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Role of MXene Materials in Hydrogen Production via Electrochemical and Photoelectrochemical Water Splitting

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ABSTRACT

The increasing demand of energy and climate change has intensified the pursuit of green hydrogen production via electrochemical and photoelectrochemical (PEC) water splitting. Various materials are being explored as catalysts for the water splitting. Among various materials MXenes, a family of two-dimensional metal carbides, nitrides, and carbonitrides have demonstrated significant promise as efficient and cost-effective catalysts for PEC water splitting. MXene materials offer high surface area, hydrophilic surface and metallic conductivity exhibiting advantage over the use of conventional noble metals. This review complies with the mechanism of water splitting, detailed overview of various MXene materials-based catalysts, challenges in design, and advances in their architecture for both hydrogen and oxygen production. The aim of this paper is to provide prospective pathways for achieving low cost and highly efficient catalyst for water splitting.

Keywords: MXene, Materials, Water Splitting, Electrochemical, Photoelectrochemical

INTRODUCTION

The global energy demand as a result of industrialization is increasing many fold each year. This has created a catastrophic increase in the consumption of fossil fuels resulting in their depletion at an exponential rate (Ang et al., 2022; Hossain, 2025). According to reports of U.S. energy information administration (EIA), the demand for energy will be increased by 50% at the end of 2050. Further, EIA has reported that the CO_2 emission rates are increasing at 0.6% per year (Andrei et al., 2022; Ang et al., 2022). These effects are significantly visible in our climate in the form of increased number of floods, temperature changes, pollution, droughts etc. Furthermore, the rapid depletion of natural resources is demanding to opt for alternative sustainable and eco-friendly energy sources (Yang et al., 2019).

Currently, renewable energy sources available in nature are hydropower, biomass, geothermal, solar, biomass, and hydrogen. Various alternatives like harvesting wind energy, thermal energy, solar energy, hydrothermal energy etc. offer sustainable energy sources. Most of these resources are not uniformly distributed and are not able to fulfil the energy requirements (Energy, 2015; Mitrašinović & Radosavljević, 2023; Tabar & Abbasi, 2019). However, out of these, solar energy is most viable and rich source of energy as nearly 120,000 TW of solar energy is reaching the earth surface (Hossain, 2025). Currently, photovoltaics (PV) is abundantly being used as a solar energy conversion technology. Currently photovoltaics with efficiency more than 30% is achieved. However, this area is suffering from low quality of electric power generation, limited life of panels due to weather changes and high temperature requirements for the photolysis (Chu et al., 2021; Tabar & Abbasi, 2019). This solar energy can be used in various other ways like production of chemical fuels and hydrogen fuel. Hydrogen is a clean fuel having high energy density, zero- carbon emission profile and water vapours as a by product. Further, it is seen as a potential fuel for the transport sector which are consuming significant amount of natural sources accounting for about 57.7% alone and contributing to about 14% of the global emission (Choi et al., 2023; Grimm et al., 2022).

Currently majority of the hydrogen production is taking place using coal gasification, biomass, fossil fuels like coal etc. Thus, most of the current technology for hydrogen production rely on natural sources which makes it less suitable for the sustainable development of clean energy source. Electrolysis is also one of the processes for hydrogen production through sustainable route that makes electricity through electricity (Choi et al., 2020, 2023; Pei et al., 2023; Xia et al., 2022). The sustainability of this process can be achieved by using fuel cells that can generate electricity from the hydrogen.

The most suitable method for achieving the goal is to use the photoelectrochemical (PEC) method which produces both H_2 and O_2 gases at different electrodes.

1. PHOTOELECTROCHEMICAL WATER SPLITTING (PEC)

In photoelectrochemical (PEC) water splitting photons from the solar radiation are absorb by the catalyst material resulting in the generation of electron-hole pairs that drives the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at their respective electrodes (Li et al., 2022; Swierk & Mallouk, 2013). PEC offer advantage over the photocatalytic method as H_2 and O_2 are produced at different electrodes so it automatically overcomes the problem of gas separation. The process is thermodynamically driven but requires to overcome the kinetic barriers through electrolysis. The reaction can be divided into further two reactions occurring at cathode and anode producing hydrogen and oxygen gases respectively.

