub> @Ti <sub>3</sub> C <sub>2</sub>	Rhodamine B (RhB)	(Rate constants) 0.02686 (RhB) (Removal rate)	20 mg catalyst + 100 mL 10 mg L <sup>-1</sup> substrate, 30 min dark adsorption	300 W Xe lamp ( $\lambda > 400$ nm)	•OH •O <sub>2</sub> <sup>-</sup>	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /ZnFe <sub>2</sub> O <sub>4</sub> nanoparticles/ Ti <sub>3</sub> C <sub>2</sub> nanosheets	Multilayer	2019	107
	Cr(vi)	Cr(vi)							
		Light off: about 70% in 90 min Light on: about 90% in 90 min							



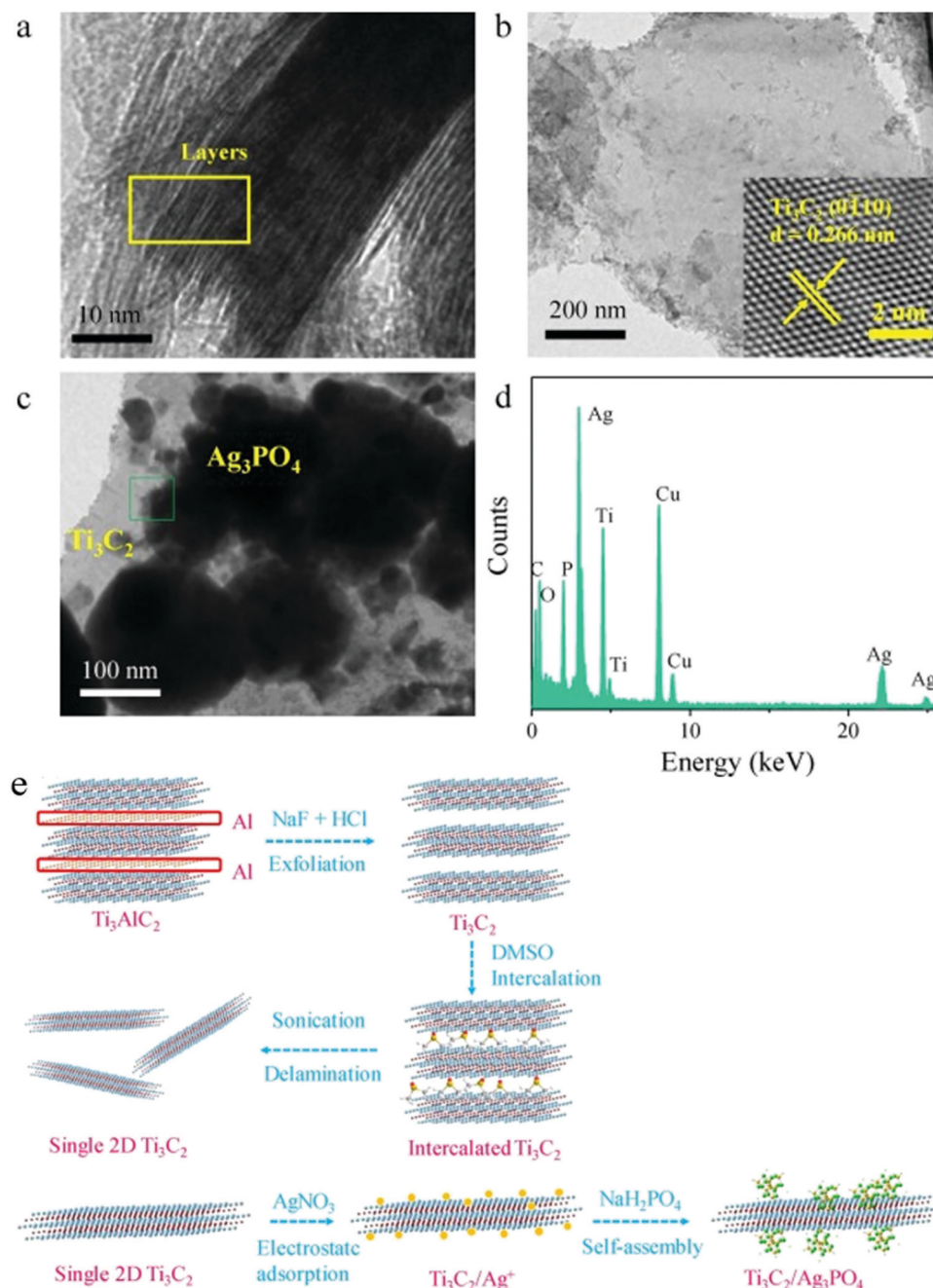


Fig. 19 TEM images of (a) bulk  $\text{Ti}_3\text{C}_2$ , (b) single  $\text{Ti}_3\text{C}_2$  sheet, (c)  $\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$  composite. (d) EDX spectra of the  $\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$  composite and (e) the schematic representation of single 2D  $\text{Ti}_3\text{C}_2$  sheets and  $\text{Ag}_3\text{PO}_4/\text{Ti}_3\text{C}_2$  synthesis.<sup>87</sup>

needs to be explored. As is known to all, the structure of pure  $\text{Ti}_3\text{C}_2\text{T}_x$  is not stable in both air and water. In air, the fresh-etched surface groups (such as  $-\text{OH}$  and  $-\text{F}$ ) can be replaced by oxygen termination after being exposed to air for a period of time; in water,  $\text{Ti}_3\text{C}_2\text{T}_x$  can even be oxidized after being replaced for 21 days in room temperature.<sup>108</sup> Thus, it needs to be explored more whether the structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  is changed during the photocatalytic reaction and if it does, how it changes.

During photocatalytic  $\text{CO}_2\text{RR}$ , although both monolayer-structured and multilayer-structured  $\text{Ti}_3\text{C}_2\text{T}_x$  exhibit high

performance, isotope detection shows that some carbon resources come from  $\text{CO}_2$  molecular; thus, there are still some ambiguities and other possibilities. For example, the valence state of "C" in  $\text{Ti}_3\text{C}_2\text{T}_x$  is mostly  $-4$ , which makes it possible for  $\text{CO}_2$  to react with  $\text{Ti}_3\text{C}_2\text{T}_x$  in order to form the CO as product; this pathway involves redox reaction rather than catalysis.

This, in all, the mechanism needs to be explored more, both during the photocatalytic reaction and the oxidation of  $\text{Ti}_3\text{C}_2\text{T}_x$  itself.



