

Showcasing cutting-edge research for catalytic hydrogen production on MXene fabricated catalysts from Dr Ejaz Hussain and Dr Khezina Rafiq's laboratory 52s, Institute of Chemistry, The Islamia University of Bahawalpur-63100, Pakistan.

Unveiling the potential of MXene-fabricated catalysts: an effective approach for H<sub>2</sub> generation from water splitting

This study represents an advanced scientific approach to generating hydrogen from water splitting. Reported catalysts (*i.e.*, TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and TiO<sub>2</sub>@C) have been found to be extremely stable and effective for hydrogen generation. The results depict that the relatively higher catalytic activities of TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> are attributed to the existence of multilayer MXenes. The findings of this study have been anticipated to guide the design of MXene-supported catalysts for hydrogen energy applications. Moreover, comprehensive assessment has made this work distinct from other reported studies in the same area.

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# Unveiling the potential of MXene-fabricated catalysts: an effective approach for H<sub>2</sub> generation from water splitting†

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Hydrogen has enough potential and can be successfully used as an alternative to the conventional fuel. It can be successfully produced from water that is not only a sustainable source but exists everywhere on earth. Additionally, its combustion releases water that is quite safe and environment friendly. The current project was designed to generate hydrogen from catalytic water splitting on TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts. To obtain the required catalytic characteristics, titania was engineered on Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> surfaces *in situ* using an ethanol-assisted solvothermal approach. After careful recovery, the catalysts were characterized and assessed for the photoreaction. All photoreactions were performed in a quartz reactor (150 mL), where hydrogen evolution activities were monitored on GC-TCD (Shimadzu-JP). The comparative activities indicated that TiO<sub>2</sub>@C and TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts deliver 9.37 and 18.57 mmol g<sup>-1</sup> h<sup>-1</sup> of hydrogen, respectively. The higher activities of TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> were attributed to the existence of higher active sites (charge trapping centres) on the multilayer MXene that progressively promote and facilitate redox reactions. Reason is that existence of titania on MXene interfaces develops heterojunctions that rectify the charge transfer; hence reduce the charge recombination (*i.e.*, back reaction). On the basis of encouraging activities, it has been concluded that the aforementioned approach holds promise to replace the costly and conventional hydrogen generation technologies.

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## Introduction

Without doubt, fossil fuels are the main sources of the world's energy, but pollution generated by their burning is enough to ruin life on earth. If the current speed of fossil fuel consumption continues, it will definitely bring a severe change in the earth's climate.<sup>1</sup> Unpredictable weather, sudden hailstorms and rain-falls are undeniable evidence of climate change. Thus, for life on earth, an alternative and green source is urgently needed.<sup>2</sup> That is why the scientific community is focusing on new and sustainable sources that not only meet the energy demand but also protect our earth and atmosphere. Additionally, excessive growth in the human population and industrialization increase these challenges. Due to high costs of conventional energy sources, developing countries are struggling to shift from fossil fuels to green and sustainable sources.<sup>3</sup>

Hydrogen is an ideal fuel due to its (i) high calorific value (150 kJ g<sup>-1</sup>), (ii) zero carbon emissions, and (iii) renewable nature.<sup>4</sup> Water is a stable molecule, and it needs 237 kJ mol<sup>-1</sup> of energy to split into hydrogen and oxygen. However, the

activation energy of the water splitting reaction can be reduced with the use of stable and effective catalysts.<sup>5</sup> For water splitting, commonly used photocatalysts are TiO<sub>2</sub>, ZrO<sub>2</sub>, ZnO, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, ZnS, CeVO<sub>4</sub>, CuO, CdS, CdZnS, g-C<sub>3</sub>N<sub>4</sub>, ZnIn<sub>2</sub>S<sub>4</sub>, and Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>.<sup>6-14</sup> However, these catalysts have been restricted due to the following drawbacks: (i) fast charge recombination; (ii) poor optical response; (iii) photocorrosion; (iv) stability and durability; and (v) improper band gaps and structural defects.<sup>15</sup> Due to the aforementioned drawbacks, these catalysts cannot split water efficiently; therefore, for progressive water splitting, improvements in the catalytic system have become necessary. Thus, modifications using co-catalysts like MXene or graphene have gained more interest due to their excellent conductivity.<sup>16</sup>

In recent decades, MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) has opened new pathways for developing stable and durable catalysts. The reason is that MXenes naturally exhibit surface terminations like -F, =O, and -OH that enhance the surface reaction ability of catalysts.<sup>17</sup> Among the MXenes family, titanium carbide (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>) has gained significant attention for energy conversion and storage applications. Due to tuneable characteristics, increased conductivity, and intrinsic features, it facilitates more active sites during photoreactions.<sup>18</sup>

Among co-catalysts, MXene and graphene have been identified as exceptional co-catalysts that can effectively promote surface charges to the active centres (*i.e.*, redox sites). Additionally, these co-catalysts have substantial selectivity and can only

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perform in optimized catalytic reactions. However, the fabrication of MXene with  $\text{TiO}_2$  for targeted applications (*i.e.*, water splitting) is quite challenging having relatively high mechanical strength.<sup>19</sup> Because the dispersion of MXene matrix on semiconductor's surfaces can be problematic, this causes agglomeration during the developmental process. Hence, the synthesis of  $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2/\text{C}$  has been found significant factor for excellent photocatalytic activities.<sup>20</sup> The advantage of MXene support is that it can become the inherent source of  $\text{TiO}_2$  growth due to Ti–C–Ti–C–Ti structural arrangements.<sup>21</sup> Additionally, the complete oxidation of  $\text{Ti}_3\text{C}_2\text{T}_x$  produces the carbide-derived carbon (CDC), which also acts as co-catalyst and promotes the photon absorption ability of semiconductor systems.<sup>22</sup> Thus, *in situ* developments of metal oxide, *i.e.*,  $\text{TiO}_2$ , on  $\text{Ti}_3\text{C}_2\text{T}_x$  and CDC are quite important to enhance the overall catalytic efficiency of the photoreaction.

In this work, we have extended the utilization of MXene using *in situ*-engineered  $\text{TiO}_2$  (*i.e.*,  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@/\text{C}$ ) *via* an ethanol-assisted solvothermal approach. The significant advantage of *in situ* growth of  $\text{TiO}_2$  has the following advantages for catalytic water splitting: (i) superior conductivity and charge transportation; (ii) formation of heterojunctions to reduce back reactions; (iii) extension of the internal optical response during photoreaction; (iv) enhanced stability and durability; (v) enhanced pool of reactive charges on the redox sites. The findings of the current project deliver encouraging examples of renewable energy systems that can be further be improved for large-scale implementation.

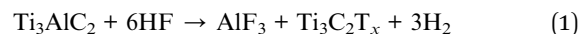
## Experimental

The details of the chemicals and instruments used in current work have been discussed in the ESI† section.

### Catalysts preparation

The scheme that was employed to design the MXene and derived catalysts is illustrated in Fig. 1. In this study,  $\text{Ti}_3\text{C}_2\text{T}_x$ , *i.e.*, titanium carbide, has been developed by the etching process, which was designed and selectively performed with HF (*ca.* 40%) [20]. Typically, 500 mg of  $\text{Ti}_3\text{AlC}_2$  was transferred to

40 mL of the aforementioned HF in a 100 mL Teflon reactor. Note that the reaction process was completed in a safe environment, *i.e.*, under a fume hood. To ensure the complete removal of aluminium, the product was vigorously stirred under gentle sonication [21]. The chemical reaction involved in this process is given in eqn (1).



To isolate  $\text{Ti}_3\text{C}_2\text{T}_x$  from the HF solution, the suspension underwent some important steps: (i) centrifugation at 5000 rpm; (ii) careful washing six times to eliminate impurities; and (iii) vacuum-drying at 85 °C.