The reactions involved in the PEC method are as:

Reaction involving hydrogen evolution at cathode:

(a) In acidic medium

$2H^+ + 2e^- \rightarrow H_2$ …….(1)

(b) In alkaline medium

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$…….(2)

Reaction involving oxygen evolution at anode:

(a) In acidic medium

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$…….(3)

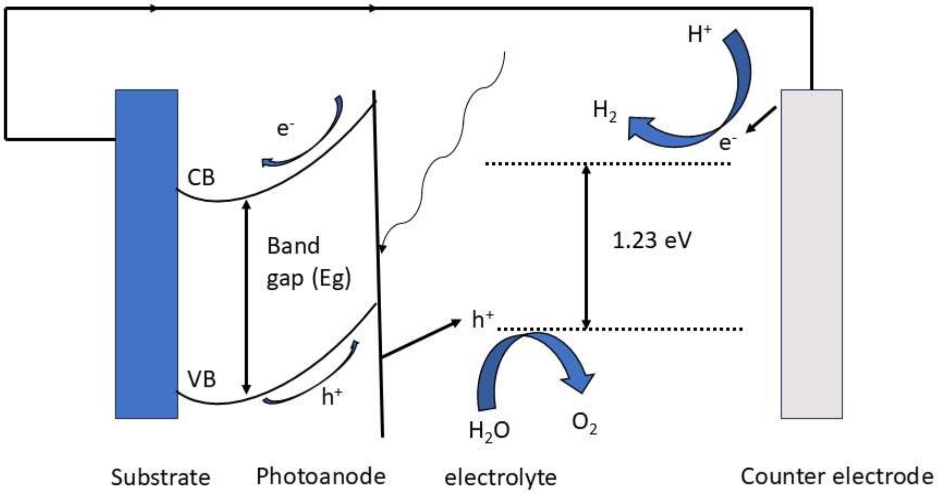
(b) In alkaline medium

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$…..(4)

The overall reaction requires a potential of 1.23V corresponding to standard Gibbs free energy change of 237 KJ/mol required for the water splitting process.

This reaction in the PEC process can be demonstrated using the schematic diagram as shown in Figure 1.

Figure 1: Schematic Illustration of PEC Water Splitting Process



Further materials must satisfy certain criteria like appropriate band gap, flat-band potentials, Schottky barrier and minimum electrical losses. Firstly, the band gap which is defined as the smallest difference between the bottom of conduction band and top of valence band must lie in the range of 1.6 eV to 2.5 eV, in order to harvest the most intense part of the solar radiation. The lower value of band gap is more than 1.23 eV because it requires to overcome the overpotential also. Further, the choice of material also depends upon the position of conduction and valence band. For water splitting it is necessary that the valence band must lie below the oxidation energy and conduction band must lie greater than the redox energy of water splitting. Further flat band potentials are important in case of semiconductor electrodes in which the work functions of electrode and counter electrode decide the flow of electrons resulting in band bending. Also, the bending of band produces a built in fi potential to prevent further flow of electron. This potential is known as Schottky potential. The major electrical energy sources involve the electrode resistance. The resistance of the semiconductor photoanode is several times larger than that of the metallic cathode. The conductivity of the semiconductor is given by