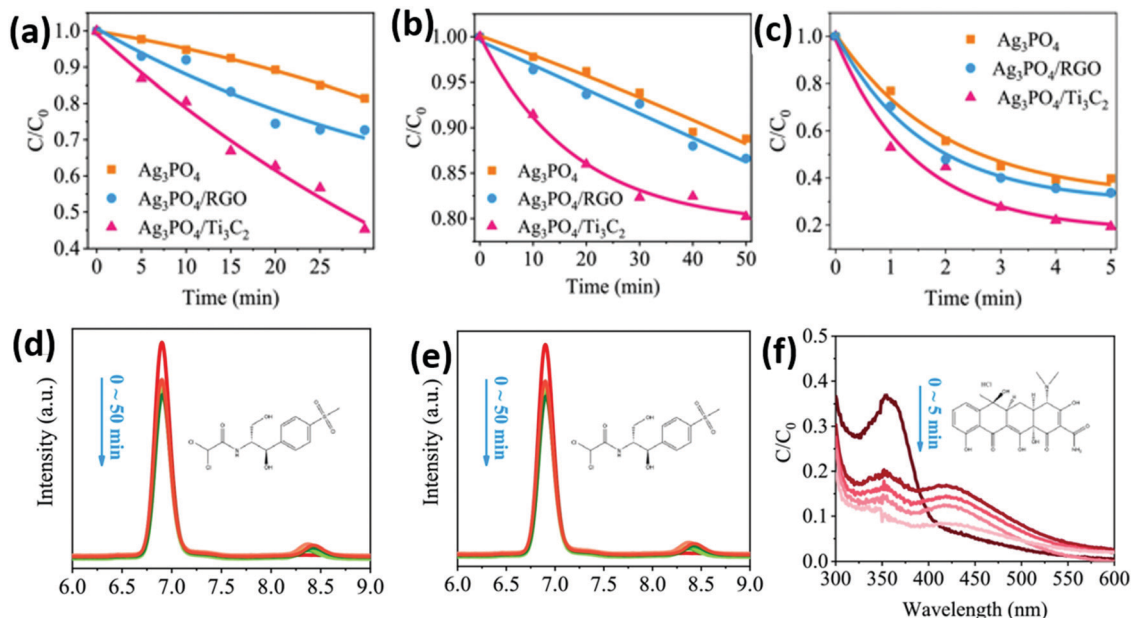


Fig. 20 Photocatalytic degradation of various pollutants by the as-prepared catalysts. (a) CPL, (b) TPL, and (c) TC-H degradation efficiency in the presence of the as-prepared catalysts under visible light irradiation ( $\lambda > 420$  nm). HPLC chromatogram of (d) CPL and (e) TPL under different degradation times using the as-prepared catalysts. (f) UV-vis absorption spectra of TC-H under different degradation times using different catalysts.<sup>87</sup>

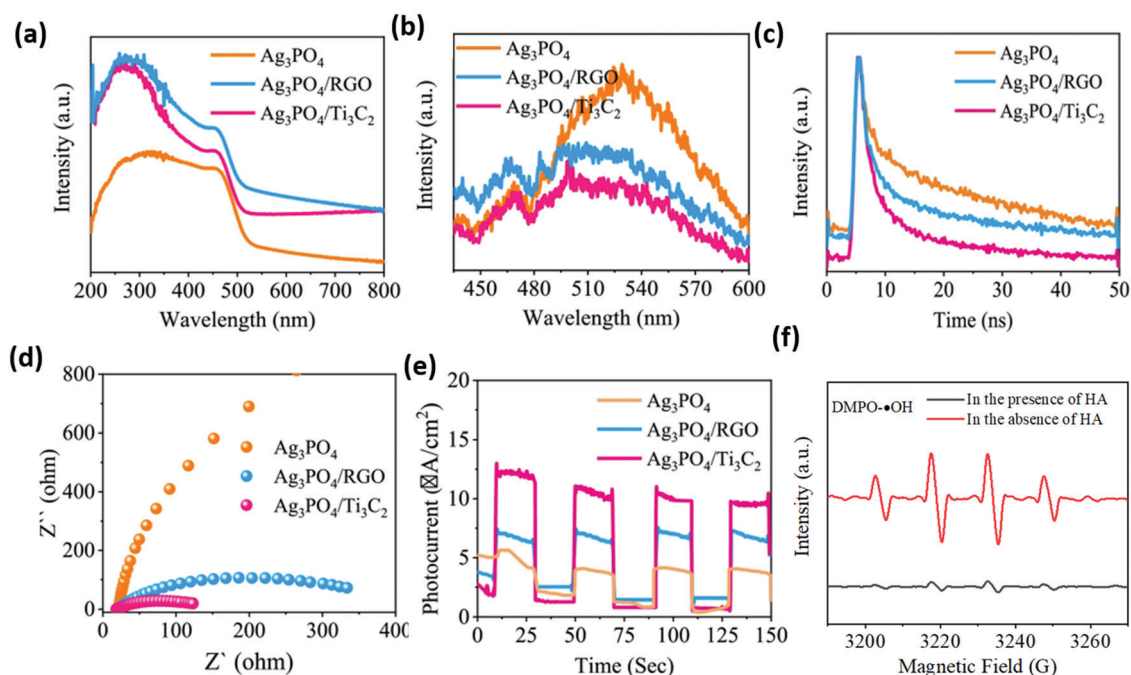


Fig. 21 UV-vis diffuse reflectance spectra (a), PL spectra (b), time-resolved PL decay spectra (c), EIS Nyquist plots (d), transient photocurrent responses (e) of the as-prepared catalysts, and DMPO spin-trapping ESR spectra for  $DMPO \cdot OH$  in the  $Ag_3PO_4/Ti_3C_2$  system in the presence or absence of HA.<sup>87</sup>

**5.2.2 Development direction.** The application of  $Ti_3C_2T_x$  in photocatalysis is meaningful not just because it obviously promotes the reaction but also due to its applications in other

new two-dimensional materials. For further applications, the following directions are necessary: to explore new methods of preparation to get structurally-stable  $Ti_3C_2T_x$ ; to explore easier





