

Role of ZnO in ZnO Nanoflake/Ti₃C₂ MXene Composites in Photocatalytic and Electrocatalytic Hydrogen Evolution

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In this chapter, we have undertaken to understand and synthesize nanomaterials that can be useful for electrocatalytic HER and photocatalytic organic pollutant degradation. Herein, we report a synergistic impact of Ti₃C₂ and ZnO for photocatalysis and electrocatalysis applications, a straightforward hydrothermal synthesis of ZnO- Ti₃C₂ MXene nanocomposites with varied weight percent of ZnO. The effectiveness of ZnO-Ti₃C₂ nanocomposites in degrading organic contaminants (such as dyes and pharmaceuticals drugs) and in the hydrogen evolution process (HER) has been thoroughly studied. Among the developed nanohybrid catalysts, ZnO-Ti₃C₂ composite with 10 wt.% ZnO (MXZnO-10) showed the highest photodegradation efficiency of 76.4% within 10 minutes of the reaction and 99.2% in 60 minutes for methylene blue (MB) dye. The longer lifetimes of electrons and holes were made possible by the synergistic interactions between 2D layered Ti₃C₂ and ZnO, which decreased the recombination rate. The MB dye was more efficiently degraded attributed to the uncombine electrons and holes. Excellent HER performance was demonstrated by the 5 wt % ZnO-Ti₃C₂ (MXZnO-5) nanocomposite with overpotential of 495 mV at 10 mA/cm² and a Tafel slope of 108 mV/dec. This work widens the application range of transition metal oxide-MXene composites, providing potential substitute materials for photocatalysis and electrocatalysis applications.

3.1 Experimental section

3.1.1 Synthesis of MXene

Ti₃C₂T_x was prepared by etching the Al layer from the as-purchased MAX (Ti₃AlC₂) phase precursor. Ti₃C₂ solution was prepared by immersing slowly 2g MAX power in a 40 mL aqueous solution of 40 wt.% HF acid in a polypropylene beaker and continuously stirred at room temperature for 24 hr. The resultant solution of Ti₃C₂ was centrifuged at 3500 rpm and washed out several times with DI water to remove AlF₃ and excess HF acid until the neutral pH of the supernatant was reached. To obtain Ti₃C₂ flakes, the solution was dispersed in 150 ml water and sonicated for 3 hrs to increase the interspacing between the layers. Further filtration was carried out followed by drying in a vacuum oven at 80° to obtain multi-layered Ti₃C₂.

3.1.2 Synthesis of ZnO-MXene

A one-pot hydrothermal process prepared ZnO-Ti₃C₂ as shown in **Figure 3.1**. Firstly 200 mg MXenes were dispersed in water and sonicated for 20 min to obtain a homogenous suspension. Then, 0.5 M concentration solution (1) of Zn(CH₃CO₂)₂·2H₂O and 0.25 M concentration solution (2) of NaOH solution were prepared separately. A white suspension was observed when solution (2) was added into solution (1) dropwise with continuous stirring. Finally, white precipitate solution and Ti₃C₂ solution were added in 33 mL DI water to make 5, 10, and 15 wt.% ZnO into MXene, named as MXZnO-5, MXZnO-10, and MXZnO-15, respectively. The product was heated in a hydrothermal autoclave vessel at 180°C temperature for 12 hrs. Finally, the resultant solution was cool down at room temperature and dried at 60 °C.

3.1.3 Dye degradation test

The catalytical degradation performance of Ti₃C₂ and ZnO-Ti₃C₂ nanocomposites was evaluated with organic pollutants, including dyes and drugs. Here, different wt.% ZnO-Ti₃C₂ catalysts were used for the degradation experiment. In contrast, Methylene blue was used as a main probing dye, and the best catalyst was applied for other organic pollutants like MO, CR, IBP, and CIP. All the experiments were carried out at pH 7. Afterward, the pH of the solution was maintained at around 3.5 and 10 using HCl and NaOH for all the experiments to check the

effect of pH on MB photodegradation. The resultant solution was exposed to 1 sun intensity at the solar simulator and removed from the catalyst-dye solution at a certain time interval. After centrifugation of the collected sample solution, the supernatant solution was used to measure UV-visible absorption and real-time MB concentration. The degradation efficiency of samples was calculated using the formula $C_0 - C / C_0 \times 100$, where C is the concentration of MB (dye solution) at a different time interval, and C_0 is the initial concentration at $t = 0$.

3.1.4 Electrochemical Measurements

A CHI660E-CH Instruments workstation was used to study the specimens at room temperature with a standard three-electrode system. All the electrochemical measurements for HER were performed in three-electrode cells with 0.5M H_2SO_4 aqueous electrolyte. Electrochemical measurements were executed with respect to 3M Ag/AgCl as a reference electrode, while a glassy carbon electrode ($d=3\text{mm}$) coated with the active materials as a working electrode and a platinum wire electrode as the counter electrode. Linear sweep voltammetry (LSV) measurements were tested at a scan rate of 10mV s^{-1} with internal resistance (iR) compensation. The double-layer capacitance of the samples (C_{dl}) was determined in the non-faradaic region (0.213V vs RHE) by measuring capacitive currents at different scan rates. The cycling stability test was performed by long-term chronopotentiometry for 10 hrs. Electrochemical impedance spectroscopy (EIS) studies were conducted in the 1e^6 KHz to 0.1 Hz frequency range.

3.1.5 Scavenging test

Scavenging experiments. The involvement of the primary reactive species (radicals, electrons, and holes) was investigated utilizing several scavenger molecules to determine the mechanism of the photocatalytic activity of $ZnO-Ti_3C_2$ nanocomposites. Initially, three types of capture scavengers were chosen: triethanolamine (EDTA, an h^+ scavenger), tert-butanol (IPA, an $OH^\bullet$ scavenger), and p-benzoquinone, (p-BQ, an $O_2^\bullet$ scavenger) to detect the main reactive species for dye degradation experiments. 3 mL of each scavenger (0.02 M) is typically dispersed in reaction solutions containing the $ZnO-Ti_3C_2$ photocatalyst and MB solution and then exposed to light for 60 minutes.

3.1.6 Preparation of working electrodes

The working electrodes were prepared by adding electroactive materials in a 1 mL solution containing 50 μL of Nafion and the mixture of ethanol and DI H_2O (1:1) followed by sonication for 20 minutes to get a homogenous solution. Afterward, the materials were dropped and cast onto the glassy carbon electrode to get a 0.15 mg/cm^2 mass loading. Further, the electrode was dried at room temperature to study the electrochemical activity of HER.

3.2 Results and discussion

3.2.1 Structural and Morphological characterization

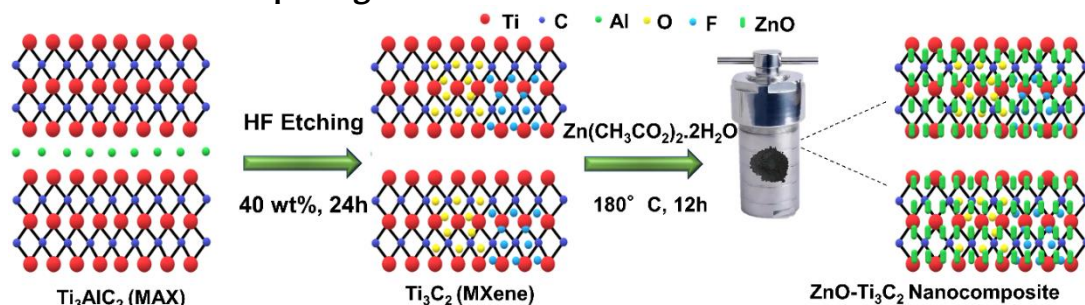


Figure 3.1: Synthesis process of Ti_3C_2 MXene from Ti_3AlC_2

Figure 3.2(a) represents the XRD patterns of Ti_3AlC_2 , Ti_3C_2 , and $ZnO-Ti_3C_2$ composites with different wt.% of ZnO NPs. The (002) peak of Ti_3C_2 shifted towards the lower angle, confirming the successful formation of Ti_3C_2 from the Ti_3AlC_2 . The bonding between the layers is decreased. The increase of the c - parameter after HF acid treatment (24 hours) is due to the selective etching of the Al layer from Ti_3AlC_2 (Husmann et al., 2020). Well-defined diffraction

peaks were observed at 2θ values of 9.4° , 19.0° , 34.0° , 36.7° , 38.8° , 41.7° , 48.4° , 56.4° , 60.2° , 65.4° , 70.3° , and 74.0° , which were indexed to the (002), (004), (100), (103), (104), (105), (107), (109), (110), (1011), (2021), and (2024) planes, respectively, according to the standard JCPDS card number 52-0875 for Ti_3AlC_2 . The highly intense peak at $2\theta = 38.8^\circ$ was not observed in Ti_3C_2 , indicating the successful removal of the Al layer. The diffraction peaks of Ti_3C_2 can be indexed to the (002), (006), (008), and (110) with some impurity peaks of the TiC and TiO_2 . These additional peaks are obtained from the precursor and oxidation of the Ti_3C_2 MXene during the etching processes. $\text{ZnO-Ti}_3\text{C}_2$ nanocomposites were synthesized using varying wt.% of ZnO, in which maximum diffraction intensities were observed in the case of the MXZnO-15 sample (**Figure 3.2 a**). In the XRD pattern of $\text{ZnO-Ti}_3\text{C}_2$ composites, ZnO peaks were observed at 2θ values of the 31.5° , 34.3° , 36.2° , 47.6° , 56.6° , 62.9° , 67.9° , and 69.4° which can be assigned to the (100), (002), (101), (102), (110), (103), (112) and (201) planes of wurtzite ZnO. These peaks are matched with the standard JCPDS card number 00-036-1451 for ZnO. The microstrain values obtained after incorporating ZnO into pristine MXene are given in **Table 3.1**. MXene showed a microstrain of 24.67, which increases up to 37.05, indicating the successful incorporation of ZnO. This suggests that the ZnO was successfully grown on the Ti_3C_2 surface.