$$\sigma = en\mu_n + ep\mu_p + z_i ei\mu_i \ldots..(5)$$

where e is the electric charge, n is the concentration of electrons, p is the concentration of holes, z_i the concentration of ions, μ_n is the mobility of electrons, μ_p is the mobility of holes, μ_i is the mobility of ions and z_i is the charge of the ion. The contribution of the ionic component can be ignored at room temperature. Due to interactions, the mobility of the charge carriers decreases with an increase in temperature but the carrier concentration increases with temperature (Millman et al., 1967). Thus, there is a competition between the two for the maximal value of conductivity. The electrical resistance can be reduced through the minimization of the thickness of the photoelectrode. But this may compromise with the required absorption thickness for the absorption of the light energy. Other losses include electrolyte resistance because of different diffusion nobilities of the ions (Feng et al., 2010; Li et al., 2013). The electrolyte also has H^+ and OH^- ions that have the highest mobility and due to which photocurrent density affected by the concentration variation of electrolyte but, its effect is not significant. All concentration increase cannot enhance the PEC cell performance. Milczarek et al. studied the effect of sulphuric acid concentration from 0.5 M to 5M and found no significant effect on the PEC performance (Milczarek et al., 2003). Ren et al. reported the variation of concentration of ethanol, ethylene glycol, glycerol, ammonia, urea, and Na_2S and found ethanol, ethylene glycol, and ammonia fuels showed an increase in photocurrent density with increase in concentration, glycerol shows decrease in photocurrent density with increase in concentration because of high viscosity, urea and Na_2S shows no significant variation in photocurrent density with concentration (Ren et al., 2013). Alkaline cations like K^+ and Ba^{2+}assumes minimal resistances at a concentration between 3M and 4M. Other contributions to electrical resistance come from electrical wires, electrical connections such as those between wires and those between wires and electrodes and measuring and control equipment.

Despite remarkable progress in the PEC process of water splitting, the practical application is invaded due to the high cost, low life and less abundance of metal catalysts such as platinum (Pt), iridium (Ir) etc. This limitation presents challenge to develop efficient, low cost and durable catalyst. In this context, MXenes have gained significant attention in the last few years. MXene have chemical formula of $M_{n+1}X_nT_n$, where M stands for early transition metal such as Ti, V, Ni, Mo etc. X stands for carbon, nitrogen or carbon nitride and T represents surface termination group including O, OH group. MXene are generally synthesized from MAX phase, where A stands for group 13 or 14 element which is replaced by selectively etching the A layer during synthesis process. The key properties of MXene includes rapid charge transport and large surface area which is desirable for the catalytic activity. Further, these materials offer advantage of combining with other catalytic materials commonly in the form of nanoparticles or nanosheets forming hybrid architectures that synergistically enhance the catalytic activity.

Mechanism of Water Splitting

Water splitting is an endothermic reaction involving a thermodynamic potential of about 1.23 eV at 298 K. Within the water electrolyser, the water splitting is consisting of two half reaction. One is the HER production as a result of water reduction at cathode and other is water oxidation at anode resulting in the OER. These hydrogen and oxygen evolution process accompanied complicated multistep mechanisms.

(a) Mechanism for the HER

The process of hydrogen production primarily depends upon the type of medium. In the acidic medium, the HER reaction proceeds through the hydronium ion reduction while in case of alkaline medium or neutral medium, the reaction involves water molecules (Bao et al., 2021; Mahmood et al., 2018). The HER process can be explained using two mechanisms. The first mechanism is known as Volmer tafel mechanisms in which first step involves the transfer of electron to the surface combining with H^+ ions in the acidic medium or H_2O in the alkaline or neutral medium. This reaction in the first step is known as Volmer reaction (Cao et al., 2022). This step results in the formation of adsorbed hydrogen atoms. These two adsorbed hydrogen atoms easily combine to form H_2 molecule.

- Volmer step
  $H_3O^+ + e^- \rightarrow H_{ads} + H_2O$…..(6)
- Tafel step
  $2H_{ads} \rightarrow H_2$…..(7)

