

MXENES 2D NANOPARTICLES: ITS PHOTOCATALYSIS PROPERTIES AND APPLICATION

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MXenes are the two-dimensional transition metal carbides and/or nitrides which have a unique layered structure and a variety of surface functional groups. These 2D nanoparticles are unique in their robust mechanical properties and excellent photocatalysis properties. It is reported that MXenes have a considerably good light absorption over a wide wavelength range and a longer charge- carrier recombination time. This makes them a wonderful light harvesting material with potential device application. In this review, I discuss in detail this upcoming material along with its synthesis, the unique properties it possesses, the composite it forms, and their application in photo-catalytic reactions.

Keywords: Mxenes, Nano-composite, Photocatalysis, Synthetic methods.

INTRODUCTION

In past two decades, advanced 2-D nanomaterials have shown piqued interest especially after the discovery of single-layer graphene in 2004 and its derivatives in later stages (1). Despite the fact that there are many 2D materials available in 2011, the vast majority includes semiconductors, semimetals, or insulators with poor electronic conductivities and carrier concentrations (2). In this continuation, advanced 2D materials need to be explored in significant quantities with distinctive micro and nanostructures for their uses outside of the microelectronics area. For this significant improvement, the fabrication of 2-D materials such as phosphorene (3), metal nanoparticles, hexagonal boron nitride(4), transition metal oxides and dichalcogenides (5), carbonitrides, layered double hydroxides(6), etc. are investigated for diverse applications(7). These atomically thin 2D materials exhibit strong electrical, mechanical, optical, and physicochemical potentials which are outstanding due to quantum confinement effect. Owing to this fact, these 2-D nanostructured materials are already utilized in variety of devices from electronic to biosensors and receives a lot of attention from researchers to academia working in the field of materials science (8). Apart from that, the ultrathin 2-D nanomaterials have a unique mix of features such as anisotropic electron transport behavior and a large surface area that makes them interesting and viable for variety of applications (9, 10). On the other hand, these materials also possess few serious drawbacks including very stable surface area which prohibit inclusion of functional groups, hydrophobicity (e.g., MoS₂, graphene), Low electrical conductivity (e.g., MoS₂, graphitic carbon nitride) and many more that limit the performance of these materials in variety of processes. For instance, the functionalization of graphene is limited to surface flaws and edges, while functionalization of MoS₂ is even more grim (11). Except for graphene and h-BN, solution-processed 2D materials have small flake sizes due to low mechanical strength, which caused 2D sheets to fracture during delamination. As a result, the discovery of alternative family of 2D materials with enhanced metallic conductivity,

hydrophilicity, processing ease, high yields, and huge flakes was desirable that can have a significant impact on the entire materials science area. To counter this, novel classes of 2-D nanomaterials known as MXenes has just emerged and have potential to solve these issues. The material is more known as 2-D transition metal carbides and carbon nitrides having general formula of $M_{n+1}X_nTx$; which is made by etching (selective) A-layers from $M_{n+1}AX_n$ (MAX) phases wherein M represents early transition metal, A represents 13/14 group elements, and X represents either carbon or a combination of nitrogen/carbon, and n ranges from 1 to 3. The Tx in the formula indicates the numerous functional groups at surface coming from diverse synthetic techniques, such as chlorine, fluorine, oxygen and hydroxyl (12).

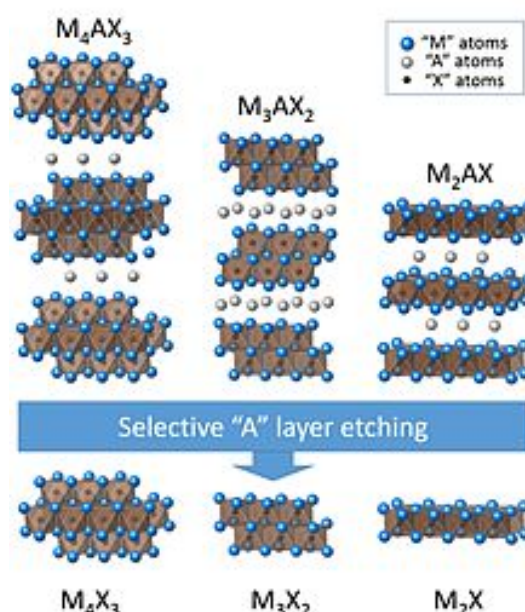


Figure 1 MXenes are produced by selective etching of the "A" element from the MAX phase structure