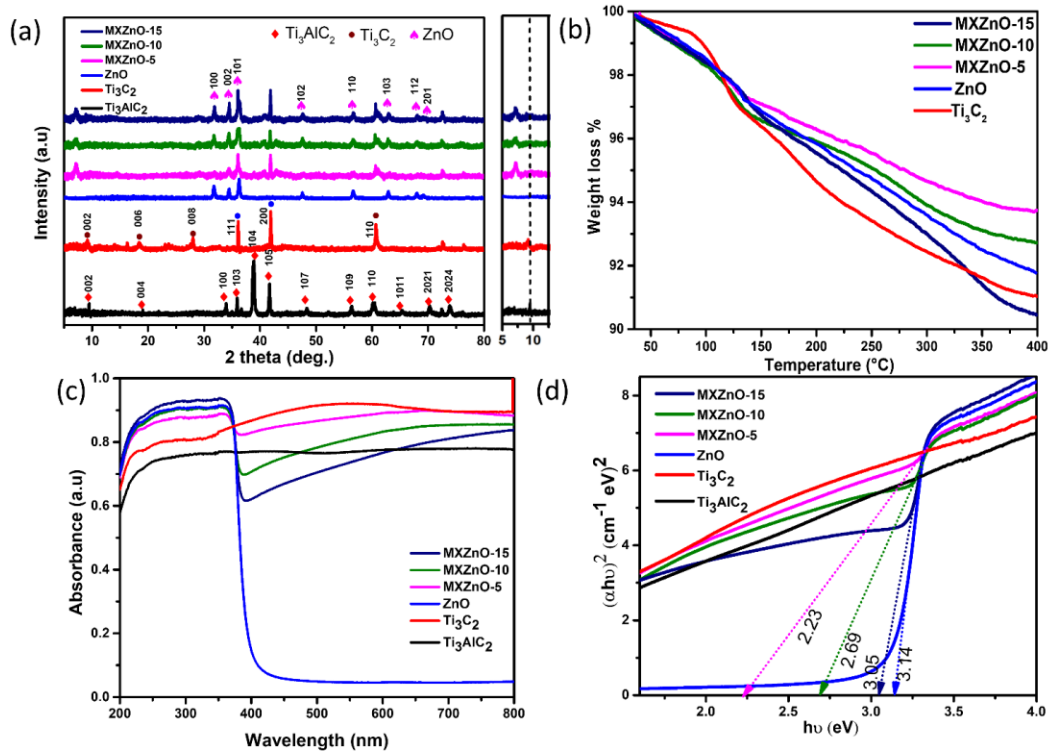


Figure 3.2: (a) XRD patterns of the Ti_3AlC_2 , Ti_3C_2 and $\text{ZnO-Ti}_3\text{C}_2$ nanocomposites. (b) TGA curves of Ti_3C_2 , ZnO and $\text{ZnO-Ti}_3\text{C}_2$ nanocomposite. (c) The UV-Vis DRS of as-prepared catalyst and (d) corresponding Tauc plots.

Table 3.1: Crystallite size, dislocation density and strain calculation of Ti_3C_2 and $\text{ZnO-Ti}_3\text{C}_2$ nanocomposite.

2θ	FWHM (β)	crystallite size(nm)	dislocation density(δ)* 10^{-3} (lines/m ²)	Microstrain (ϵ)* 10^{-3}
9.17	0.45	18.24	3.01	24.67
7.15	0.47	17.69	3.19	32.69
7.02	0.52	15.83	3.99	37.22
7.14	0.53	15.63	4.09	37.06

Figure 3.2(b) shows the TGA curve of all the prepared ZnO-Ti₃C₂ with different wt.% of ZnO under a nitrogen atmosphere between room temperature to 450°C. The weight of Ti₃C₂ decreased drastically between 85°C to 170°C. In contrast, the TGA curve of the ZnO-Ti₃C₂ composites shows the weight loss from room temperature to 200°C owing to removing the surface-bonded group of -F, -OH, -O, and H₂O. Pristine ZnO shows higher stability compared to Ti₃C₂ and MXZnO-15. It can be observed from the TGA results that MXZnO-5 and MXZnO-10 have less mass % degradation than the Ti₃C₂ and MXZnO-15. Additionally, MXZnO-5 shows the highest thermal stability and char residues. After incorporating a higher ZnO percentage, MXZnO-15 composition becomes less thermally stable. Diffuse reflectance UV-vis spectroscopy is an essential technique to understand the photocatalytic activity of ZnO incorporated Ti₃C₂. **Figure 3.2(c)** shows the UV- vis absorbance spectra of MXZnO-5, MXZnO-10, MXZnO-15, ZnO, Ti₃C₂ and Ti₃AlC₂. All the samples displayed absorbance spectra ranging from 200 to 800 nm. Ti₃AlC₂ shows a straight line without any absorption edge, but the Ti₃C₂ showed the absorption edge at 520 nm, indicating the oxidation process happened in a small portion of Ti₃C₂ to TiO₂. ZnO-Ti₃C₂ composites display the absorption edge at 357 nm, which shows the incorporation of ZnO particles. The bandgaps of all samples were estimated by Tauc plot, following the theory of P. Kubelka and F. Munk (Makula et al., 2018) and the following equation.

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where α , h , ν , A , and E_g represent the absorption coefficient, Planck's constant, light frequency, direct transition constant, and bandgap, respectively. The bandgap of MXZnO-5, MXZnO-10, MXZnO-15, and ZnO was determined through the Tauc plot as 2.23, 2.69, 3.05, and 3.14 eV, respectively, as shown in **Figure 3.2(d)**. The bandgap is drastically decreased in the case of ZnO-Ti₃C₂ composites compared to ZnO, which can be attributed to the presence of metallic Ti₃C₂. (Dong et al., 2018) In addition, the bandgap lowered from 3.14 to 2.23 because of the increased metallic Ti₃C₂ doping, which may have caused more oxygen vacancies to develop. MXZnO-10 is anticipated to display superior photocatalytic degradation than pure ZnO due to its smaller bandgap of 2.69 eV. The MXZnO-5 composition has the lowest bandgap and surface area compared to other ZnO-Ti₃C₂ compositions, affecting interfacial interaction between Ti₃C₂ and ZnO. A distinct morphology of the as-produced ZnO-Ti₃C₂ multilayer composites is shown in Figure 3.3 by high magnification scanning electron microscopy (SEM). **Figure 3.3 (a and b)** represent the SEM images of the Ti₃AlC₂ phase and Ti₃C₂, respectively. The HF treatment results in a specific stack of individual sheets of multilayer Ti₃C₂ after the etching of Al from the Ti₃AlC₂. It can be noticed from the inset magnified SEM image in **Figures 3.3 (a and b)** that the average Ti₃AlC₂ grain is below 20 μ m, and in the exfoliated Ti₃C₂, the layer thickness varies between 2 nm-10 nm. As confirmed by BET analysis, **Figure 3.3 (c and d)** denote the ZnO anchored Ti₃C₂, showing an increased surface area. Synthesis of pristine ZnO shows the highly dense and uniform rice-like nanoflakes structure as seen in **Figure 3.3 (e and f)**.

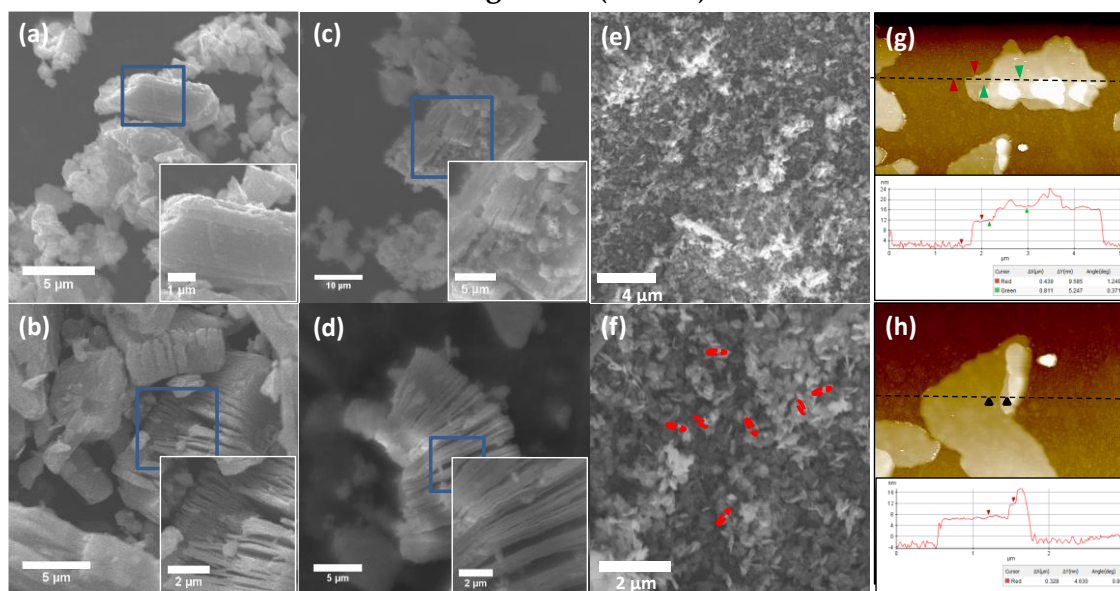


Figure 3.3: Morphological and structural observation of catalysts: (a) SEM images of Ti_3AlC_2 , (b) Ti_3C_2 , (c) MXZnO-15 , (d) MXZnO-5 nanocomposites and (e and f) pristine ZnO nanoflakes. Inset images are corresponding large magnification SEM images. Atomic force microscopy (AFM) of (g and h) delaminated Ti_3C_2 MXene and corresponding height profiles.

AFM of Ti_3C_2 was taken after the etching, washing, sonication, and centrifugation from Ti_3AlC_2 . The as-synthesized Ti_3C_2 shows the single, double, or multilayer. The thickness of the layer was around 4.6 nm and 9.5 nm, which can be due to the single and double-layered Ti_3C_2 as shown in **Figure 3.3 (g and h)**. The energy-dispersive X-ray spectroscopy technique was further conducted on the colored square district labeled to study the distribution of Ti, Zn, C, O, F, and Al in the multilayer ZnO- Ti_3C_2 composite, as shown in **Figure 3.4**. The less intense Al peaks denote Al's replacement from Ti_3AlC_2 with surface groups like O and OH. The O element was observed in EDX owing to the formation of ZnO, TiO_2 , and surface termination group with F, OH, and O.