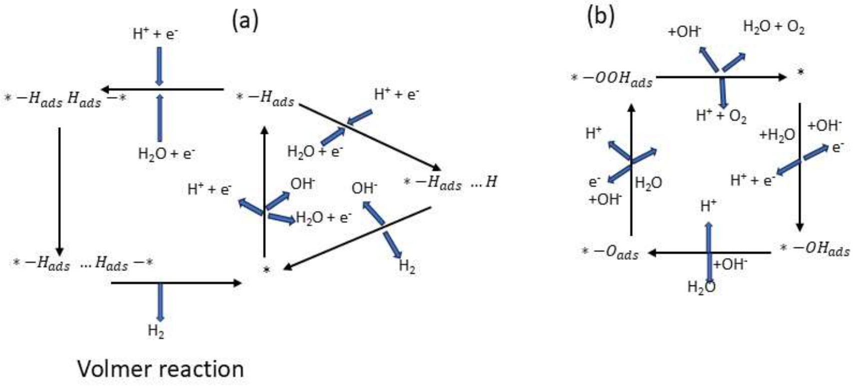
The second mechanism for the hydrogen production is known as the Volmer-Heyrovsky reaction. The first step in this mechanism is same as that of Volmer Tafel mechanism which involves the transfer of electron resulting in the formation of H^+ ions in the acidic medium or H_2O in the alkaline or neutral medium (Shi et al., 2022; Xiao et al., 2014). In the second process, adsorbed hydrogen combines with the electron and H^+ ion to form H_2 molecule.

- Volmer step
  $H_3O^+ + e^- \rightarrow H_{ads} + H_2O$ …..(8)
- Heyrovsky step
  $H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O$…..(9)

(b) Mechanism for the OER

OER reaction is more complicated in comparison to HER as it requires the four electrons while 2 electrons are required in the HER reaction (Song et al., 2020). In the alkaline medium, OH^- is adsorbed at the catalyst preferably over the surface sites and form $^*OH$ after oxidation. Further this $^*OH$ combine with OH^- to form H_2O and $^*O$ molecules (Tang et al., 2022). Further this $^*O$ combine with OH^- to form $^*OOH$ which produces O_2 and H_2O when combine with OH^-. These HER and OER pathways can be summarized in Figure 2.

Figure 2: HER (a) and OER (b) Mechanisms in Acidic and Alkaline Medium



2. MXENE-BASED HYBRID MATERIALS FOR WATER SPLITTING

The dependency on noble-metal catalysts such as platinum for photocathode and ruthenium oxide for photoanode presents a major challenge due to the scarcity and high cost of these materials. This issue opens the search for earth abundant materials with high catalytic activity and stability. Within this area two dimensional materials like transition metal carbides, nitrides, have gained significant attention due to their high conductivity, large surface area, and tunable band gap. These materials have shown as potential catalysts or conductive support for enhancing catalytic activity and stability. Thus, this current review is focused on the water splitting performance of MXenes when hybridized with noble and non-noble metal single atom nanoparticles, metal oxides, phosphides, layered double hydroxides (LDHs), transition metal chalcogenides (TMCs), and carbon-based materials.

One of the effective interface engineering techniques to enhance the catalytic active sites can be achieved by incorporating the single atom catalysts (SACs) and nanoparticles on MXenes. One of the V_2CT_xMXene immobilized with platinum (Pt) exhibited remarkable HER activity with low value of overpotential of 27.1 mV at 10 mA/cm^2 in acidic medium of 0.5 M H_2SO_4 and 63.1 mV in the alkaline medium of 0.1 M KOH solution (Park et al., 2022). The underline performance is attributed to the enhanced electron transfer and optimal hydrogen adsorption induced due to interaction of Pt with oxygen terminations on the surface. Further, Zhao et al. have reported the Co SACs on three MXene materials namely V_2CT_x, Nb_2CT_x, $Ti_3C_2T_x$ and exhibiting bifunctional HER and OER catalytic activity owing to redistribution of electronic density that lowers the energy barriers for reaction intermediates (Zhao et al., 2023). Pt and Ag nanoparticles also showed excellent catalytic activity when deposited on MXene. Yuan et al. has reported the Pt nanoparticles grown on tetrabutylammonium hydroxide (TBAOH) treated $Ti_3C_2T_x$ exhibited low overpotential of 55mV in acidic electrolytes (Yuan et al., 2019). While in case of Ag nanoparticles on V_2CT_xMXene hybrid exhibited excellent HER and OER activity with overpotentials of 32 and 310 mV, respectively in alkaline medium (Haider et al., 2023).