In this study,  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@/\text{C}$  catalysts were synthesized *via* an ethanol-assisted solvothermal approach.<sup>23</sup> The  $\text{Ti}_3\text{C}_2\text{T}_x$  was used as a precursor material because it has an inherent titanium source for the growth of  $\text{TiO}_2$  due to Ti–C–Ti–C–Ti structural arrangements.<sup>24</sup> Typically, 200 mg of the aforementioned precursor support was dispersed in 40 mL of mixture solvents (with 80 : 20 water/ethanol ratios) and sonicated for 10 min. For the *in situ* growth of  $\text{TiO}_2$  on  $\text{Ti}_3\text{C}_2\text{T}_x$ , this mixture was transferred to a Teflon-lined autoclave reactor for 2 h at 180 °C. The reaction was continued for a further 4 h to achieve the complete oxidation of MXene so that it is successfully transformed into the high-textured  $\text{TiO}_2@/\text{C}$  product. It has been noted that optimized conditions are necessary to obtain the complete oxidation of MXene for developing high-quality  $\text{TiO}_2$  catalyst textures *in situ* on the surfaces of carbide.<sup>25</sup> After hydrothermal reaction, catalysts were recovered by vacuum filtration. To remove the impurities or unreacted precursors, catalysts were thoroughly rinsed with the ethanol/acetone mixture (80 : 20 v/v ratios). To eliminate the moisture from layered structures, catalysts were vacuum dried at 95 °C for 5 h.

### Photocatalytic activities

Photocatalytic water splitting reactions for hydrogen generation were carried out using a PLS-SXE300 lamp. The photoreactions were performed in a 150 mL quartz reactor, where a 20 mg dose of catalysts was optimised for 50 mL of pure water.  $\text{H}_2$  and  $\text{O}_2$

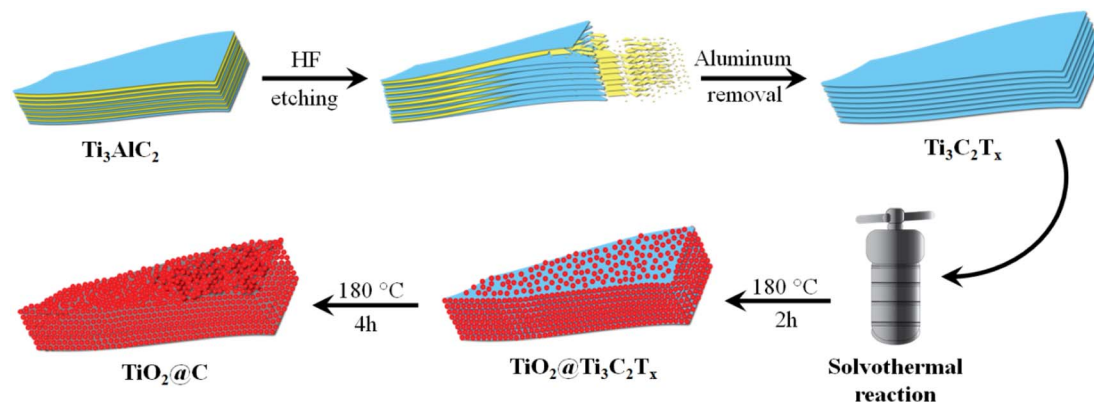


Fig. 1 Graphical illustration for the synthesis of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@/\text{C}$  catalysts.



generation rates were quantified by taking gas samples (0.5 mL per syringe) from the headspace of the photoreactor. For the accurate analysis, high-purity argon served as the carrier gas. A specialized molecular sieve capillary column was used for gas separation. The gases were quantified using the internal calibration curves of the gas chromatography system (GC-TCD, Shimadzu, 2010).<sup>26</sup> Quantum efficiencies (QEs) were calculated using eqn (2). Note that these measurements were executed under controlled conditions.

$$QE = \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100 \quad (2)$$

## Results and discussions

The synthesis scheme of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{TiO}_2@\text{C}$  catalysts is shown in Fig. 1. Various characterization techniques have been employed to study the structural, morphological, optical, magnetic, and chemical properties of the synthesized catalysts, which have been discussed below.

### XRD analyses

The XRD patterns of  $\text{Ti}_3\text{AlC}_2$  (MAX),  $\text{Ti}_3\text{C}_2\text{T}_x$  (MXene),  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$  are described in Fig. 2a. XRD is an excellent tool that can accurately provide significant insights about

structural transformations.<sup>27</sup> Results of this study indicate that the XRD pattern of pristine  $\text{Ti}_3\text{AlC}_2$  closely matches JCPDS No. 52-0875, validating its purity with hexagonal crystalline structure.<sup>28</sup> Notably, the XRD patterns of  $\text{Ti}_3\text{C}_2\text{T}_x$  display broader lattice planes (002) as compared to  $\text{Ti}_3\text{AlC}_2$ . It is worth mentioning that shift of the (002) planes towards smaller angles along with the disappearance of the characteristic peak at  $39^\circ$  (*i.e.*, corresponds to (104) planes) indicate the complete removal of aluminium atoms (in the form of  $\text{AlF}_3$ ).<sup>29</sup> These results confirm the phase purity and successful transformation of MAX to  $\text{Ti}_3\text{C}_2\text{T}_x$  structures. The  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts exhibit the inherent diffractions of  $\text{TiO}_2$  (anatase) along with the  $\text{Ti}_3\text{C}_2\text{T}_x$  XRD patterns. The changes in diffraction pattern confirm the *in situ* growth of  $\text{TiO}_2$  over  $\text{Ti}_3\text{C}_2\text{T}_x$  surfaces. On the other hand, the peak positions of  $\text{TiO}_2@\text{C}$  confirm the anatase structure and are exactly matched with PDF#73-1764.<sup>30</sup> Additionally, removal of  $\text{Ti}_3\text{C}_2\text{T}_x$  diffraction peaks confirms the complete conversion (*i.e.*, oxidation) of Ti–C–Ti–C–Ti to the  $\text{TiO}_2@\text{C}$ .<sup>31</sup> XRD pattern and their corresponding *hkl* values for as reported catalysts have been tabulated in Table S1.† The structural changes observed in XRD results provide valuable insights into catalyst performance.

### FTIR analyses

The FTIR analysis (Fig. 2b) of  $\text{Ti}_3\text{AlC}_2$  revealed the bending vibrations of the Ti–Al–C bond at  $505 \text{ cm}^{-1}$ . The etching of

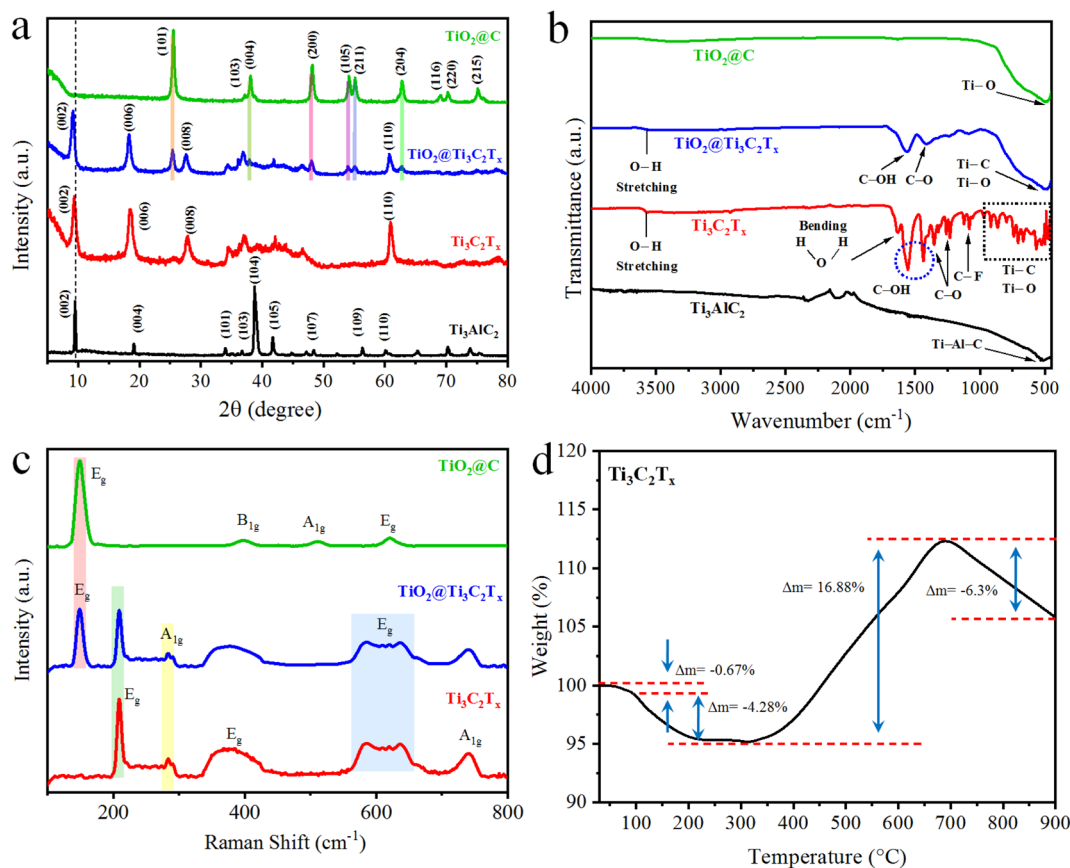


Fig. 2 (a) XRD pattern; (b) FTIR results of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$ ; (c) Raman spectroscopy results of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$ ; (d) TGA of  $\text{Ti}_3\text{C}_2\text{T}_x$ .