In past few years, plenty of MXene compositions are investigated which includes 30+ experimentally synthesized MXene compositions and dozens of theoretically predicted

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potential compositions; this is due to the different type of atomic structure and available range of M elements. Hence, the family of 2D materials is continuously expanding (13-16). Furthermore, MXenes properties can be tweaked by changing the ratios of M or X elements in conjunction with the surface terminations (17, 18). Their unique chemical and physical properties (say, electrochemical, thermal conductivity, excellent electronic conductivity, optoelectronic, customized surface chemistry, good ion intercalation activity and adjustable interlayer spacing, ultrathin 2D sheet-like shape) enable this material to be more practiced in applications like photocatalysis, super-capacitors, conductive electrodes, energy conversion, electrochemical energy storage, water splitting and purification, nonlinear photonics, electromagnetics, absorbers, bio-sensing, biomedical applications and many more (19-26). Additionally, MXenes are also acts as an efficient adsorbent for a variety of compounds and ionic species, broadening their uses in ion sieving, catalysts, and sensors, thanks to their broad specific area and rich surface functional groups (20, 27, 28). Besides that, MXenes comprise a large number of exposed metal sites and high electronic conductivity due to which rapid transfer or separation of photo-excited electron-hole pairs is ascertained for photocatalytic processes (29, 30). Despite all, MXenes have few limitations, including poor oxygen stability, low flexibility and restacking, all of which limit their applicability in diverse applications (31, 32). Subsequently, MXenes based composites have emerged as a trend that could potentially improve their characteristics to provide stable and versatile material for their mass production and ease of process integration (29). MXenes have been effectively merged with a variety of materials to form MXene-based composites, including metals, Nano-spheres, and polymers, high-quality graphene, carbon nanotubes, metal sulphides, providing improved mechanical, electrical, chemical, structural, and physical properties, ease of fabrication, and tunable capabilities (12, 33-36). MXenes have a high degree of flexibility in conjunction with their 2-D shape and layered structure which enables their composite formation easy for photocatalytic application (30). More crucially, MXenes' interlayer spacing may be changed without breaking their layered arrangement, surface structure tunability (without impacting the overall conductivity), hydrophobicity and the absorbed functional groups (37).

In this work, several attempts have been taken in this study to elaborate sections in order to provide readers with a wide understanding of the ramifications of MXenes composites for photocatalysis and their properties. The first section in this work outlines the various synthesis procedures used in the fabrication of MXenes. Another subsequent section is further expanded on the synthesis of variety of MXenes based composites which includes MXenes-polymer composites, MXenes-Oxide Composites and MXenes-CNT composites. The third section discusses the current advancements in the use of MXenes/MXenes composite for photocatalysis applications. Finally, prospects and current challenges pertaining to MXenes are summarized. Finally, the concluding remarks of MXenes for photocatalysis applications are discussed to address the scope of MXenes in present problems.

MXene for photocatalysis

MXenes is indeed a wonderful and upcoming material for photocatalysis applications. It is used for various key

photocatalysis activities which include water splitting, carbon dioxide reduction, nitrogen fixation and degradation of several pollutants. The key factors which contribute to the tremendous photocatalytic activity of MXenes are: (a) The wet chemical etching synthesis results in plentiful functional groups which in turn lead to close contact interface between MXenes and other semiconductors. (b) The tunable band gap, which can be attained by optimizing and controlling surface chemistry. (c) The metal kernels in the layered structures lead to greater conductivity and electron acceptability. MXene based structures play multiple roles in different steps of photocatalysis process as a whole. These include: (a) acting as a tough support system (b) enhancing reactant absorption (c) restraining photocatalysis size, and most importantly (d) promoting charge carrier separation. In this section we would be discussing various aspects MXenes which are responsible for its excellent photo-catalytic properties also their potential practical applications in photocatalysis reactions.