In recent years, transition metal oxide (TMOs) such as Co_3O_4, NiO, and Fe_3O_4 are extensively explored for OER catalytic activity. However, these material exhibit poor HER activity owing to poor conductivity. Incorporating these TMOs with MXenes enhances the conductivity as well provide higher surface area leading to increase in the catalytic activity. Lu et al. has reported the overpotential value of 300 mV at 10 mA/cm^2 in the alkaline medium in case of $Co_3O_4/Ti_3C_2T_x$ (Lu et al., 2020). Furthermore, ZnO nanoparticles in $Ti_3C_2T_x$ with uniform distribution showcase overpotential of 422 mV in acidic medium (Saini et al., 2022). Bifunctional oxides like Fe_3O_4 on MXene also demonstrated excellent HER and OER overpotentials as well as stability over extended cycles (Vikraman et al., 2022).

Transition metal phosphides (TMPs) such as CoP, Ni_2P, NiCoP also exhibit excellent catalytic activity for both HER and OER. This is due to the synergistic effect between the metal and phosphorous centers facilitates proton and hydride adsorption, resulting in accelerated evolution of hydrogen. Incorporating TMPs with MXenes tunes the electronic structure and exposes abundant sites. For instance, NiCoP integration with $Ti_3C_2T_x$ significantly lowers the HER overpotential to 71 mV at 10 mA/cm^2 (Niu et al., 2022). Further, Selven et al. has reported the enhancement in OER activity by introducing CoP nanorods on the top layer of $Ti_3C_2T_x$ (Selvam et al., 2019). The observed enhancement is attributed to the increase in the surface area due to the tensile stress induced by the CoP nanorods.

Layered double hydroxides (LDHs) represent another class of materials synergistically paired with MXenes for effective water splitting activity. Although LDH have limited surface area and thus low conductivity and water splitting efficiency. However, MXene with LDH overcome these limitations by preventing restacking and enhancing interfacial charge transfer (Cheng & Wang, 2022). Yu et al. has reported the mesoporous NiFe-LDH coupled with 3D $Ti_3C_2T_x$ MXene on nickel form exhibiting enhanced HER and OER activity due accelerated charge transport and increased active site exposure (M. Yu et al., 2019). Further, Wen et al. fabricated Ce-doped NiFe-layered double hydroxide nanoflakes on $Ti_3C_2T_x$ exhibiting an overpotential of 260 mV (Wen et al., 2021).

Transition metal chalcogenides (TMCs), including sulphides and selenides of Ni, Co, and Fe are often employed for HER but their applications are limited due to their poor stability and conductivity (Hu et al., 2023; Yin et al., 2020). When these TMCs bonded to MXene nanosheets, significant increase in the electron transfer efficiency has been observed. Studies on NiS_2 deposited on V_2CT_xMXene achieved and HER overpotential of 179 mV at 10 mA/cm^2 (Kuang et al., 2019). Jiang et al. has fabricated $NiSe_2$ nanocrystals wrapped with ultrathin MXene nanosheet of $Ti_3C_2T_x$ with overpotential value of 200 mV hybrid (Jiang et al., 2019). For OER, sulfurized NiCoLDH/MXene transformed into metal oxyhydroxides achieving as low as overpotential of 365 mV. Further, there are MXene based hybrid materials which shows significant catalytic activity (Cui et al., 2020; Zahra & Rizwan, 2022). Such dynamic surface reconstruction highlights the complexity and promising potential of TMC-MXene hybrid materials. Further, the various MXene hybrid materials with electrolyte used and corresponding overpotential have been summarized in Table 1.