aluminium was confirmed by the removal of the  $505\text{ cm}^{-1}$  peak, whereas new vibration patterns are attributed to surface termination ( $\text{T}_x = \text{O}, -\text{F}, -\text{OH}$ ).<sup>32</sup> FTIR results indicate that the vibrations observed at  $566\text{ cm}^{-1}$ ,  $706\text{ cm}^{-1}$ ,  $855\text{ cm}^{-1}$ , and  $922\text{ cm}^{-1}$  are attributed to the Ti-C/Ti-O stretching vibrations. The O-terminations on the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface caused Ti-O vibrations at  $617\text{ cm}^{-1}$ . F-terminations are observed at  $1057$  and  $1097\text{ cm}^{-1}$ , whereas O-H terminations are detected at  $1399$  and  $1437\text{ cm}^{-1}$ .<sup>33</sup> The vibrations at  $1229$  and  $1343\text{ cm}^{-1}$  are attributed to adsorb/atmospheric  $\text{CO}_2$ .<sup>34</sup> These results confirm the formation of a multilayer  $\text{Ti}_3\text{C}_2\text{T}_x$  structure. In the FTIR results of  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  catalysts, the strong vibration at  $480\text{ cm}^{-1}$  confirms the formation of  $\text{TiO}_2$  over  $\text{Ti}_3\text{C}_2\text{T}_x$ . The aforementioned results also demonstrate the surface terminations ( $=\text{O}$  and  $-\text{OH}$ ) along with Ti-C vibrations of  $\text{Ti}_3\text{C}_2\text{T}_x$ . For  $\text{TiO}_2@/\text{C}$ , the Ti-O peak was detected at a frequency of  $480\text{ cm}^{-1}$ . The presence of adsorbed water molecules on the catalyst surface was observed at  $1628$  (bending vibrations) and  $3550\text{ cm}^{-1}$  (stretching vibrations).<sup>35</sup> The absence of any Ti-C peaks confirms that all Ti-C-Ti-C-Ti bonds were completely converted into  $\text{TiO}_2@/\text{C}$ , which underwent heterostructures to enhance the activity performances of catalysts during photoreactions.

### Raman analyses

The Raman results for  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{Ti}_3\text{C}_2\text{T}_x@/\text{TiO}_2$ , and  $\text{TiO}_2@/\text{C}$  were obtained in the  $100\text{--}800\text{ cm}^{-1}$  region (Fig. 2c). MXenes ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) belong to the  $\text{D}_{3d}$  point group, and their vibrations can be described using Mulliken symbols as  $2(N-2) E_g + (N-2) A_{1g} + 2(N-2) E_u + (N-2) A_{2u}$ , where  $N$  represents the number of atoms per unit cell (*i.e.*, five in the case of  $\text{Ti}_3\text{C}_2$ ).<sup>36</sup> The  $E_g$  and  $E_u$  are doubly degenerate modes (mostly  $E_g$  is used for representation), while  $E_g$  and  $A_{1g}$  are the only Raman-active vibration modes. In MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ), four Raman modes are active:  $E_g$  and  $A_{1g}$  signify the in-plane and out-of-plane vibration of Ti atoms, along with two additional vibration modes of C atoms (Fig. S1†).<sup>37</sup> The Raman frequency of  $208\text{ cm}^{-1}$  ( $E_g$  mode) is attributed to in-plane vibrations of Ti and C atoms. The carbon layer vibrations appear at higher frequencies ( $500\text{--}800\text{ cm}^{-1}$ ). The presence of surface terminations ( $=\text{O}, -\text{F}, -\text{OH}$ ) causes more vibrations due to the increased atoms in the unit cell. The Raman results of  $\text{Ti}_3\text{C}_2\text{T}_x$  show three regions: lower frequencies for entire flake vibrations, mid-frequency for surface terminations, and higher frequencies for carbon and surface terminations (Fig. S1†).<sup>36</sup> The  $E_g$  corresponds to in-plane vibrations, and  $A_{1g}$  corresponds to out-of-plane vibrations. The Raman vibrations around  $600\text{ cm}^{-1}$  ( $E_g$  mode) were attributed to the C-O vibrations. As compared to the pristine  $\text{Ti}_3\text{C}_2\text{T}_x$ , the Raman peaks of  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  indicate the formation of titanium dioxides, with the vibrations at  $147\text{ cm}^{-1}$  that correspond to the anatase phase. Moreover, the Raman spectrum of  $\text{TiO}_2@/\text{C}$  exhibits Raman vibrations at  $148\text{ cm}^{-1}$  ( $E_g$ ),  $397\text{ cm}^{-1}$  ( $B_{1g}$ ),  $510\text{ cm}^{-1}$  ( $A_{1g}$ ) and  $620\text{ cm}^{-1}$  ( $E_g$ ). These vibrations were attributed to the oxygen atoms of O-Ti-O (correspond to the anatase phase).<sup>38</sup>

### TGA analysis

Thermal gravimetric analysis (TGA) of  $\text{Ti}_3\text{C}_2\text{T}_x$  in an oxygen atmosphere was conducted to observe changes as the temperature increased up to  $900\text{ }^\circ\text{C}$ .<sup>39</sup> The results (Fig. 2d) demonstrate four weight-change steps. The first weight change was due to the loss of water adsorbed on the surface of  $\text{Ti}_3\text{C}_2\text{T}_x$ . In the second step, the surface terminations and bonded water were released up to  $319\text{ }^\circ\text{C}$ .<sup>40</sup> Further increases in temperature led to the oxidation of  $\text{Ti}_3\text{C}_2\text{T}_x$ , resulting in a subsequent 19.98% increase in mass. The oxidation of  $\text{Ti}_3\text{C}_2\text{T}_x$  started at  $320\text{ }^\circ\text{C}$  and finally began to decompose at  $729\text{ }^\circ\text{C}$ .<sup>41</sup> TGA results revealed the thermal stability of  $\text{Ti}_3\text{C}_2\text{T}_x$  in an oxygen atmosphere and  $\text{TiO}_2$  formation (oxidation) on its surface.