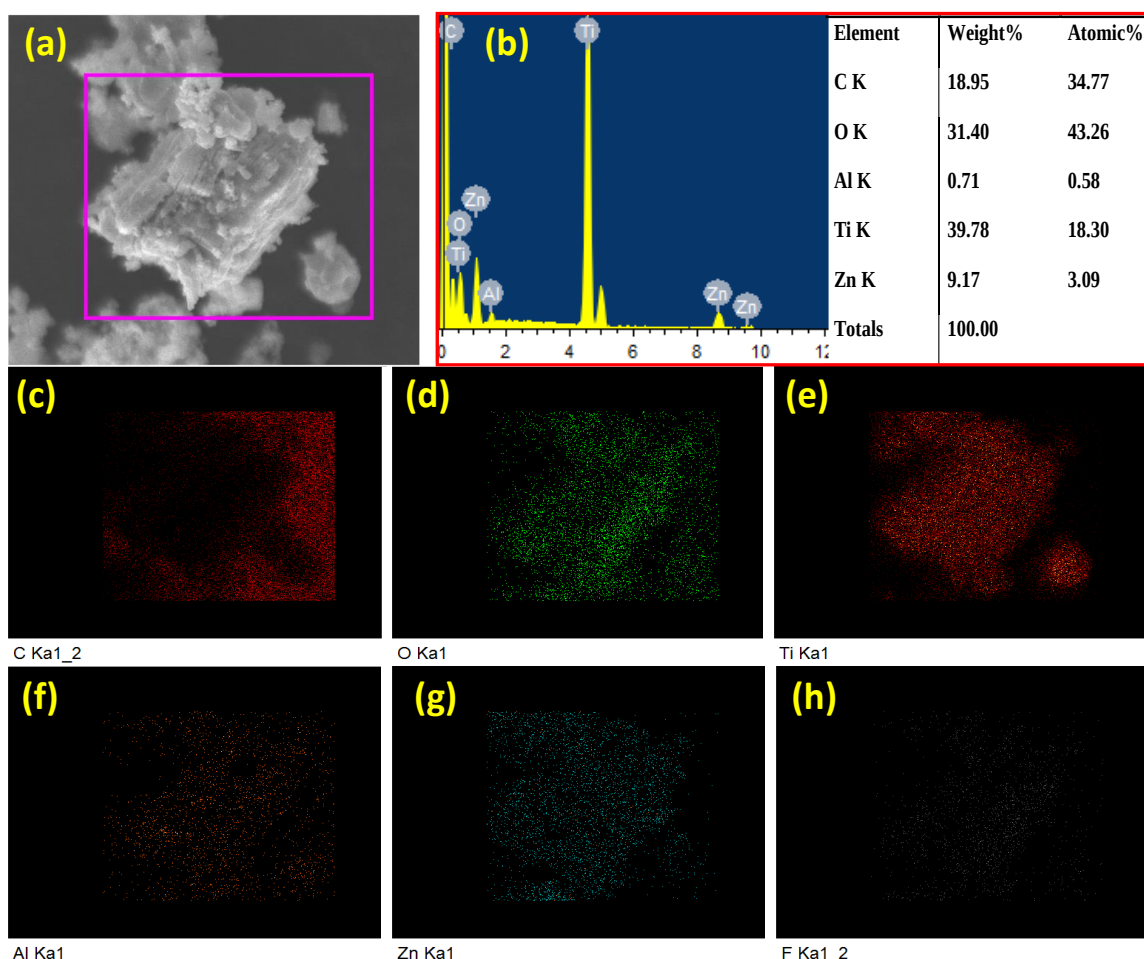


Figure 3.4: SEM image of ZnO- Ti_3C_2 nanocomposite (a) and corresponding EDX analysis and EDX elemental table (b); EDX elemental mapping of ZnO- Ti_3C_2 (c-h).

The surface morphology and component distribution were further characterized by TEM. In the ZnO- Ti_3C_2 nanocomposite in **Figure 3.5(a)**, ZnO exhibits the rod and rice-like structure over the MXene sheets. The elemental mapping further reveals the distribution, and SEM image **Figure 3.5(b)** shows the HRTEM image of the ZnO- Ti_3C_2 nanocomposite, which shows the lattice fringes of the ZnO. In **Figure 3.5(c)**, the measured interplanar distance of 0.246 nm corresponds to the (101) plane of ZnO, which is identical to the value calculated from the standard XRD JCPDS card No 00-036-1451 of ZnO. The selected area electron diffraction SAED pattern in **Figure 3.5(d)** shows a combination of diffraction rings of ZnO (201, 210, and 302) and hexagonal diffraction spots of Ti_3C_2 . The same type of SAED patterns have been reported previously for ZnO- Ti_3C_2 and other Ti_3C_2 composites.(Ta et al., 2020)

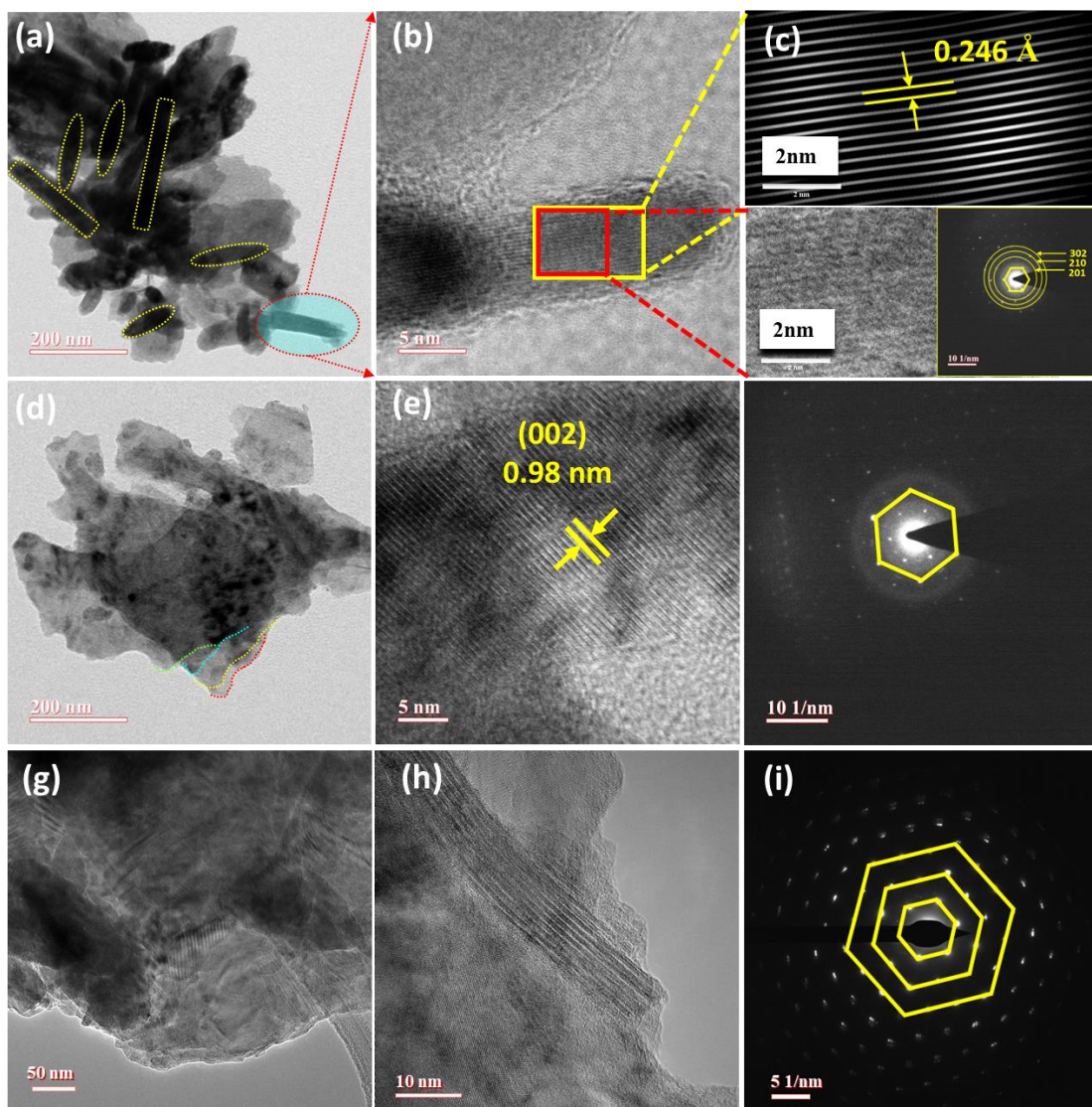


Figure 3.5: Low and high magnification TEM images and corresponding SAED patterns of as prepared MXZnO-15 catalyst (a-c), Ti_3C_2 (d-f) and Ti_3AlC_2 (g-i).

The layered structure of MXene can be observed in **Figure 3.5(d)**, demonstrating the removal of the Al layer from Ti_3AlC_2 . **Figure 3.5(e)** exhibits the lattice spacing of ~ 0.98 nm due to the etching process corresponding to (002), which is further confirmed by the XRD, located at $2\theta = 9.17^\circ$. **Figure 3.5(f and i)** represent the SAED pattern of Ti_3C_2 , and Ti_3AlC_2 , respectively. The symmetrical hexagonal pattern seen in the SAED patterns of the ZnO- Ti_3C_2 , and Ti_3AlC_2 indicates the hexagonal crystal structure is maintained after the HF treatment and hydrothermal reaction. **Figure 3.6(a)** shows the pore size distribution, demonstrating mesopore voids ranging from 10 to 50 Å. The previous studies revealed that MXene has pores distribution ranging from 4 to 100 nm, which mainly depends upon the formation of TiO_2 between the space of layers. **Figure 3.6(b and c)** shows the N_2 adsorption/desorption isotherms and multipoint BET of the Ti_3C_2 and the ZnO- Ti_3C_2 nanocomposites. Type IV isotherms with apparent hysteresis loops are seen in pristine Ti_3C_2 and ZnO- Ti_3C_2 nanocomposites, caused by mesoporous voids between the Ti_3C_2 layers. As can be observed, all samples have volumes ranging from 0.0068 to 0.0321 cc/g. The average BJH pore diameter is centered at 40.2–46.62 Å, as shown in **Table 3.2**. BET surface area and pore volume increase with the increasing metal oxide in MXene materials. The Surface area of Pristine ZnO is 22.47 m^2/g , which is much higher than MXene (6.55 m^2/g). When ZnO is incorporated into the layered MXene, ZnO goes in between the MXene layer, increasing the interlayer spacing and providing more surface area for the composite. The average pore diameter increased with the ZnO incorporation and then decreased further. It can be inferred that mesoporosity can provide a way for loading larger amounts of guest molecules, and the material can boost photocatalytic

and electrocatalytic performance. The specific surface area obtained from the BET method for Ti_3C_2 , MXZnO-5, MXZnO-10, and MXZnO-15 is 6.55, 13.06, 25.58, and 31.79 m^2/g . All the ZnO- Ti_3C_2 composite shows a higher surface area compare to pure Ti_3C_2 . The enhancement in the surface area is due to the formation of ZnO particles on the Ti_3C_2 layer and increased interlayer spacing between the Ti_3C_2 layers. The higher surface area of ZnO- Ti_3C_2 was expected to improve the performances of photocatalysis and electrocatalysis, due to the more surface interaction between the catalysis and dye molecules or electrolyte solution.