Table 1: MXene-Based Materials for Water Splitting

Sr. No.	**Catalyst**	**Electrolyte**	**HER Overpotentials (@ 10 mA/cm^2)**	**Reference**
1.	Pt(SAC)V_2CT_x	0.5 M H_2SO_4 0.1 M KOH	27.1 mV 63.1 mV	28
2.	Pt(SAC)TBAOH-$Ti_3C_2T_x$	0.5 M H_2SO_4	55 mV	30
3.	Ag(NP)V_2CT_x	1 M KOH	32mV	31
4.	Co_3O_4- $Ti_3C_2T_x$	1 M KOH	300mV	32
5.	ZnO -$Ti_3C_2T_x$	0.5 M H_2SO_4	422mV	33
6.	$Co_3O_4^{-}$ $Ti_3C_2T_x$	1 M KOH	52mV	34
7.	$Fe_3O_4^{-}$ $Ti_3C_2T_x$	1 M KOH	63 mV	34
8.	$NiCoP^{-}$ $Ti_3C_2T_x$	1 M KOH	71 mV	35
9.	CoP^{-} $Ti_3C_2T_x$	1 M KOH	230 mV	36
10.	NiFe(LDH) $Ti_3C_2T_x$	1 M KOH	205 mV	38
11.	Ce doped NiFe(LDH) $Ti_3C_2T_x$	1 M KOH	260 mV	39
12.	NiS_2-VC_2T_x	1 M KOH	179 mV	42
13.	$NiSe_2$- $Ti_3C_2T_x$	0.5 M H_2SO_4	200 mV	43
14.	Pt $Ti_3C_2T_x$	0.5 M H_2SO_4	62 mV	44
15.	CNT-V_2CT_x	1 M KOH	27 mV	45
Photoelectrochemical Cell				
	Catalyst	**Electrolyte**		**Reference**

16.	TiO_2-Ti_3C_2	0.5 M Na_2SO_4	Photocurrent 1.96 mA/cm^2	46
17.	MX@C/Mo:$BiVO_4$	1 M KOH_4	Photocurrent 1.23 mA/cm^2	47
18.	α-Fe2O3/MXene NRs	1 M NaOH	Photocurrent 1.23 mA/cm^2	48
19.	MNs/α-Fe2O3	1 M NaOH	Photocurrent 1.02 mA/cm^2	49
20.	Co-Pi/MNs/α-Fe2O3	1 M NaOH	Photocurrent 3.2 mA/cm^2	50

From the perspective of photoelectrochemical (PEC) water splitting. MXene based hybrid systems also manifest substantial potential. As photoelectrodes, MXene serve primarily as conductive supports and electronic modulators that improve charge transfer and separation. For instance, $TiO_2/Ti_3C_2T_x$ composites act as photoanodes where MXene facilitates the hole transport resulting in an efficient OER (X. Yu et al., 2019). MXene quantum dots with tunable surface functional groups and electronic properties have been shown to enhance charge separation and $BiVO_4$ and α-Fe_2O_3 (Nguyen et al., 2020; Song et al., 2022; Yang et al., 2021; Ye et al., 2021). The photoelectrochemical cell parameters for different materials have been summarized in Table 1.

CONCLUSION

This work presents a review of MXene and hybrid-Mxene materials for the photoelectrochemical water splitting. This paper incorporates the phenomenon of water splitting and various pathways in the acidic and alkaline medium. It can be concluded that the exploration of diverse MXene compositions, including mixed transition metal MXenes showing promises pathways to tailor electronic structures and thus catalytic properties. For advancing PEC water splitting technologies. Surface reconstruction during electrochemical reactionnecessitates in situ analytical methods such as Raman spectroscopy and X-ray absorption spectroscopy for structural evolution and to understand active species. Despite these advancements, challenges remain in fully harnessing MXene-hybrids for water splitting. A key issue is the control and understanding of active catalytic sites, tuning of compositions, and surface termination groups.

In Summary, Mxene-based hybrid materials offer a versatile and promising platform for advancing PEC water splitting technologies. Their intrinsic attributes of high conductivity, large surface area, and tunable surface chemistry, and structural flexibility, combined with synergistic integration of secondary catalytic materials, have led to significant improvements in catalytic efficiency and stability. MXene based materials not only promise to meet growing clean energy demand but also contribute to a sustainable energy future by enabling green hydrogen generation through solar to fuel conversion.

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