### SEM studies

Field-emission scanning electron microscopy (FESEM) was utilized to analyse the surface features and characteristics of catalyst.<sup>42</sup> The SEM results of  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{TiO}_2@/\text{C}$  are demonstrated in Fig. 3a–d. The SEM results of commercial  $\text{Ti}_3\text{AlC}_2$  powder (Fig. 3a) demonstrate the solid block structure with smooth surfaces. The etching of  $\text{Ti}_3\text{AlC}_2$  produces accordion-like multilayer nanosheets loosely bound together,<sup>43</sup> as shown in Fig. 3b. The MXene layers are clearly separated as compared to the MAX powder that confirms the successful exfoliation (*i.e.*, aluminium removal). The expansive 2D structure of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets offers an abundance of active sites and terminations (*i.e.*,  $-\text{O}, -\text{OH}, -\text{F}$ ) that improve the interactions with reactants for hydrogen generation.<sup>44</sup> The *in situ* growth of anatase  $\text{TiO}_2$  over the  $\text{Ti}_3\text{C}_2\text{T}_x$  *via* hydrothermal reactions is revealed in Fig. 3c. The result illustrates the uniform distribution of  $\text{TiO}_2$  particles over the  $\text{Ti}_3\text{C}_2\text{T}_x$  surfaces and within the structure of  $\text{Ti}_3\text{C}_2\text{T}_x$ .<sup>45</sup> The complete oxidation of MXene produced  $\text{TiO}_2@/\text{C}$  catalysts having uniform dispersion of  $\text{TiO}_2$  across the material. Fig. 3d illustrates a significant difference when compared to pristine anatase (see Fig. S2†). The  $\text{TiO}_2$  derived from  $\text{Ti}_3\text{C}_2\text{T}_x$  showcases significantly higher crystallinity compared to other forms of  $\text{TiO}_2$ .<sup>46</sup>

### AFM analysis

Atomic force microscopy (AFM) provides detailed insights into the surface features, morphology, and size distribution of  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  catalysts at nearly atomic scale.<sup>47</sup> The detailed 2D topographical images are exhibited in Fig. 4a and b. A scan area of  $2.17 \times 2.17\text{ }\mu\text{m}$  was utilized to assess the height (thickness) distribution within the range of  $0.8\text{ }\mu\text{m}$ . The recorded average thickness of  $0.445\text{ }\mu\text{m}$  is validated in Fig. 4c. Moreover, Fig. 4d and e reveals three-dimensional results that provide insights to the surface features and roughness of the  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$  photocatalysts.<sup>48</sup>

### XPS analyses

The oxidation states and chemical compositions of as-synthesized catalysts were studied by X-ray photoelectron spectroscopy (XPS).<sup>49</sup> The comparative results (survey scans) of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@/\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{TiO}_2@/\text{C}$  are illustrated in Fig. 5a.



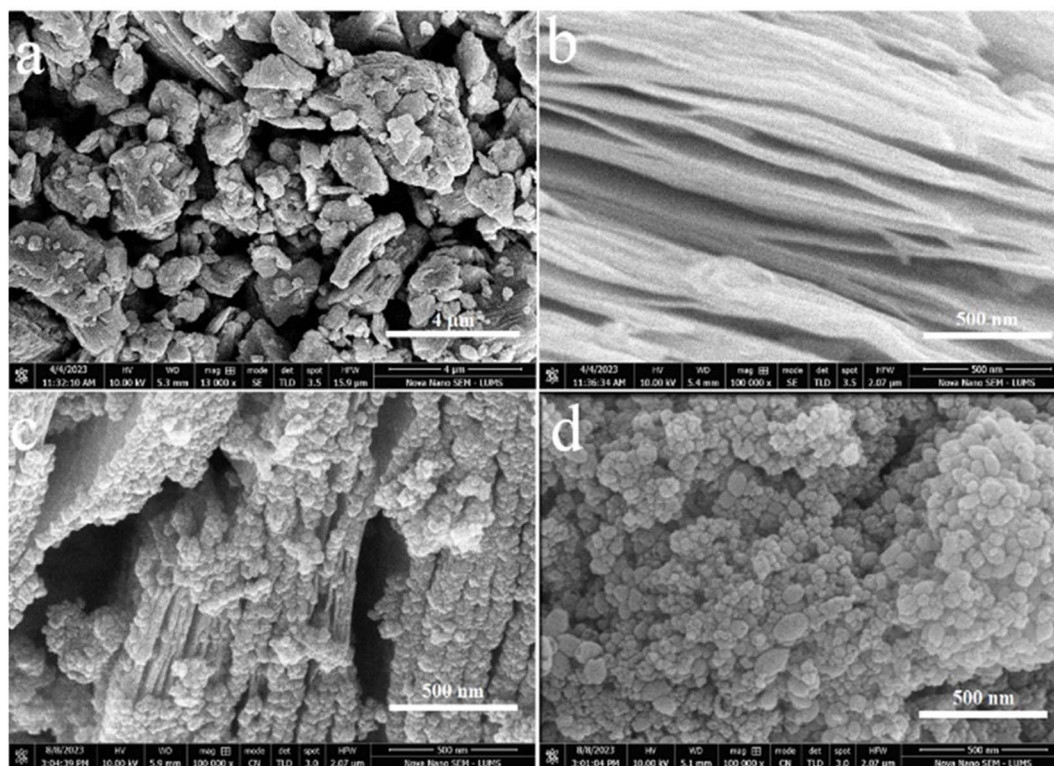


Fig. 3 (a) SEM results of MAX ( $\text{Ti}_3\text{AlC}_2$ ); (b) MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ); (c)  $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_x$ ; (d)  $\text{TiO}_2@ \text{C}$ .

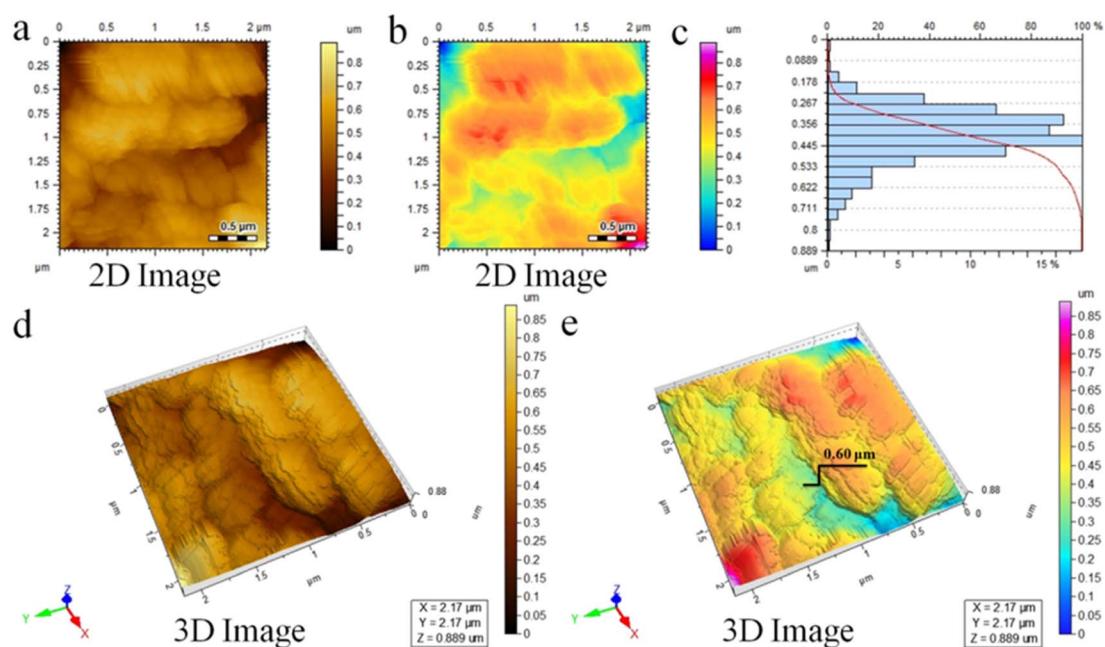


Fig. 4 AFM results of the  $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_x$  photocatalysts: (a and b) 2D-tapping modes, (c) thickness distribution, and (d and e) 3D images.