Roles of MXenes in enhancing photocatalysis activity

The lower Fermi Levels of MXenes is primarily responsible for its light harvesting properties (38, 39). In the following section we will discuss various other factors which contribute to the overall photocatalysis activity of MXenes:

Promotion of photo-generated charge carrier separation:

Recombination of photo-generated charge carriers is a serious limitation of all the light dependent processes and photocatalysis is no exception. As a matter of fact, the competence of a photocatalysis reaction is proportional to a proficient separation of the charge carriers which in turn is governed by the rate of recombination of electrons and holes. In order to overcome this limitation and to increase the charge separation efficiency, a co-catalyst along with the photocatalyst is employed (40). These co-catalysts provide an alternative and longer pathway to the photogenerated electrons. For instance MXeneTi₃C₂ can be used as a co-catalyst in CdS based devices. On the basis of density functional theory Ti₃C₂ exhibits Fermi level value of -0.05 V. This value is close to metals and is more positive than the conduction band of several n-type semiconducting materials. On using it with CdS a Schottky junction is formed between the two materials which in turn accumulate photo-generated electrons and subsequent charge separation. The conductivity of such systems is more positive than most n-type semiconductors thereby, making it a potential co-catalyst for electron transfer as well as accumulation (41). The photo excited electrons of CdS migrate from conduction band to Ti₃C₂ because of its lower Fermi level. Because of metal like electrical conductivity of Ti₃C₂ this electron acts as a free electron and is used as a reducing agent for various photocatalytic applications (42).

Acting as a perfect Substrate material: Large surface area and robust mechanical strength of MXene makes it an ideal candidate for growth and uniform dispersion of various photocatalytic materials including TiO₂, CdS and MoS₂ (43-48). They act as support materials to the nanosheets of photocatalyst, maximize the exposed active sites and most importantly in some cases function as precursors for in situ growth of related metal oxide based photocatalysts. These precursors based photocatalysts are found to have fluffy structures with increased specific surface area. Besides the close contact between the photocatalyst and the precursor leads to improved separation and migration of photogenerated

charge carriers thereby improving the photocatalytic activity (47, 49).

Decreased photo-catalyst size: An important aspect of nanomaterials application is their small size. Due to the large surface to volume aspect these materials have high surface energy and tend to agglomerate. This aggregation of catalysts decreases their contact area with the reactants hence decreasing their efficiency. If we consider MXene based materials in this light, the wet chemical etching method by which they are prepared results in large number of functional groups. These surface functional groups provide surface active sites for photocatalysis reactions, thereby increasing the total photocatalytic surface and also preventing agglomeration (50, 51). The catalytic efficiency of catalyzed reactions also depends upon the reactant adsorption. The presence of multiple functional groups increases the reactant adsorption capacity of various photocatalytic applications. The negatively charged surface of MXenes the positively charged reactants are adsorbed efficiently. The porous structures of MXenes further add to the adsorption capacity (52).

MXenes for photocatalytic Nitrogen fixation: Nitrogen is an important feedstock ingredient for the manufacture of industrially important ammonia. The classic Haber-Bosch process for ammonia manufacture is an energy exhausting process (53) mainly because of the involvement of high energy Nitrogen bonds. Of late photocatalytic Nitrogen fixation has garnered a lot of interest as a clean energy process and MXenes based materials are being studied in this regard (24). Though the exact mechanism of N_2 fixation is not yet fully established but in a broader sense we can assume that the N_2 molecules are chemi-adsorbed on the MXenes substrate. This adsorption takes place in various ways some of which include Nitrogen binding to Ti-Ti dimmers and trimers. It is proposed that this adsorption leads to lengthening and resultant weakening of Nitrogen-Nitrogen triple bond which is beneficial for photocatalyzed reduction reaction of N_2 .

A few studies have been done in this regard. Liu and coworkers (54) synthesized $AgInS_2/Ti_3C_2$ composite for photocatalytic N_2 fixation. With the aim to create a direct Z-scheme heterojunction between Ti_3C_2 and $AgInS_2$ they used hydrothermal route to synthesize $AgInS_2/Ti_3C_2$ composites. This Z-scheme heterojunction could maximize the photo induced reduction and oxidation and hence photocatalytic efficiency of system. The TEM images of the synthesized composite material showed the uniform distribution of $AgInS_2$ NPs on the surface of the Ti_3C_2 , which lead to a greater contact interface between the two of them. This large contact interface could be a proposed reason for better photocatalytic activity but also for efficient chemisorption's of the N_2 molecule.