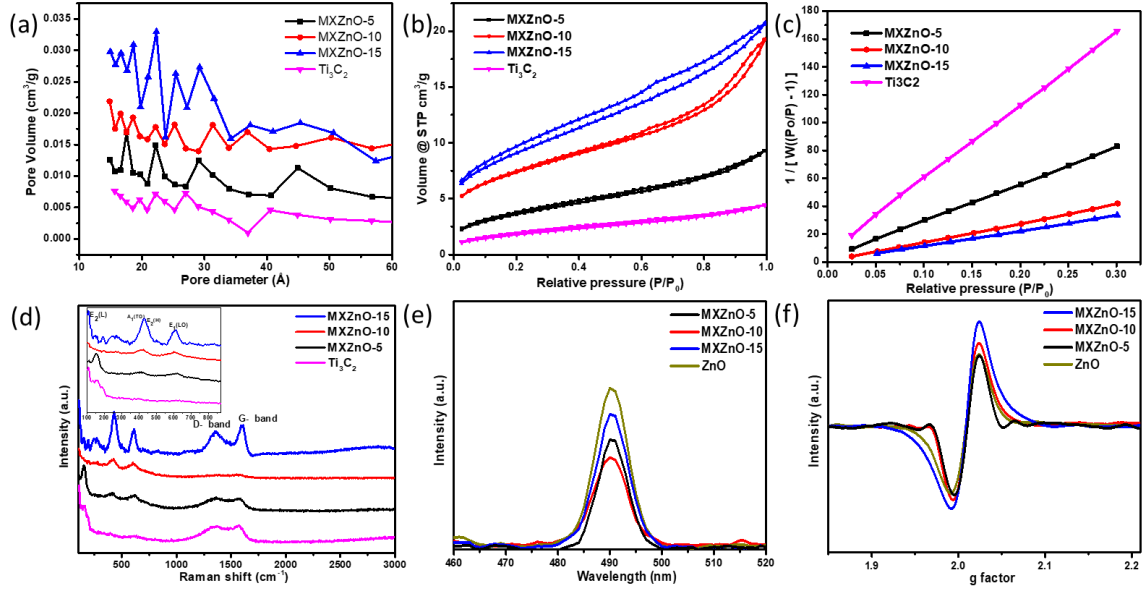


Figure 3.6: (a) Pore size distribution, (b) Nitrogen adsorption isotherm and (c) multi-point BET plots of Ti_3C_2 and Ti_3C_2 -ZnO nanocomposites. (d) Raman spectra of Ti_3C_2 and Ti_3C_2 -ZnO nanocomposites. (e) Photoluminescence spectra and (f) electron paramagnetic resonance spectra of pristine ZnO and Ti_3C_2 -ZnO nanocomposites.

Table 3.2: BET surface area and BJH pore size distribution data of pristine MXene and ZnO- Ti_3C_2 nanocomposites

Photocatalyst	BET surface area (m^2/g)	Average pore diameter (Å)	Average pore volume (cc/g)
MXene	6.55	42	0.00681
MXZnO-5	13.06	43.84	0.01432
MXZnO-10	25.58	46.62	0.02981
MXZnO-15	31.79	40.4	0.0321

Figure 3.6 (d) shows the Raman spectra of Ti_3C_2 , ZnO- Ti_3C_2 nanocomposites in the 150–3500 cm^{-1} region. Compared to the pristine Ti_3C_2 MXenes, the Raman peaks of ZnO- Ti_3C_2 nanocomposites indicate the successful incorporation of ZnO with MXene (Inset image **Figure 4 d**). The peaks around 267 cm^{-1} , 430 cm^{-1} , and 607 cm^{-1} can be ascribed to the $\text{E}_g(1)$; A_{1g} and $\text{B}_{1g}(2)$, and $\text{E}_g(2)$ vibration modes of C and O bonds and Ti-C vibrations, respectively. (Ta et al., 2020) The Raman peaks at 164 cm^{-1} , 400 cm^{-1} , and 628 cm^{-1} correspond to TiO_2 vibrational modes. (Cai et al., 2014) These results further demonstrate the formation of TiO_2 after the oxidization treatment of Ti_3C_2 MXene shown in XRD. The two broad peaks at 1370 cm^{-1} and 1575 cm^{-1} are represented by the D- and G- modes of graphitic carbon. The increased intensities of D- and G- bands in ZnO- Ti_3C_2 nanocomposites indicate the formation of carbon as observed in the XPS plot of the C atom at 284.9 eV. Furthermore, the low intensity of Raman peaks indicates the amorphous carbon content and insufficient oxygen during the process. **Figure 3.6 (e)** shows the PL spectra of the ZnO

nanostructure and ZnO-Ti₃C₂ composites. Lower PL intensity is associated with a lower electron-hole recombination rate and vice versa, which leads to improved photocatalytic efficacy. The emission peak of pristine ZnO and ZnO-Ti₃C₂ composites was observed with a green emission band around 500 nm, which is commonly attributed to energy level defects in hybrid composites related to singly ionized oxygen vacancy. The PL intensities of all nanohybrid structures are significantly lower than pure ZnO, owing to the effective separation of electron and hole pairs via the Schottky junction. The PL intensity of MXZnO-10 is the lowest compared to other composites, indicating the highest inhibition for electron-hole recombination, hence the higher carrier lifetime. These findings show hybrid structures are projected to outperform pristine ZnO in photocatalytic activity. Electron paramagnetic resonance (EPR) spectra were used to investigate the catalyst's oxygen vacancies (**Figure 3.6 (f)**). In contrast to other ZnO-Ti₃C₂ composites, the ZnO showed a poor EPR signal. The ZnO and ZnO-Ti₃C₂ nanocomposites showed a signal with a G factor of 2.008, which was consistent with the e⁻ captured on the oxygen and carbon vacancy sites. (Liao et al., 2020) ZnO in the synthesis process might have some defect sites leading to the creation of oxygen vacant sites, as observed from the EPR spectra. Meanwhile, in the doped MXenes, ZnO and various terminal Ti sites induce a redox activity to create defect sites leading to oxygen vacancies. The formation of increased oxygen vacancies with increased ZnO doping in MXene can be observed from the EPR spectra, where the signal intensity increases with increasing doping concentration. This fact can be corroborated by the XPS result where the doped MXene showed an increase in the oxygen vacancies. The formation of the oxygen vacancy in the composited can also be induced during the oxidation of the MXene into TiO₂. This oxygen vacancy may be due to the defects obtained in the TiO₂ lattice or leaving a surface group like -O, -OH. Some of the previous literature has reported that oxygen vacancies were created in the TiO₂ crystal lattice obtained during the HF etching process. (Fang et al., 2019) Furthermore, an oxygen vacancy signal was observed on MXZnO-10 nanocomposites, suggesting that composites had a higher concentration for better photocatalyst activity.

The surface chemical and electronic state of the ZnO-Ti₃C₂ composite were investigated in detail using XPS analysis for the F 1s, O 1s, C 1s, Ti 2p, Al 2p, and Zn 2p; the results are shown in **Figure 3.7 a**. The survey spectrum of the MXene and MXZnO-10 catalyst, indicating the presence of Ti 2p, C 1s, F 1s, Zn 2p, and O 2p. **Figure 3.7(b-h)** shows the various high-resolution spectrum of individual elements. A small quantity of Al in XPS indicates the residue derived due to the lack of complete etching of Ti₃C₂. This shows the co-existence of the main surface functional groups like oxide (-O-), hydroxyl (-OH), and -F in XPS can be due to the possible surface termination group of Ti₃C₂F₂. F-. The presence of O is due to the surface termination of Ti₃C₂(OH)₂. (Cao et al., 2017b) The XPS results confirm the presence of oxide and hydroxyl groups on the surface of MXZnO-10, providing a channel for redox reaction on the surface of the materials, which can help in efficient photocatalytic degradation. **Figure 3.7 (f)** shows the C 1s XPS spectra, fitted using three main components at 281.30, 284.91, and 289.11 eV, which may originate from Ti-C-T_x (where T_x is O, OH, or F), graphitic C-C and C-O/C-F, respectively. The Ti-C peak obtained by the oxidation of the Ti₃C₂ was presumed to result from the formation of TiO₂ and carbon during the etching process. The small amount of TiO₂ is beneficial owing to its photocatalytic efficiency.⁴⁹ **Figure 3.7 (g)**, showing Ti 2P high-resolution spectrum, indicated peaks at 458.73 and 46.5 eV corresponding to Ti 2P_{3/2} and Ti 2P_{1/2}, respectively, indicating the partial oxidation of the Ti₃C₂. Ti 2P peaks at 455.12 and 454.38 eV are attributed to C-Ti³⁺-T_x and C-Ti²⁺-T_x. (Pandey et al., 2018) The O 1S spectra of Ti₃C₂ exhibit the two binding energy peaks at 530.8 and 532.8 eV can be assigned to Ti-O, and C-Ti-(OH)_x, respectively, as demonstrated in **Figure 3.7 (h)**. (Rakhi et al., 2015) Two prominent binding energy peaks of Zn 2p in **Figure 3.7(e)** spotted at 1021.77 and 1044.87 eV with spin separation of 23.1 eV were attributed to Zn 2P_{3/2} and Zn 2P_{1/2}, respectively. The significant component in the F 1S spectrum observed at a binding energy of 684.68 and 685.82 correspond to Ti-F and Al-F, respectively.