The XPS results of  $\text{Ti}_3\text{C}_2\text{T}_x$  demonstrate the existence of fluorine terminations due to the use of HF during its synthesis.<sup>50</sup> The binding energies of titanium  $2p_{3/2}$  and  $2p_{1/2}$  were observed at 455.1 and 461.3 eV (see Fig. 5b), which confirms the existence of Ti-C bonds along with various other surface terminations (*i.e.*,

$=\text{O}$ ,  $-\text{OH}$ ).<sup>51</sup> This spectroscopic study provides a detailed material's composition as well as its surface features. In  $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_x$  catalysts, the formation of  $\text{TiO}_2$  over the  $\text{Ti}_3\text{C}_2\text{T}_x$  surfaces was confirmed by the shifting of  $2p_{3/2}$  and  $2p_{1/2}$  peaks to 459.3 eV and 465 eV, respectively.<sup>52</sup> The results depict that



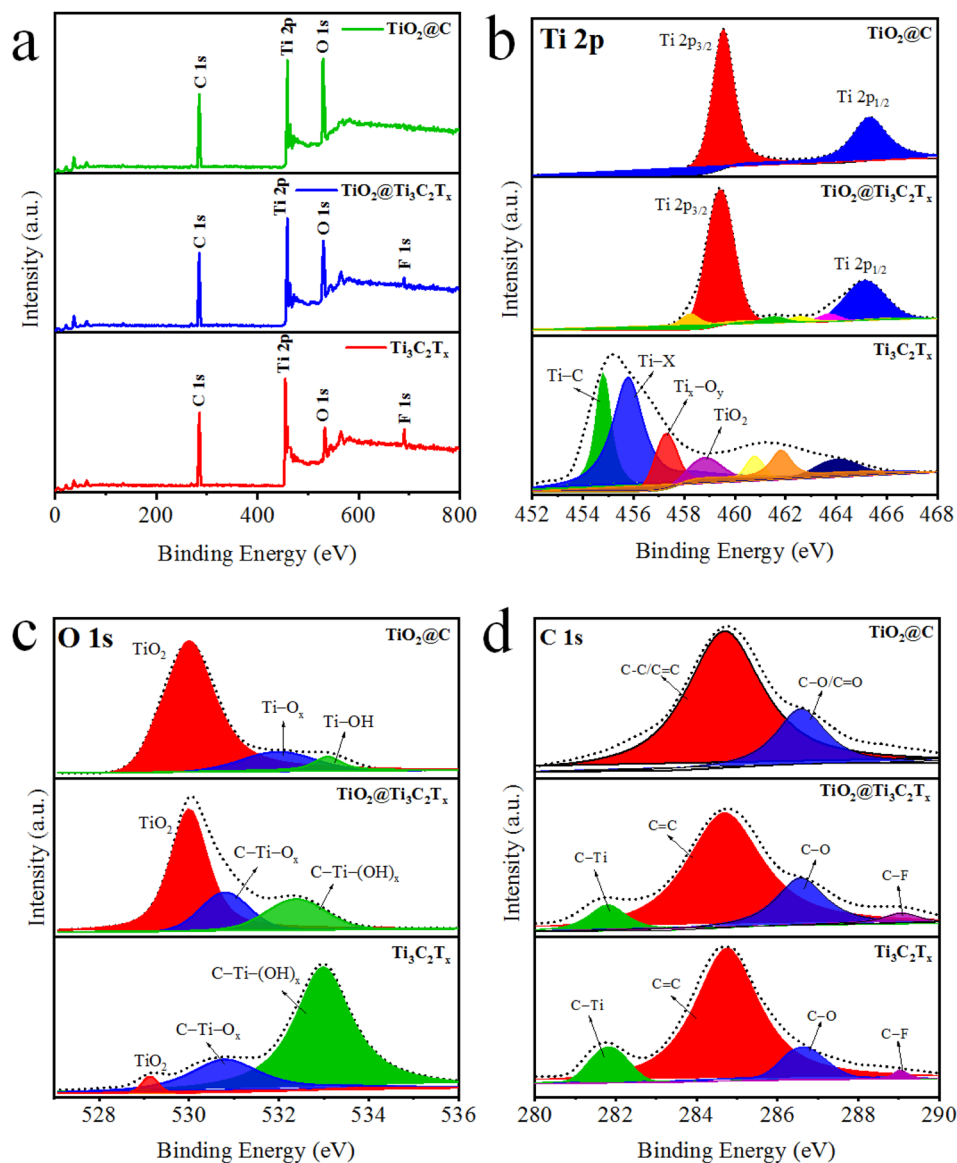


Fig. 5 (a) Survey scans, (b) Ti 2p, (c) O 1s, and (d) C 1s XPS results of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{TiO}_2@ \text{C}$ .

complete oxidations of  $\text{Ti}_3\text{C}_2\text{T}_x$  cause the removal of surface termination. Note: termination that exists on MXene layered structure. Fig. 5c demonstrates O 1s peaks for the  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{TiO}_2@ \text{C}$  catalysts. The  $\text{Ti}_3\text{C}_2\text{T}_x$  exhibits C-Ti-(OH)<sub>x</sub>, C-Ti-O<sub>x</sub> and TiO<sub>2</sub> peaks at binding energies of 532.98, 530.78, and 529.18 eV, respectively.<sup>53</sup> The increased intensity of Ti-O bonds and decreased intensity of C-Ti peaks indicate the *in situ* growth of TiO<sub>2</sub> on the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface. Results depict that oxygen terminal groups were transformed into TiO<sub>2</sub>. The C 1s XPS results demonstrate four peaks fitted at 281.88, 284.88, 286.58, and 289.18 eV, which were assigned to the C-Ti, C=C, C-O, and C-F bonds, respectively (Fig. 5d). The intensities of the C-Ti and C-F peaks decrease in  $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@ \text{C}$  catalysts (as oxidation progresses), which converts the Ti-C bonds into Ti-O bonds.<sup>54</sup>

#### UV-vis/DRS and PL studies

The optical properties of as-synthesized catalysts were obtained using UV-vis diffuse reflectance absorption spectra as shown in Fig. 6a. The UV-vis/DRS results demonstrate the ability of TiO<sub>2</sub>, TiO<sub>2</sub>@C, TiO<sub>2</sub>@ $\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{Ti}_3\text{C}_2\text{T}_x$  to absorb photons, and then bandgap energy values were estimated using the Tauc plot method (Fig. S3†).<sup>55</sup> TiO<sub>2</sub> (anatase) displays absorption in the UV region with a bandgap energy of 3.1 eV, whereas  $\text{Ti}_3\text{C}_2\text{T}_x$  (MXene) exhibits photon absorption across the entire visible and UV region. The *in situ* growth of TiO<sub>2</sub> over  $\text{Ti}_3\text{C}_2\text{T}_x$  displays an increase in photon absorption.<sup>56</sup> The increase in light absorption is due to the presence of black-coloured MXene and carbide-derived carbon (CDC).<sup>57</sup>

The charge separation, transfer, and recombination were studied *via* the photoluminescence (PL) technique. The PL intensity of pristine TiO<sub>2</sub> indicates higher recombination of photoexcited charges (back reaction).<sup>13,58</sup> The PL intensities of