Hao and coworkers synthesized a ternary $RuO_2/TiO_2/Ti_3C_2$ composite for photocatalytic N_2 Fixation (55). They made use of the fact that Ti_3C_2 is a possible potential 2D precursor for TiO_2 . The synthesis was aimed to utilize the components of the composite as light harvester (TiO_2), electron mediator (Ti_3C_2) and N_2 adsorber (RuO_2) thereby making a complete pathway for photocatalyzed N_2 fixation. The possible mechanism could be proposed based on the TEM images. The images revealed that the RuO_2 nanoparticles were mainly distributed on MXenes rather than TiO_2 . A mechanism was proposed that the photo-generated electron first transfer from TiO_2 to Ti_3C_2 and

further pass on to RuO_2 for reducing the NO_2 adsorbed on it. The introduction of an electron mediator could be definitely linked to prolonged time for charge carrier recombination and hence increased photo efficiency of the reaction.

MXene mediated photocatalytic CO_2 reduction: CO_2 can be touted as necessary evil resulting from human activities and an important and efficient way of CO_2 mitigation is its photocatalytic reduction into carbon fuels (56). Several semiconducting materials have been studied in this context which include TiO_2 (57, 58), CdS (59, 60), $ZnIn_2S_4$ (47, 61). An important way of enhancing the efficiency and yield of such reactions is by combining them with MXenes. Low and coworkers (49) reported hierarchical rice crust type Titania/MXenes structure for photocatalyzed CO_2 reduction. Ti_3C_2 twined as a precursor material to grow TiO_2 nanoparticles on Ti_3C_2 sheets by simple calcination giving rise to fluffy rice crust like structures. The voids present in the fluffy structure of the composite increased the surface area available for CO_2 reduction multiple times with several surface-active sites for CO_2 reduction.

It is imperative to note that the TiO_2/Ti_3C_2 composites exhibits different photocurrent curves in contrast with the wholesome components thereby hinting the probable mechanism of the photocatalytic reaction. In case of TiO_2 a spike in anodic photocurrent was observed upon illumination which was attributed to the fast electron migration from TiO_2 to cathode. The photoelectron hence generated recombined with the holes thereby decreasing photocurrent density. In case of the TiO_2/Ti_3C_2 composite, the photocurrent density showed a gradient increase upon light irradiation. This increase indicated that before recombining with the hole, the photoelectron migrated to Ti_3C_2 thereby separating the electron hole for a longer time. Another interesting observation that was made was the gradual decrease in photocurrent density even after light was turned off. The absence of abrupt decrease of photocurrent indicated electron reservoir properties MXenes which in turn is proved useful multielectron reaction of the CO_2 reduction.

Another metal oxide to be composited with MXenes is for CO_2 reduction is CeO_2 (62). The reduction reaction took place via formation of Schottky junction. Tang et al utilized hydrothermal route to prepare several CeO_2/Ti_3C_2 composites of varying compositions. Apart from studying the charge carrier utilization and their separation they also worked on optimization of composite composition. They reported that CeO_2 samples with 5% by weight of Ti_3C_2 exhibited the best photocatalytic activity. With an aim to create 2D/2D composite Cao et al. synthesized Ti_3C_2/Bi_2WO_6 composites (52). These composites had an interesting layer by layer structure, which gives them a huge interfacial contact area leading to greater charge migration. The Atomic Force Microscopy results revealed a stacking, layer by layer structure leading to a better interface charge migration. It was also revealed that the thickness of Bi_2WO_6 in the composite was less than that of pure Bi_2WO_6 . This indicated that MXenes possibly arrested the growth of Bi_2WO_6 thereby limiting the film thickness. An interesting optical study revealed the possible mechanistic pathway of the composite action. It was observed that the absorption edge of Bi_2WO_6 did not change after loading it with Ti_3C_2 it did exhibit an intense absorption in the visible (420-800 nm) range. This indicated that the composite material could not be directly used for generating electron-hole pairs

but can accelerate the photocatalyzed reaction by photo-thermal effect. On employing the composite for CO₂ reduction, it was observed that the photocatalytic activity of the composite was about 4.6 times higher than that of pure Bi₂WO₆ for methanol production. The isotopic labeling of carbon revealed that the source of organic compound formed in the reaction was CO₂. The study thus concluded that the enhanced activity of this composite material could be attributed photo-thermal effects along with enhanced charge carrier efficiency and enlarged surface area.