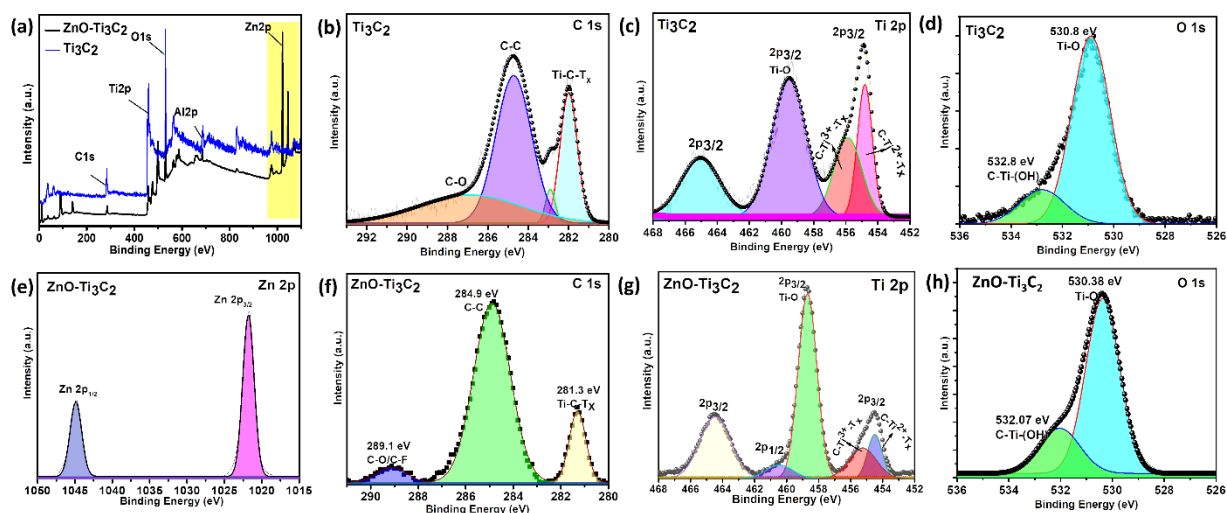


Figure 3.7. XPS spectra of as-prepared catalyst: (a) survey spectra of Ti_3C_2 MXene and Ti_3C_2 ZnO- Ti_3C_2 nanocomposite. (b) High-resolution spectra of C 1s, (c) Ti 2p, and (d) O 1s regions for Ti_3C_2 MXene. High-resolution spectra of (e) Zn 2p, (f) C 1s, (g) Ti 2p, and (h) O 1s regions for ZnO- Ti_3C_2 nanocomposite (MXZnO-10)

3.2.2 Photocatalytic activity

The photocatalytic dye degradation test of MB was performed using the pristine Ti_3C_2 , pristine ZnO, and different composites of ZnO- Ti_3C_2 after 24 h etching Ti_3AlC_2 as shown in **Figure 3.8 (a-e)**. The absorbance spectra of 40 ml MB (20 μM) were recorded between the time range of 0 to 60 min in the presence of the different ZnO- Ti_3C_2 composites. Amongst all catalysts, MXZnO-10 showed excellent degradation performance with 76.4% in 10 min for MB dye and 99.2% in 60 minutes for MB dye. The MXZnO-10 catalyst was used to degrade the other two dyes MO and CR and drugs like IBP and CIF. Pristine ZnO nanoflakes were also tested for degradation of MB, which showed 66.2% of degradation efficiency in 60 min. Before starting the photocatalytic degradation, the catalyst and dye solution was stirred for 10 min in the dark to avoid the photocatalytic effect. The MB solution fades over time, eventually becoming a colorless solution. From the UV-vis absorption graphs, MB clearly showed strong absorption at 665 nm and 292 nm with one shoulder peak at 614 nm, which drastically reduced in 10 min after exposure to the catalyst. A graph is plotted between C/C_0 and the time interval showing the MB degradation where C is the residual MB concentration at time t , and C_0 is the initial MB concentration at $t = 0$, shown in **Figure 3.8 (f)**. Furthermore, the plot displays photocatalytic degradation of MB without any catalyst, and it showed the lowest degradation percentage. **Figure 3.8 (f)** reveals that at the same time, the pristine Ti_3C_2 has the lowest degradation performance, only 7.4% in 10 min, compared to ZnO- Ti_3C_2 nanocomposites, which are primarily controlled by surface property and its termination groups. In the initial 10 mins, MB without catalyst, MXZnO-5, MXZnO-10, and MXZnO-15 showed degradation percentages of 1%, 62.3%, 76.4%, and 25.4%, respectively. The comparative study reveals that MXZnO-10's maximum degradation performance of almost 76.4% in 10 mins, as shown in **Figure 3.8 (i)**. During 60 mins, MB without catalyst, MXZnO-5, MXZnO-10, and MXZnO-15 demonstrated 43.3%, 97.3%, 99.2%, and 96.1% degradation, respectively. **Table 3.3** shows a comparative performance of various oxides and MXene-based catalysts on the degradation of some common dyes obtained from the literature. Compared with other composite materials reported, the prepared catalyst showed the highest degradation of 93% within 30 minutes. The incorporation of ZnO in Ti_3C_2 enhanced photocatalytic degradation owing to the low bandgap of ZnO- Ti_3C_2 compared to pristine ZnO, which increases the faster charge transfer towards the water molecule to produce active radicals after exposure to sunlight. The previous study shows that Ti_3C_2 has an effective electron acceptor, which supports photocatalytic activity by suppressing the recombination rate with the combined effect of ZnO- Ti_3C_2 . The higher absorption results in high charge generation and less recombination of MXZnO-10 due to the lower bandgap. MXZnO-10 generates more electron and hole pairs than others, quickly transferring from ZnO to Ti_3C_2 to overcome the recombination rate.

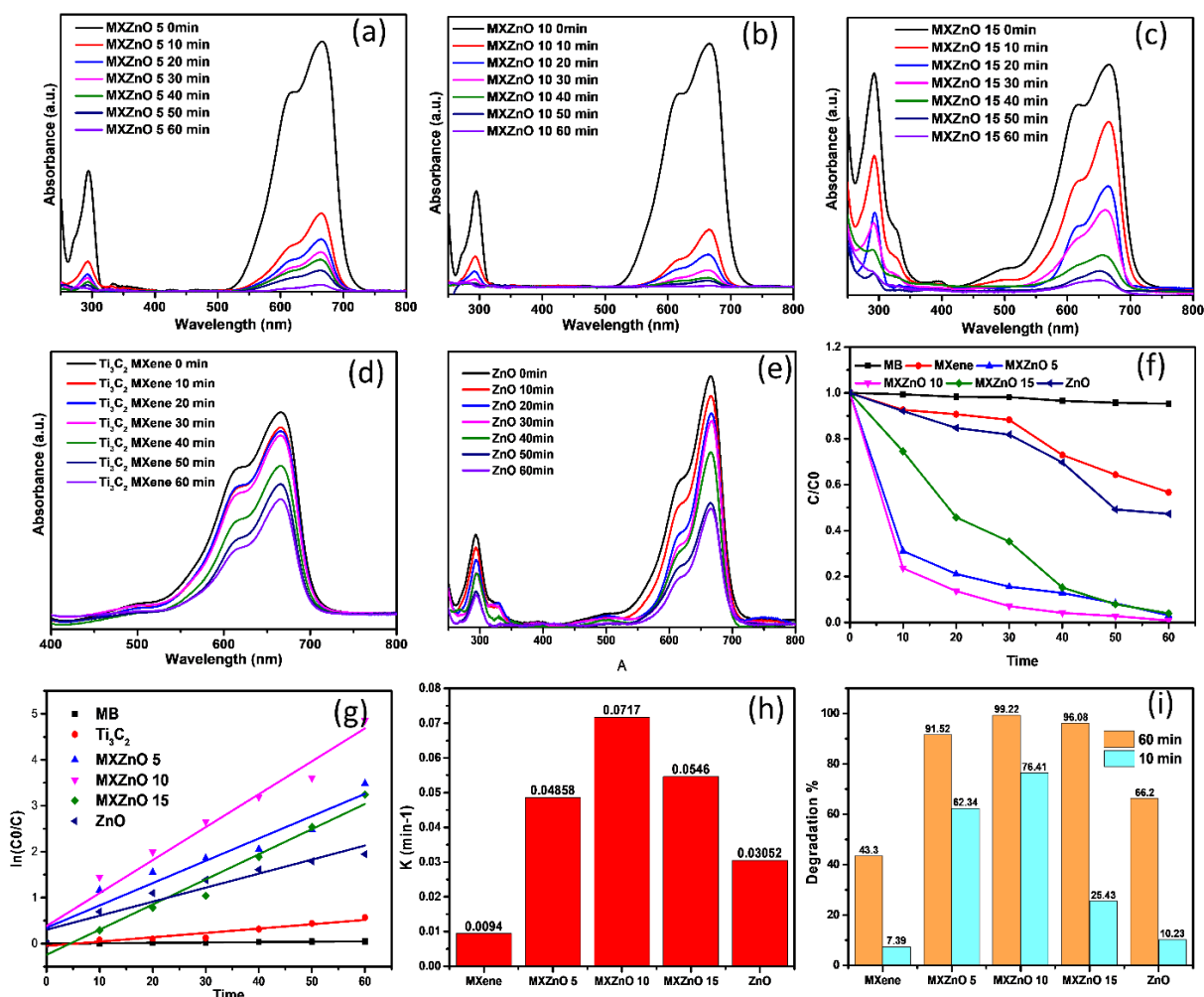


Figure 3.8. The absorption spectra showing time evolution of the photocatalytic degradation of MB over (a) MXZnO-5, (b) MXZnO-10, (c) MXZnO-15, (d) pristine Ti_3C_2 MXene, and (e) pristine ZnO. (f and g) The variation of photocatalytic degradation of MB dye over Ti_3C_2 and ZnO- Ti_3C_2 nanocomposite with a time of irradiations. (h) The rate constant and (i) degradation percentage of MB at 10 and 60 min with Ti_3C_2 MXene and ZnO- Ti_3C_2 nanocomposite

Table 3.3: Evaluation of rate constant, R^2 and photodegradation efficiency for methylene blue using different photocatalyst

Photocatalyst	$K(\text{min}^{-1})$	R^2	Degradation %
MXene	0.0094	0.91094	43.3
MXZnO-5	0.04858	0.91843	91.52
MXZnO-10	0.0717	0.96158	99.22
MXZnO-15	0.0546	0.96713	96.08
ZnO	0.03052	0.91231	66.2

Furthermore, the uncombined electron and hole pairs help to degrade the MB dye. The degradation of MB occurs through the oxidation process, leading to the breaking of the aromatic ring into smaller products via three steps - decolorization, degradation, and mineralization. (Laishram et al., 2018) The mineralization/degradation of the organic dye was further investigated by High-performance liquid chromatography (HPLC), in which peaks

disappear at a higher retention time (dye substrate) and appear at a lower retention time after 60 min of irradiation, as shown in **Figure 3.9**.