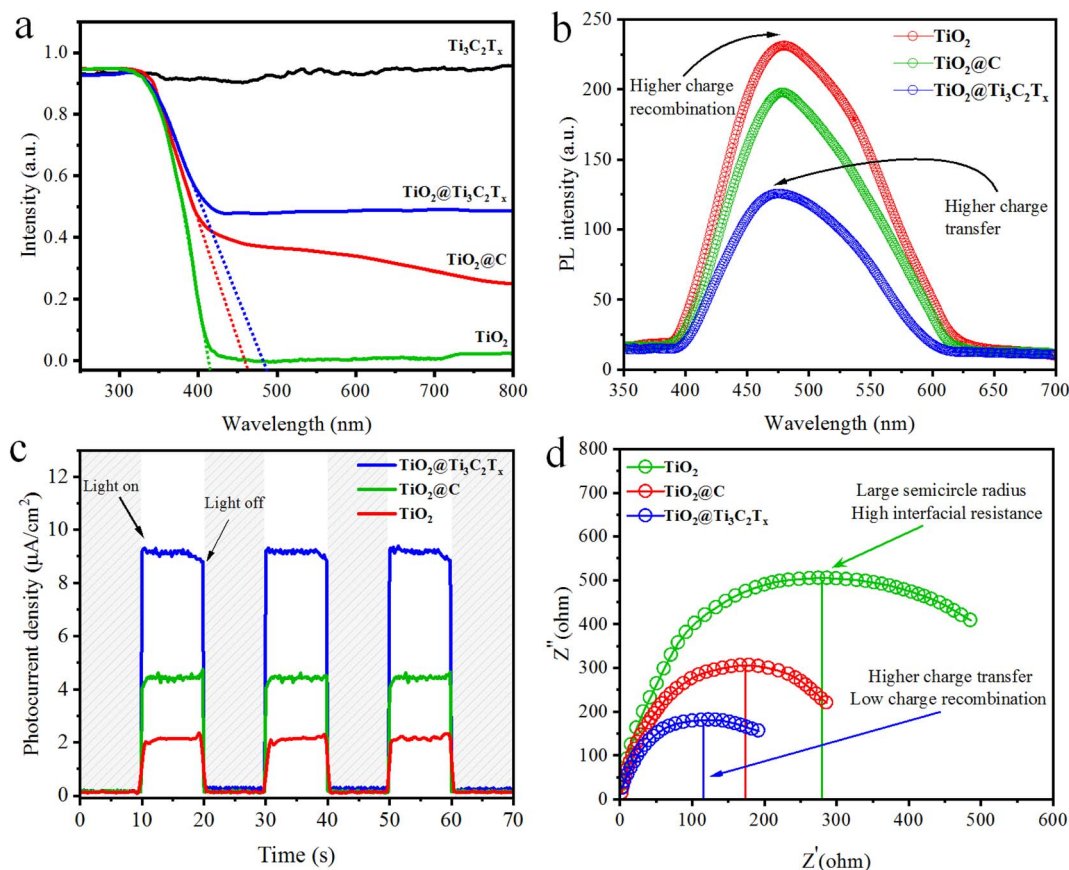


Fig. 6 (a) UV-vis/DRS, (b) PL, (c) photocurrent response, and (d) EIS results of  $\text{TiO}_2$ ,  $\text{TiO}_2@\text{C}$ , and  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts.

synthesized catalysts suggest that  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  has less charge recombination and can deliver relatively higher  $\text{H}_2$  production; see Fig. 6b. The improvements in electron transport and charge separation are attributed to the development of an *in situ* heterojunction.<sup>59</sup>

### TPC and EIS studies

Electrochemical impedance spectroscopy (EIS) and transient photocurrent (TPC) responses were used to study the charge transfer efficiency. The TPC responses of  $\text{TiO}_2$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$  were analysed with on/off cycles (Fig. 6c). The results demonstrate that  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts exhibit a higher photocurrent response as compared to  $\text{TiO}_2$  and  $\text{TiO}_2@\text{C}$ . The higher photoresponse is attributed to the higher charge separation.<sup>60</sup>

EIS measurements for  $\text{TiO}_2$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$  catalysts are shown in Fig. 6d.  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  shows a smaller semicircle diameter, which suggests improved interface carrier transfer and decreased interface resistance.  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts exhibit improved charge separation efficiency and improved charge transfer across interfaces. The lower interface resistance indicates the improved photocatalytic efficiencies.<sup>52</sup>

### BET surface area analyses

The surface area of the prepared photocatalysts was determined through nitrogen adsorption–desorption isotherms using BET measurements, as depicted in Fig. 7a–c. All catalysts exhibit typical IV isotherms and  $\text{H}_3$  hysteresis loops according to Brunauer–Deming–Deming–Teller (BDDT) classifications.<sup>61</sup> The surface areas of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$ , and  $\text{TiO}_2@\text{C}$  are 8.12, 32.57 and 28.17  $\text{m}^2 \text{g}^{-1}$ , respectively. The larger surface area of  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  is due to the *in situ* distributions of  $\text{TiO}_2$  particles over  $\text{Ti}_3\text{C}_2\text{T}_x$ ; hence, the possibility of agglomeration between  $\text{TiO}_2$  particles becomes quite low.<sup>62</sup> Pore size distributions were calculated and are depicted in Fig. 7a–c, revealing very close pore size distributions with a peak centered at *ca.* 5.0 nm. The  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$  catalysts are approximately twice as mesoporous compared to pristine  $\text{Ti}_3\text{C}_2\text{T}_x$ .<sup>63</sup> Therefore, the *in situ* growth of  $\text{TiO}_2$  over  $\text{Ti}_3\text{C}_2\text{T}_x$  provides a larger and more mesoporous surface area for enhanced  $\text{H}_2$  and  $\text{O}_2$  evolution reactions.

### EPR and VSM studies

The presence and properties of oxygen vacancies were investigated utilizing electron paramagnetic resonance (EPR) spectroscopy.<sup>64</sup> It is evident from the results (Fig. S4†) that no EPR signal appeared in the pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  sample. On the other hand, a distinct signal featuring a G factor of 2.005 was



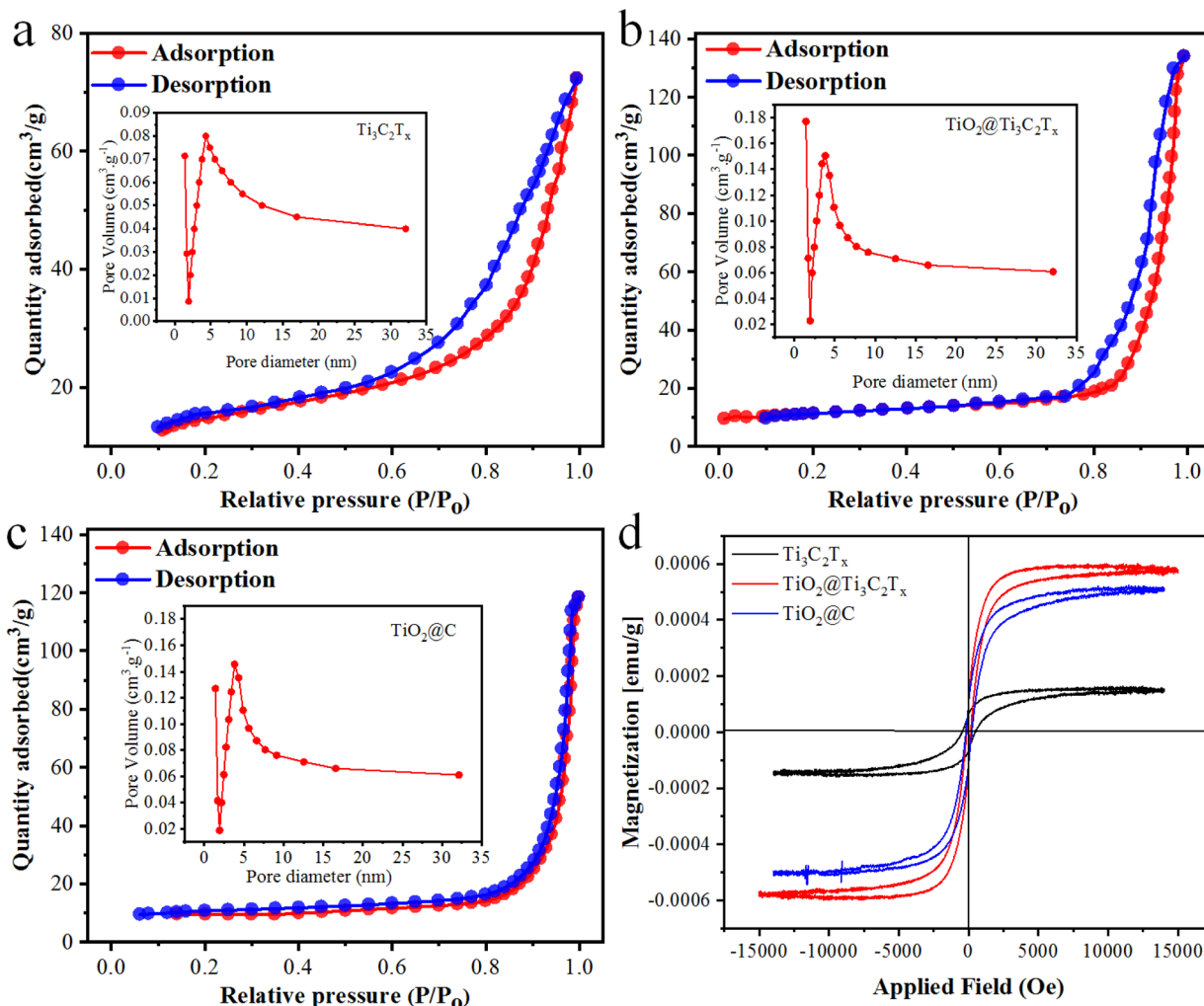


Fig. 7 BET results of (a)  $\text{Ti}_3\text{C}_2\text{T}_x$ , (b)  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$ , and (c)  $\text{TiO}_2@\text{C}$  catalysts, and (d) VSM hysteresis loop of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$  catalysts.