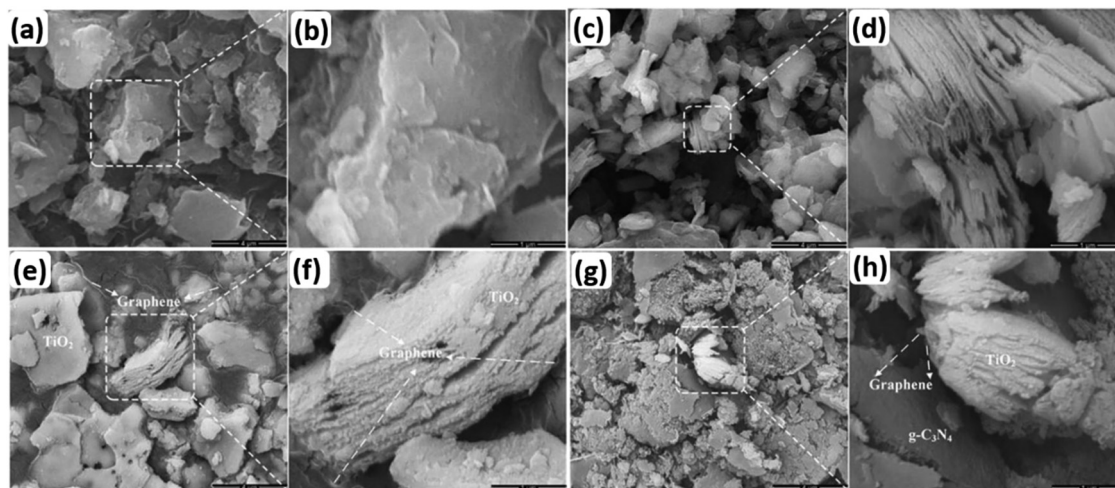


Fig. 22 SEM images of  $C_3N_4$  (a and b),  $Ti_3C_2$  (c and d), heated  $Ti_3C_2$  (e and f), and graphene layers anchored  $TiO_2/g-C_3N_4$  (g and h).<sup>105</sup>

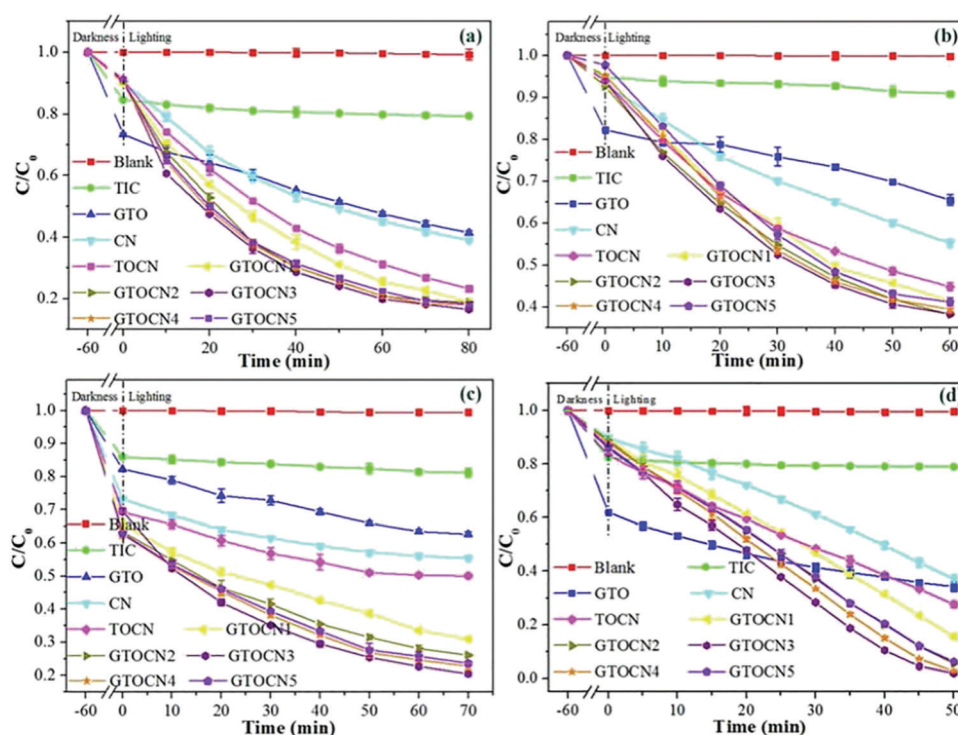


Fig. 23 The photocatalytic degradation performance of TC (a), CIP (b), BPA (c), and RhB (d) by photocatalysts under visible light irradiation.<sup>105</sup>