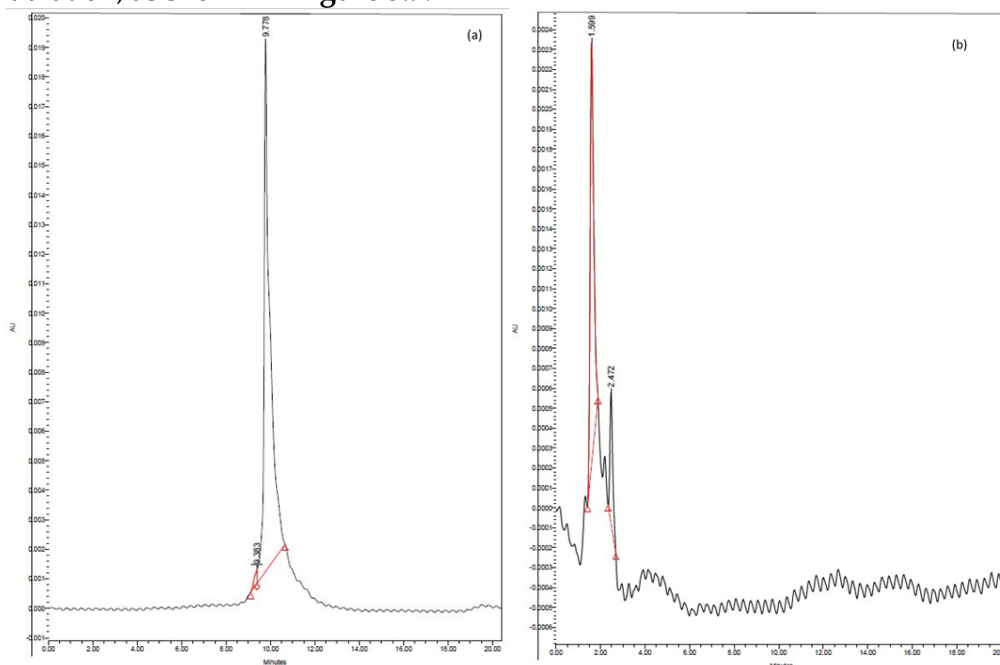


Figure 3.9: High-performance liquid chromatography of MXZnO-10, initially (a) and after (b) the 60 min photodegradation at the wavelength of 254 nm.

Further to determine the apparent degradation rate graph plotted between $\ln(C_0/C)$ and time as shown in **Figure 3.6 (g)**. To measure the degradation rate, the kinetics of the reaction is described using a pseudo-first-order equation

$$-\ln C/C_0 = K_{app}t$$

Where C is the concentration of MB at time t and C_0 is the concentration of MB at $t = 0$. K_{app} is the apparent reaction rate constant at time t . The degradation rate constants (K) and linear regression coefficient degree (R^2) were calculated from the slope using linear regression, as shown in **Table 3.3**. It reveals that MXZnO-10 demonstrated the highest degradation rate at 0.071 min^{-1} among three MXene nanocomposites tested with MB organic dye, and pristine Ti_3C_2 shows the lowest K at 0.0094 min^{-1} (**Figure 3.8 h**). The lower K value of MXZnO-15 at 0.054 min^{-1} due to ZnO's higher stacking into Ti_3C_2 , leading to more agglomeration of ZnO particles, promoting lesser interfacial interaction and faster recombination rate between photogenerated electrons and holes. The degradation of organic MB dye is dependent upon various other factors like MB concentration, catalyst concentration, source of irradiation, illuminance time, and the nature of the catalyst. The enhancement in the performance of the MXZnO-10 catalyst is due to the efficient separation of electron and hole charge carriers with a longer lifespan. MXene as an effective electron acceptor can be easily channelized through its layer structure by hindering electron-hole recombination and thereby enhancing photocatalytic degradation. More importantly, the layered stack structure formed generally increases the charge transfer efficiency. The generated active species participate in the reaction during photocatalytic degradation, such as hydroxyl radicals ($\cdot\text{OH}$), photogenerated holes (h^+), and superoxide radical anions ($\text{O}_2^{\cdot-}$) play a central role in the photocatalytic degradation of MB. In MXZnO-10, the catalyst ZnO has been well distributed over the MXene layers, providing better interfacial interaction to help the MB degradation, as observed from the SEM image **Figure 3.3 (c)**.

The pH of the solution disturbs the hydroxyl radicals and catalyst surface interaction which affects the photodegradation of organic dyes, as demonstrated in **Figure 3.10 (a and b)**. The pH-dependent study investigated at three different pHs of 3.5, 7, and 10 at the concentration of $20 \mu\text{M}$ with MXZnO-10 catalyst loading of 40 mg/L . The equilibrium between the photocatalyst and the dye solution was achieved for 10 minutes. The results revealed that as the pH increased to basic pH, the overall methylene blue degradation efficiency increased and showed the highest removal efficiency. Generally, the degradation capacity is lesser at lower pH than the neutral and acidic

medium because of the electrostatic repulsion force between positively charged photocatalyst and cationic MB. The positive charge at photocatalyst ZnO-Ti₃C₂ may be due to a highly protonated hydroxyl surface group.(Ying et al., 2015) At pH 3.5, methylene blue achieved the highest degradation of 86.83% in 10 min, indicating that electrostatic interactions are less dominant than H bonding between the MXene hydroxyl group and MB leading to higher degradation.⁵⁴ At pH= 10, negative charges such as [Ti-F]⁻ and [Ti-O]-H⁺ were produced at the surface of ZnO-Ti₃C₂, further enhanced by ZnO nanoflakes when it reacted to cationic MB dye.³⁰ Several radical trapping investigations were done to demonstrate the photocatalytic dye process and define the most relevant effects of various species on photocatalytic activity. Several radical trapping investigations were evaluated to demonstrate the photocatalytic dye degradation process and to define the most relevant effects of various species on the photocatalytic activity, as demonstrated in **Figure 3.10 (d)**. Initially, three varieties of scavengers were selected: triethanolamine (EDTA, an h⁺ scavenger), tert-butanol (IPA, an OH^{*} scavenger), and p-benzoquinone, (p-BQ, an O²⁻ scavenger) to detect the main reactive species for dye degradation experiments. Typically, 3 mL of scavenger (20mM) is mixed in MB solutions containing the ZnO-Ti₃C₂ photocatalyst and then exposed to light for 60 minutes. The addition of an EDTA quencher in the solution had a major effect on the efficiency of MB degradation, indicating the importance of holes. The addition of p-BQ and IPA scavengers reduces the efficiency of MB photocatalysis to roughly 36.26% and 11.48%, respectively, showing that radicals play an important role in photocatalytic processes. As a result, it has been established that the contribution of *O²⁻ and *OH radicals drive the MB solution's photocatalytic mechanism towards MXZnO-10 composites, whereas h⁺ showed a major effect in the degradation process. **Figure 3.10 (c)** depicts a bar diagram of methylene blue's dark adsorption and photocatalytic degradation percentage on the MXZnO-10 catalyst. Adsorption-desorption equilibrium was observed for sixty-minute and obtained less degradation efficiency than photodegradation. The degradation of ZnO, Ti₃C₂, MXZnO-5, MXZnO-10 and MXZnO-15 were obtained to be 16.24%, 15.15%, 32.06%, 38.93% and 34.18%, respectively.

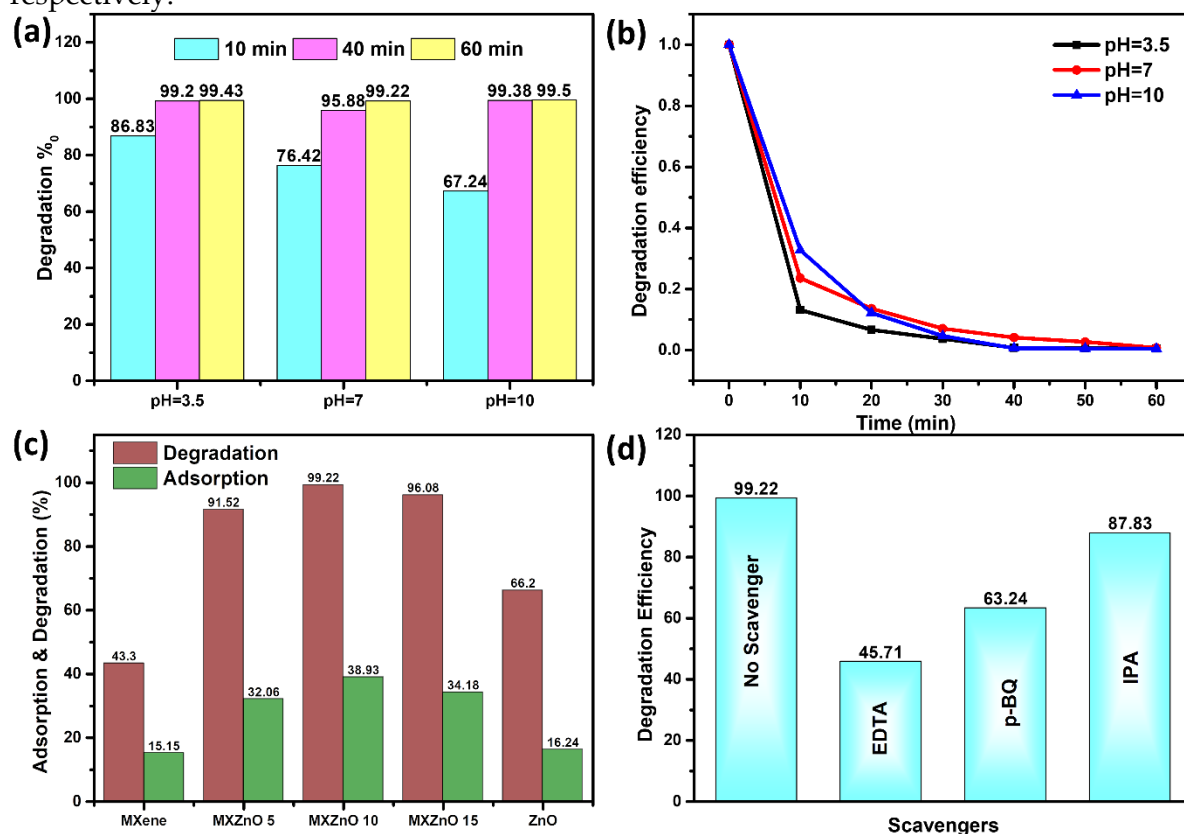


Figure 3.10. (a) Degradation percentage and (b) degradation efficiency of MB at different pH values (c) Adsorption and degradation percentage study of pristine Ti₃C₂, pristine ZnO and ZnO-Ti₃C₂ nanocomposites. (d) Degradation efficiency of MXZnO-10 catalyst with different scavengers.