observed in both the  $\text{TiO}_2@\text{C}$  and  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts, indicating the trap and transfer of unpaired electrons. Notably, a higher signal was observed in the  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts as compared to the  $\text{TiO}_2@\text{C}$  catalysts.<sup>64</sup> Some recent reports suggest that the existence of oxygen vacancies is more challenging for photocatalytic  $\text{H}_2$  evolution reactions.<sup>65</sup>

The magnetic properties of the as-synthesized catalysts were examined *via* the vibrating-sample magnetometry (VSM) technique (Fig. 7d). This analysis provides crucial insights into saturated magnetic intensity (Ms), residual magnetic intensity (Mr), coercivity (Hc), and squareness ratio.<sup>66</sup> The  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  and  $\text{TiO}_2@\text{C}$  photocatalysts exhibit Mr values of 0.064 and 0.071  $\text{emu g}^{-1}$  respectively. By using the VSM plots, the magnetic parameters (Ms, Mr, Hc, and squareness ratio) of the as-synthesized catalysts are tabulated in Table S2.†

### Water splitting activities

The hydrogen and oxygen evolution rates have been measured to evaluate the catalytic performances. Fig. 8a and b indicate the

activities in  $\text{mmol g}^{-1}$  and  $\text{mmol g}^{-1} \text{h}^{-1}$ , respectively. The results demonstrate that  $\text{H}_2$  and  $\text{O}_2$  generation increases linearly with the irradiation time for each photocatalytic reaction. It has been observed that  $\text{TiO}_2@\text{C}$  and  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts exhibit 9.37 and 18.57  $\text{mmol g}^{-1} \text{h}^{-1}$  of hydrogen, respectively. The  $\text{O}_2$  production rate was approximately half that of the  $\text{H}_2$  production rate. It is worth mentioning that the activity in the case of  $\text{TiO}_2@\text{C}$  is two times higher, while for  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$ , it is five times higher than pristine  $\text{TiO}_2$ . The comparison of  $\text{H}_2$  and  $\text{O}_2$  evolution rates of  $\text{TiO}_2$ ,  $\text{TiO}_2@\text{C}$  and  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  catalysts and their %QE are tabulated in Table S3.† The higher catalytic performances of  $\text{TiO}_2@\text{Ti}_3\text{C}_2\text{T}_x$  are attributed to the existence of multilayer structures that contribute relatively higher active sites to promote water reduction reactions. Additionally, during the photoreaction, the formation of heterojunctions and Schottky barriers at the interfaces enhances the charge transfer to promote and drag water splitting reactions.<sup>67</sup> Additionally, the higher surface area also has a considerable impact on the photocatalytic activity. In  $\text{TiO}_2@\text{C}$  catalysts, carbide-derived carbon (CDC) serves as an electron acceptor



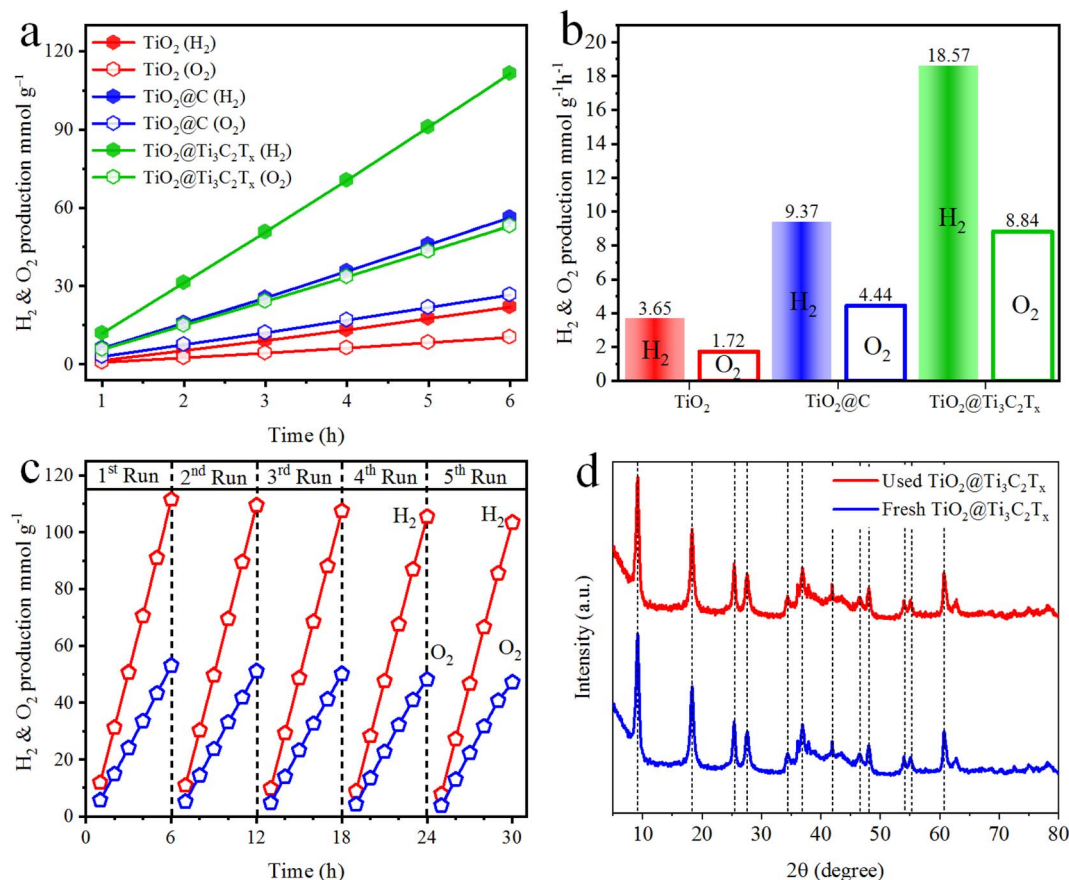


Fig. 8 Hydrogen and oxygen production activities of TiO<sub>2</sub>, TiO<sub>2</sub>@C, and TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (a) mmol g<sup>-1</sup> and (b) mmol g<sup>-1</sup> h<sup>-1</sup>; (c) recyclability and (d) XRD results of fresh and used TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts.

and drags charges to improve H<sub>2</sub> and O<sub>2</sub> production rates.<sup>68</sup> Comparatively, TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is a promising catalyst for water splitting reactions due to its layered structures, higher charge transfer, and large number of active sites available for redox reactions.

Photocatalyst stability and its reusability are crucial factors in accessing the catalyst's practicability. The recycling studies were carried out for five consecutive cycles using TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts. It is noteworthy that the photocatalytic activity remained steady even after five cycles (Fig. 8c). The slight decrease in activity was caused by catalyst deposition on the inner surface of the reactor wall.<sup>35</sup> The XRD analysis of both fresh and used TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts was compared, and it was found that there was no significant difference in crystallinity, as shown in Fig. 8d. These findings suggest that TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts have exceptional stability, which is due to the *in situ*-grown TiO<sub>2</sub> over the MXene structures.<sup>69</sup>

### Charge transfer and water splitting mechanisms

In a photocatalytic reaction, photons have greater energy than the band gaps, *i.e.*,  $\geq E_G$ , when the excitation of charges occurs on the surfaces of semiconductors. During excitation, electrons start to move from the valence band (VB) to the conduction band (CB) of the semiconductor, leaving behind the electrons

deficient charges, *i.e.*, holes.<sup>70</sup> Fig. 9a demonstrates the water splitting process during the photocatalytic reaction. It has been found that TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> exhibits higher catalytic efficiencies relative to the TiO<sub>2</sub>@C catalysts. Higher H<sub>2</sub> and O<sub>2</sub> evolution efficiencies in the case of TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> are attributed to the presence of electron promoters, *i.e.*, MXene. It is obvious that MXene's exceptional conductivity contributes to the transportation of electrons to active sites, where a water reduction reaction occurs to generate hydrogen.<sup>71</sup> Additionally, due to the layered structure of MXene, electron trapping and transfer become relatively high, where electrons can stay on redox sites for further utilization/consumption.<sup>18</sup> During the photoreaction, a dynamic equilibrium is established between MXene and TiO<sub>2</sub>, which aligns the Fermi energy ( $E_F$ ) of the TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> photocatalyst to develop a new quasi-Fermi state,  $E_F^*$ .<sup>72</sup> Moreover, due to the higher work function of MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>), the feasibility of electron population on the TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> system increases, which is why these catalysts contribute relatively higher rates of hydrogen evolution in photoreaction.<sup>73</sup> MXene develops heterojunctions with TiO<sub>2</sub>; hence, it enhances the feasibility to quench and transfer the charges during photoreaction. That is why TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> effectively promotes electron transfer to the  $E_{CB}^*$  of TiO<sub>2</sub>.<sup>74</sup> It is worth mentioning that due to