methods of preparation to get monolayered  $Ti_3C_2T_x$ ; to explore more effective combination between  $Ti_3C_2T_x$  and the base photocatalyst; to explore methods of regulating the surface groups and interlayer groups; to explore other application in the MXene family; to explore the mechanism.

$Ti_3C_2T_x$  is the earliest material in the MXene family; thus, the improvement of its application in photocatalysis represents a great significance for the application of the whole family.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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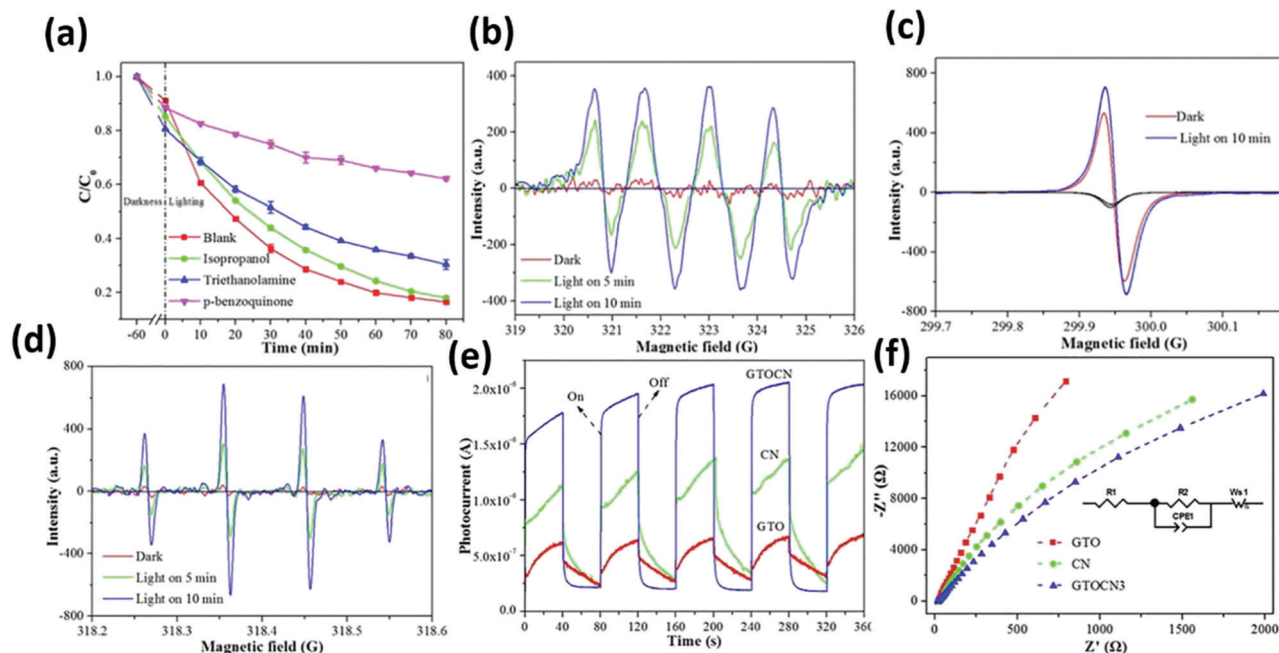


Fig. 24 Trapping experiment for the photocatalytic degradation of TC over GTOCN3 (a); ESR spectra of GTOCN3 for (b)  $\text{DMPO} \cdot \text{O}_2^-$ , (c)  $\text{TEMPO} \cdot \text{h}^+$ , (d)  $\text{DMPO} \cdot \text{OH}$  in the dark and under visible light irradiation,  $I$ - $T$  curves under visible light irradiation (e) and the EIS response (f) of the samples.<sup>105</sup>

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