The stability of the MXZnO-10 catalyst was investigated through the degradation of MB over six cycles under optimum conditions. A photocatalytic degradation efficiency and bar diagram of the reusability of the MXZnO-10 catalyst is shown in **Figure 3.11 (a and b)**. After the photodegradation reaction, MXZnO-10 composite was collected by centrifugation after each cycle and washed twice using DI water, followed by ethanol to remove any sticky degradation products. Finally, the catalyst was dried overnight at room temperature before the use next cycle. Degradation efficiency was 93 % in the fourth cycle and 92 % in the sixth cycle. In the third cycle, the degradation efficiency increases from 71.57 to 72.51 (in the initial 10 mins), indicating strong interfacial interaction even after the second cycle. However, the overall efficiency is reduced in the third cycle from 97.72 to 96.05 % (in 60 min). When the MXZnO-10 catalyst was utilized up to the sixth cycle, the degrading efficiency dropped by nearly 7.3 percent, as shown in Figure 3.11 (b). This might be due to an irreversible change in the catalyst during each cycle which affects the activity of the catalyst due to loss in active sites. Furthermore, XRD measurements were carried out for the fourth and sixth cycles to observe the deterioration of the catalyst, which indicates the very minute change in XRD peak intensity as shown in **Figure 3.11 (c)**. It can be concluded that the MXZnO-10 catalyst appears to be stable, allowing it to be reused for multiple cycles.

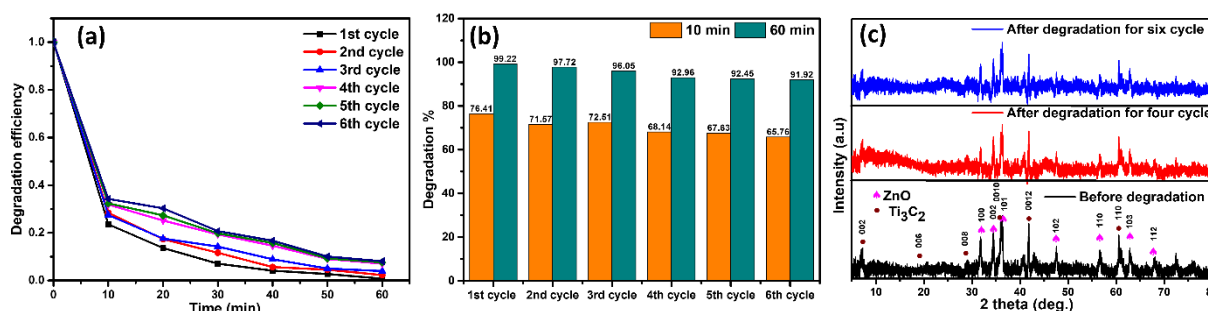


Figure 3.11. (a) Degradation efficiency up to 6th cycles and (b) degradation percentage up to 6th cycles of as synthesized MXZnO-10 catalyst and (c) XRD measurement before and after degradation for four and six cycle.

Figure 3.12 (a and b) show the degradation of dyes (cresol red; CR and methyl orange; MO), and **3.12 (c and d)** show degradation of anti-inflammatory and antibiotic drug degradation (ibuprofen; IBP and ciprofloxacin; CIF) using MXZnO-10 catalyst. CR obtained two characteristic absorption peaks at 434 and 573 nm, as shown in **Figure 3.12 (a)**. (Huang et al., 2021) The absorption peak intensity with time indicates the degradation of CR by the MXZnO-10 catalyst. The complete degradation was obtained at 220 min with redshift, indicating the degradation into lower hydrocarbon molecules. Methyl orange absorbance measurement exhibits the two peaks at ~265 and ~266 nm shown in **Figure 3.12 (b)**. (Tsuji et al., 2018) The decrease of 265 nm peaks indicates the cleavage of the azo bond, and methyl orange solution becomes decolorized after irradiating sunlight for 120 mins. **Figure 3.12 (c)** shows the absorption spectra of IBP with different time irradiation under solar light. One absorption band was observed at 222 nm associated with the π - π^* transition owing to the aromatic character of IBU. (Choina et al., 2013) The degradation graph of CIP shown in **Figure 3.12 (d)** indicates the characteristic peak at ~276 nm. (Yang et al., 2016) Additionally, 72% degradation was obtained in 110 mins using MXZnO-10 catalyst. The different electrostatic interactions between the Ti₃C₂ surface and organic pollutant molecule account for the significant difference in effective removal.

Figure 3.12 (e) schematically depicts a proposed mechanism for the ZnO-Ti₃C₂ nanocomposite structure's improved photocatalytic performance in the presence of electrons and holes. The improved photocatalytic performance may be ascribed as follow: The Fermi level of Ti₃C₂ MXene is lower than the conduction band (CB) of ZnO, and ZnO's work function is more significant than Ti₃C₂. (Low et al., 2018) When light interacts with the ZnO-Ti₃C₂ hybrid structure, generated electrons flow rapidly from ZnO's CB to Ti₃C₂, and the Schottky barrier prevents them from returning. Superoxide anion radicals ($\bullet\text{O}_2^-$) are expected to form due to these produced electrons attacking O₂ molecules. Meanwhile, holes in ZnO's valence band (VB) interact with H₂O or OH ions, resulting in $\bullet\text{OH}$ radicals. MB can then be degraded harmless compounds by reacting with

active radicals such as $\cdot\text{OH}$ and $\cdot\text{O}_2^-$. The entire photodegradation procedure can be summarized as follows:

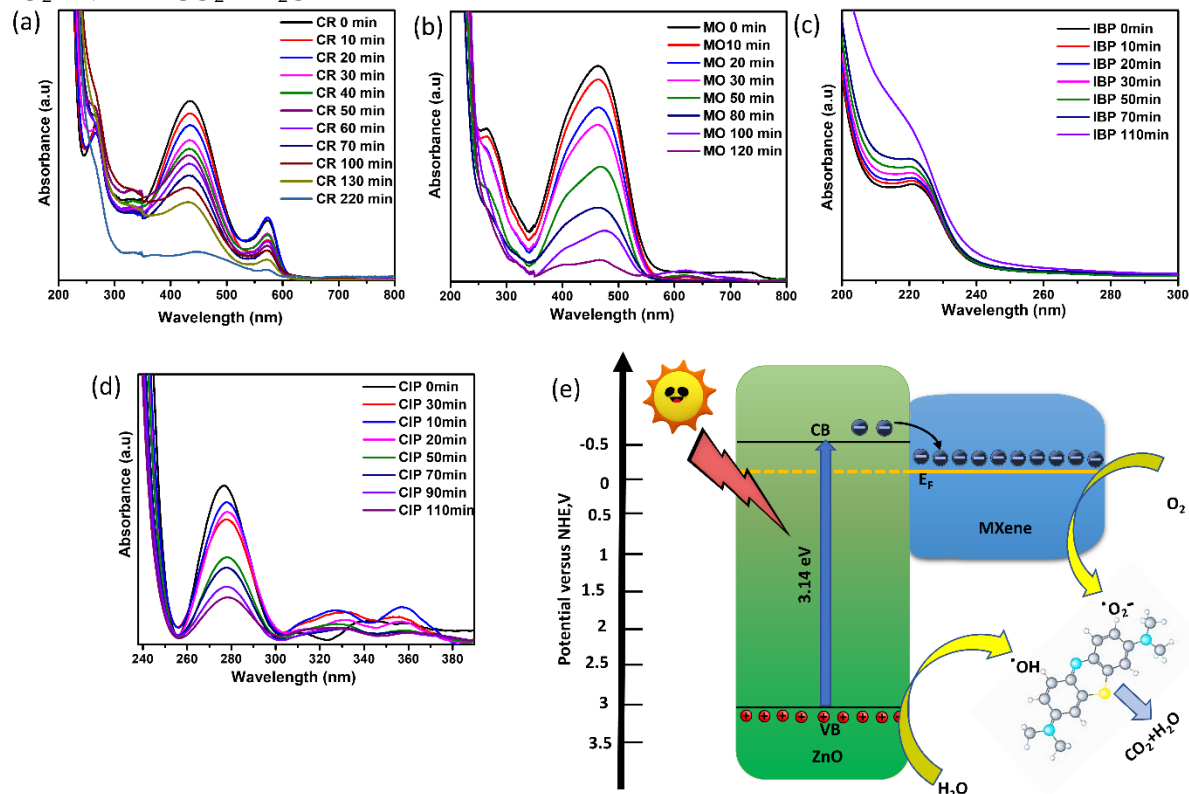
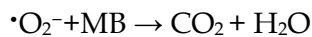
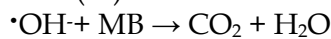
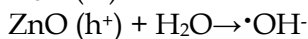
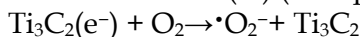
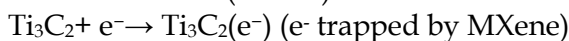
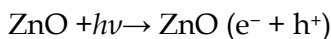


Figure 3.12. Adsorption curve of Cresol red (a), methyl orange (b), ibuprofen (c) and ciprofloxacin (d) with the as-synthesized MXZnO-10 catalyst. (e) Charge carrier transfer mechanism from ZnO to MXene in ZnO-Ti₃C₂ nanocomposite

3.2.2 Electrocatalytic activity

In general, metal oxides are used in photocatalytic water splitting compared to the electrocatalytic application due to the low electric conductivity. Many researchers have used transition metal oxides for the HER application. (Wang et al., 2021) The ZnO-MXene nanocomposites synthesized and studied are the first of their kind for HER application to obtain cheaper electrocatalysts for green hydrogen production. **Figure 3.13** (a) shows the anodic polarization curves for HER of the materials. The MXZnO-5 exhibited an onset overpotential of 422mV and MXZnO-10 of 588mV. For determining the HER activity of the electrocatalyst, the overpotential at 10 mA/cm² is a significant factor. MXZnO-5 and MXZnO-10 exhibited an overpotential of 495mV and 573mV, respectively, at an anodic 10 mA /cm² current density. Even though the observed overpotentials are far higher than the standard Pt/C (~38mV @ -10mA/cm²) (Liu et al., 2018b), a significant ~40% reduction in the onset overpotential is observed by MXZnO-5 and a ~18% reduction for MXZnO-10 at 10mA/cm² with the inculcation of ZnO to the MXene layers. Hence This reduction in overpotential can be attributed to the synergy between ZnO and Ti₃C₂ due to an increase in OH functional groups on the surface of ZnO-Ti₃C₂. **Figure 3.13** (b) shows the catalytic materials' Capacitive current vs Scan rate. MXZnO-5, MXZnO-10 and pristine Ti₃C₂ show a double layer capacitance (*C_{dl}*) of 0.68 mF/cm², 0.53 mF/cm², and 0.59 mF/cm², respectively. The significantly lower *C_{dl}* of MXZnO-10 nanocomposite can be understood that ZnO nanoparticles hinder the catalytically active sites in the non-faradaic region (**Figure 3.14**). Electrochemically active surface area (ECSA) was measured to evaluate the

electrochemical double-layer capacitance of the catalyst. The electrochemical capacitance was calculated using the cyclic voltammograms to measure the non-Faradaic capacitive current associated with double-layer charging.