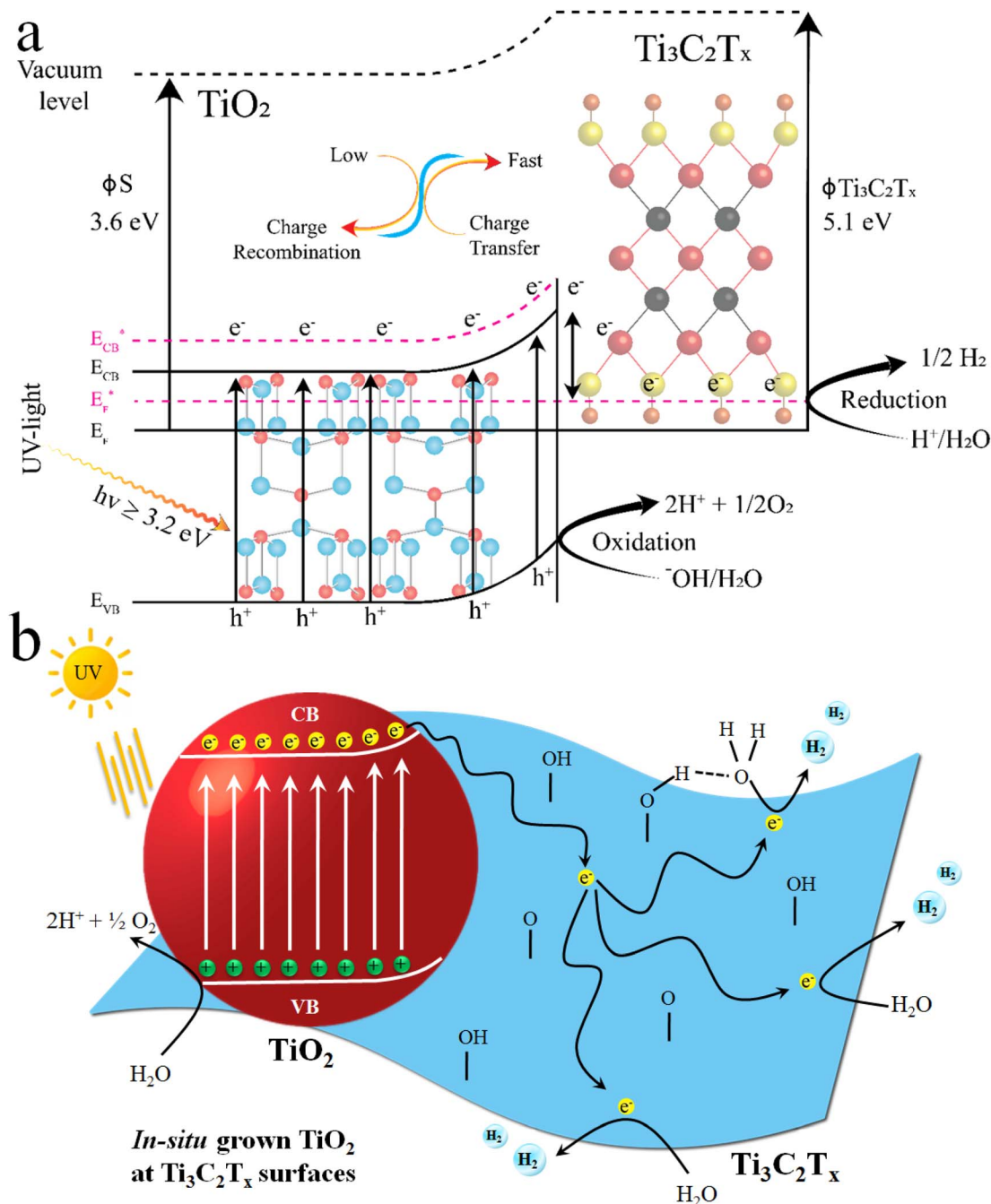
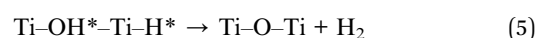
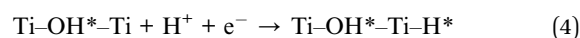
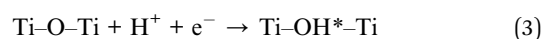


Fig. 9 (a) Charge transfer on  $TiO_2@Ti_3C_2T_x$  catalysts; (b) mechanism of water splitting over  $TiO_2@Ti_3C_2T_x$  catalysts.

heterojunctions, the Schottky barrier at the interface suppressed the charge recombination (*i.e.*, back reaction).

On the other hand, during catalytic water splitting, oxygen-carrying moieties, *i.e.*,  $\cdot OH$ , or peroxide  $\cdot O_2$ , undergo oxidation with holes.<sup>75</sup> During photoreactions, MXene layers favour the generation of O vacancies when they become exposed to or come into contact with water.<sup>76</sup> The hydrogen evolution process over  $TiO_2@Ti_3C_2T_x$  catalysts is initiated with the protonation of  $\cdot O$  terminations during photoreaction (photon absorptions). It is worth mentioning that in photoreaction protons inherently

adsorb on the  $\cdot O$  sites instead of Ti sites to *in situ* develop the  $TiO_2@Ti_3C_2(OH)_x$  structures (see eqn (3)–(5)). Subsequently, the adjacent Ti site undergoes protonation. This protonation then favours the enhancement and promotion of catalytic hydrogen.<sup>77</sup> The catalytic reaction is demonstrated in eqn (3)–(5).



These above chemical reactions prove the process of protonation and charge transfer involved in hydrogen generation.<sup>77</sup> Fig. 9b illustrates the photoreaction and catalytic hydrogen and oxygen generation over TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts. In the case of TiO<sub>2</sub>@C catalysts (see Fig. S5†), photogenerated electrons are quenched by the CDC layers to drag the water splitting reactions.<sup>68</sup>

## Conclusions

TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> catalysts have been successfully synthesised and employed for water splitting reactions. In this project, an ethanol-assisted solvothermal approach was introduced to achieve the required morphologies and catalytic characteristics. Typically, TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and TiO<sub>2</sub>@C catalysts were optimized and assessed for comparative activities. The morphology and optical characteristics were assessed *via* XRD, FTIR, Raman spectroscopy, TGA, SEM, AFM, UV-vis/DRS, XPS, PL, TPC, EIS, BET, EPR, and VSM. The results confirm the morphology, excellent optical response, and charge transfer that indicate the speciality of the current work. The results show that TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> exhibits higher catalytic activity, *i.e.*, 18.57 mmol g<sup>-1</sup> h<sup>-1</sup> of H<sub>2</sub> and 8.84 mmol g<sup>-1</sup> h<sup>-1</sup> of O<sub>2</sub>, which is almost double the activity of TiO<sub>2</sub>@C. It is worth mentioning that the higher activity of TiO<sub>2</sub>@Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> is attributed to the existence of titania on MXene multilayers that offer more reactive sites and redox centres. The results indicate that heterojunctions between titania and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> executed the rectification and charge transfer to active sites (*i.e.*, redox centres). Additionally, heterojunctions rectify and reduce the back flow of charges during the photoreaction. This significant factor anticipates the consequences of higher catalytic efficiencies. Based on results and activities, it has been anticipated that the current study holds promise to replace costly and conventional catalysts. Although there are many challenges ahead, the described approach has great potential to deliver sustainable hydrogen for the proper implementation of green technologies.

## Data availability

The data and necessary protocols of this study have been included as part of the ESI.†

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

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