Another interesting aspect of material science employed in using MXenes for photocatalytic reduction of CO₂ is the effect of reducing a particle to quantum size. Zeng group (63) synthesized Ti₃C₂ quantum dot supported Cu₂O nanowires for photocatalytic CO₂ reduction. The study reported detailed synthesis process which comprised of separate synthesis of the copper oxide nanowire and MXenes quantum dots and then harvesting the surface charge difference between them to couple the materials via self-assembling process. The Transmission Electron Microscopy images revealed that the Ti₃C₂ quantum dots were uniformly distributed over the nanowires while the EDX analysis further confirmed the homogeneous distribution of Ti, C, Cu and O in the sample. The group also prepared different samples by varying MXenes content in the composite. The increase in Ti₃C₂ ratio led to more stable composites because apparently MXenes covered the surface of Cu₂O nanowires and protected it from photo corrosion. The simulated energy level diagram of Ti₃C₂ quantum dots exhibited the Fermi level as -0.523V which is more negative than Ti₃C₂ nanoparticles as a result the photo-generated electrons which accumulate on the quantum dot surface can easily reduce CO₂ to methanol instead of carbon monoxide. The work also emphasized the fact that the tuning of MXenes quantum dot size plays a significant role in the reaction efficiency thereby by putting forth the importance of size dependence in photocatalytic activity.

Gao research team and others groups (64, 65, 66, 67, 68, 69, 70) studied organic, dye-sensitized and perovskite nanomaterials for photocatalytic reduction of CO₂. These inorganic materials possess proper band gap, good photo stability and longer lifetime for charge carriers. The study showcased the increased MXenes catalytic activity on loading them with CsPbBr₃. The TEM studies revealed an even distribution of cubic CsPbBr₃ crystals onto the MXenes surface which was further confirmed by EDX elemental analysis. The coupling of CsPbBr₃ with MXenes significantly extended the photogenerated charge carrier lifetime, hence offering better CO₂ reduction efficiency.

Conclusion

In this work we have discussed how MXenes have emerged as an important 2-D material and present the studies which establish them as a potential device material. However, there are certain challenges to be addressed before they can be utilized for large scale applications. Some of the key issues to be addressed are; First and the foremost challenge with MXenes is their synthetic approach. Most common method of synthesis includes etching and exfoliation by hydrofluoric acid and other harsh chemicals which are corrosive. They are not only unsafe to handle but are harmful for the environment as well. Apart from this the surface terminated groups produced during the synthetic process have a direct influence on the

electronic properties. Thus, development of a greener and more sustainable approach with a greater control over surface functional groups is a key issue to be addressed. Second issue to be addressed is a better comprehension of the photocatalytic mechanism of MXenes. It is believed that the terminal functional groups on the surface of MXenes based photocatalysis play a crucial role in the electronic properties and the interfacial charge transfer mechanism yet a clear picture of charge carrier dynamics is yet to be worked upon. This mechanistic approach is also crucial for a better control over the reaction phenomenon. For instance, the while the photo generated electrons act as a reducing agent, the MXenes based material could be oxidized into a different species thereby making the regeneration difficult. A more detailed time-resolved study on interfacial charge transfer will make us better equipped for fabrication of MXenes based devices. Last but not the least improvement of photocatalytic performance of MXenes based photocatalysis needs to be dealt in a better way. One of the measures could be synthesis of MXenes based composites or maybe high efficiency MXenes quantum dots. Several permutations and combinations of materials may lead to a potentially better photo-catalyst and multidisciplinary research is the need of the hour to bring out an economical, sustainable and industrially applicable in the future.

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