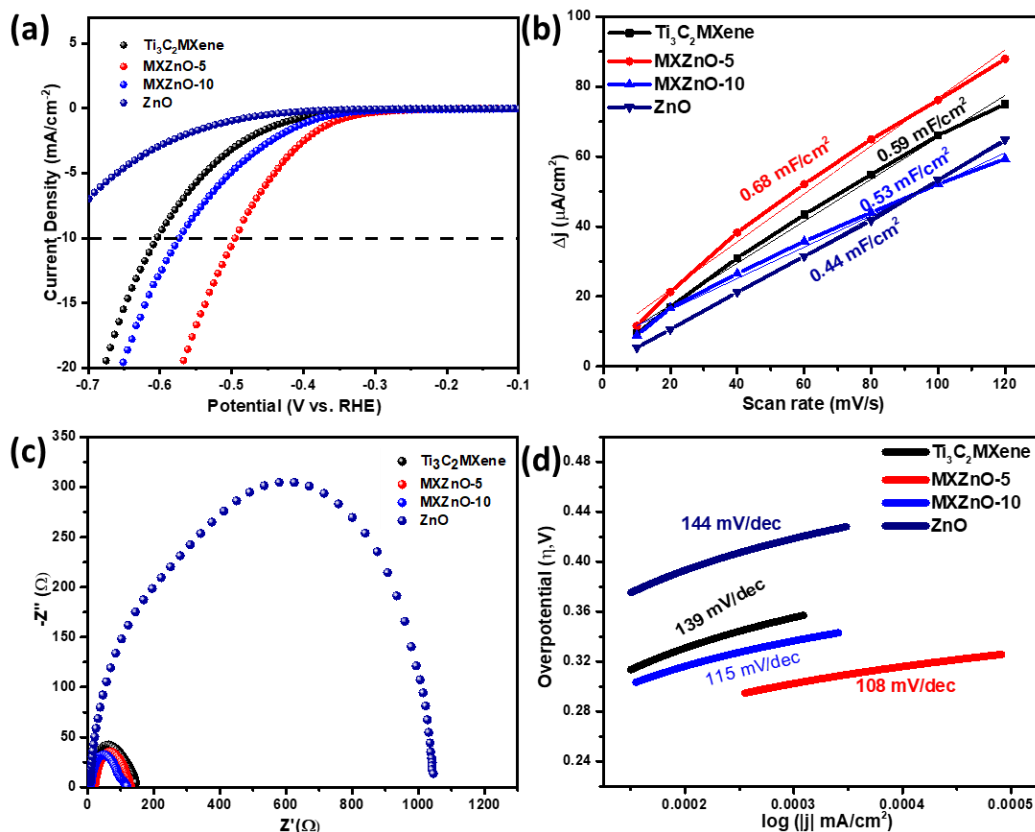


Figure 3.13. (a) HER polarization curves of as synthesized samples at a scan rate of 10mV/s, (b) corresponding scan rate vs current density with Cdl values, (c) Impedance spectra of catalyst, (d) Tafel plot for the catalyst derived from the polarization plot

The scan rate is directly proportional to the double layer charging current, normalized on the geometric area of the electrode. Hence, the ECSA of the catalyst can be calculated as:

$$ECSA = C_{dl} / C_s$$

C_{dl} was derived from a linear fitted slope by plotting the current as a function of the scan rate. The specific capacitances (C_s) were chosen according to the previously reported value (0.035 mF cm⁻² in 0.5 M H₂SO₄). (McCrory et al., 2013) The obtained C_{dl} values of MXZnO-5, MXZnO-10, Ti₃C₂ and ZnO are 0.34, 0.265, 0.295 and 0.22 mF/cm². ECSA values are determined as 9.71, 7.57, 8.42 and 6.28 mF/cm². In contrast, the synergy between ZnO and MXene can be observed in the faradaic region reflected in the polarization curves. Nafion binder concentration and the deposition rate of the materials were kept standard throughout the study to understand the relative catalytic performances because it has a crucial effect on HER performance. **Figure 3.13 (c)** shows the Nyquist plots of the composites at 531mV with respect to E_{RHE}. The diffusive layer resistance at the electrode/electrolyte interface is undeterminable due to the absence of the Warburg response at the lower frequency region, attributed to the H₂ gas bubbles screening the conducting electrode surface in the Faradaic potential domain. The Z_{real} intercept at high frequency for all three materials indicates a significant electrode resistance R_e. The charge transfer resistance R_{CT} of the systems, which is characteristic of the HER process, was determined from the semi-circular loop at the mid-frequency region. The R_{CT} of pristine Ti₃C₂, MXZnO-5, and MXZnO-10 are 127Ω, 109 Ω, and 110 Ω, respectively with MXZnO-5 having the least resistance among all. The charge transfer resistance (R_{ct}) exhibited supports the observed overpotentials of the corresponding composites. **Figure 3.13 (d)** shows the Tafel slopes of the materials. Tafel plots were fitted to the Tafel equation (η=b log j + a) to explore the HER mechanism, where b is the Tafel slope, and j designates the ratio of current density to the exchange current density. The Tafel

slope of pristine Ti_3C_2 is 139 mV/dec, which is higher than MXZnO-5 (108 mV/dec), MXZnO-10 (115 mV/dec), and lower than pristine ZnO (144 mV/dec).

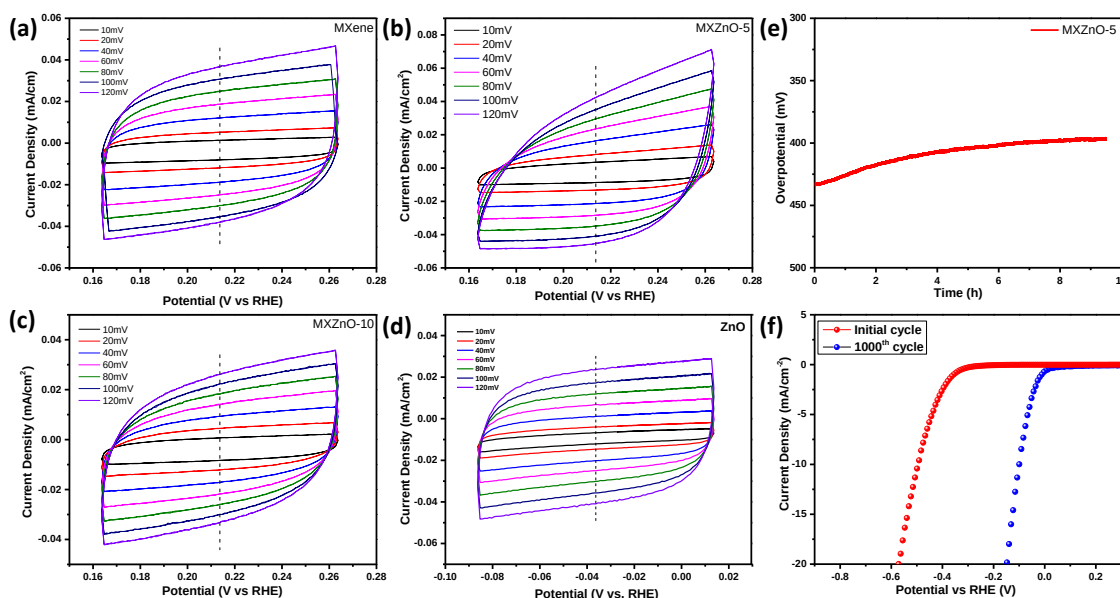


Figure 3.14: (a-d) Cyclic voltammograms of MXene, MXZnO-5, MXZnO-10 and ZnO within different rates ranging from 10 to 120 mV s^{-1} in the region from 0.165 to 0.26 V. (e) HER polarization curves of MXZnO-5 sample, before and after the 1000th cycle. (f) Stability for MxZnO-5 using chronopotentiometry at 5 mA cm^{-2} for 10 h.

The cyclic stability of the MXZnO-5 was studied by performing (Figure 3.14 f) a CV test over the non-faradaic region. After 1000 cycles, high electrocatalytic performance is observed with a reduction in overpotential. This is attributed to the continuous exfoliation of the MXene layers in the presence of Pt (counter electrode) at pH~0. Additionally, a temporal study on the performance of MXZnO-5 was carried out using chronopotentiometry at 5 mA cm^{-1} current density. The stability of MXZnO-5 was studied, and Figure 3.14 e shows its 10hr stability.

3.3 Conclusion

In summary, 2D $\text{ZnO-Ti}_3\text{C}_2$ nanohybrid catalysts with varying wt.% of ZnO were synthesized through in-situ hydrothermal methods and demonstrated their performance as photocatalysts and electrocatalysts for hydrogen evolution reaction. The physicochemical properties of the samples were thoroughly analyzed by various characterization techniques such as SEM, TEM, TGA, XRD, and XPS, ascertaining the successful formation of $\text{ZnO-Ti}_3\text{C}_2$ nanohybrid. A series of experiments were carried out with various $\text{ZnO-Ti}_3\text{C}_2$ composites to investigate photocatalytic degradation and its kinetics. The experimental data revealed that the MXZnO-10 nanohybrid sample has a high MB degradation capacity of 99.2% after an irradiation time of 60 min with a high reproducibility, reusability, and stability through six catalytic cycles. The Chronopotentiometry, polarization curves, Nyquist, and Tafel plots demonstrated that $\text{ZnO-Ti}_3\text{C}_2$ nanocomposites were a stable and durable HER electrocatalyst compared to pristine MXene. Among the materials, MXZnO-5 shows the lowest overpotential of 495 mV at anodic 10 mA/cm^2 current density, a small Tafel slope of 108 mV/dec, and a contact resistance of 109 Ω . The photo- and electrocatalysis performance of hydrothermally synthesized 2D $\text{ZnO-Ti}_3\text{C}_2$ nanohybrids has been confirmed as an excellent nanostructure composition for photocatalytic, and electrocatalytic applications.

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