

MXENE AS FUTURE POTENTIAL PHOTOACTIVE CO-CATALYST MATERIAL FOR EFFICIENT VISIBLE LIGHT PHOTODEGRADATION OF PERSISTENT ORGANIC CONTAMINANTS: A REVIEW

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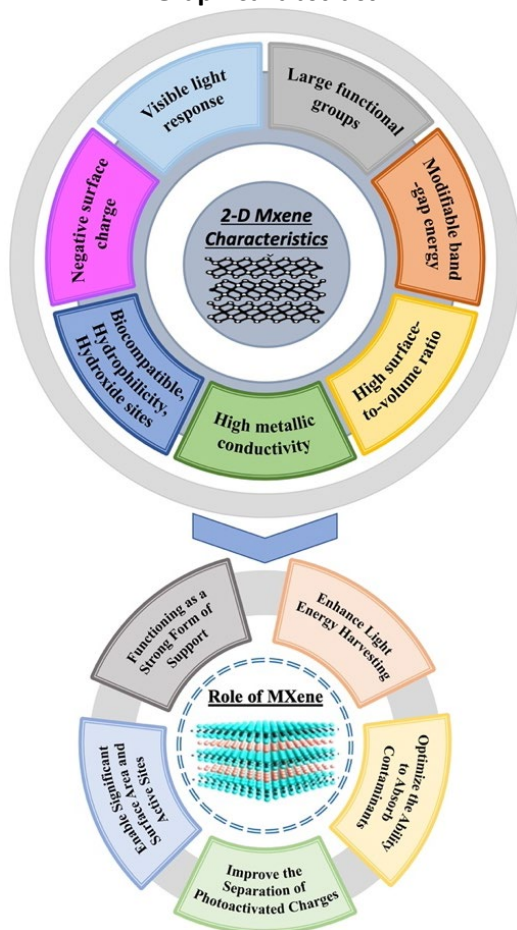
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Graphical abstract



Abstract

Advanced oxidation strategies (AOSs), which are regarded as an eco-friendly approach, are being evaluated as a potential technique to address the escalating energy crisis and environmental issues stemming from the industrial revolution. Traditional wastewater treatment techniques often result in the emission of possibly harmful by-products. Therefore, various semiconductor photocatalysts such as TiO_2 , ZnO , $g\text{-C}_3\text{N}_4$, CdS , WO_3 , and ZnS have been under continuous investigation to fulfill the need for efficient treatment of wastewater in a cost-effective approach. However, there is a pressing need to develop engineering strategies for these photocatalytic materials to generate strong capabilities for maintaining high stability, effectively separating charges, and harvesting visible light. This need for innovation arises from the inherently low efficiency of the reactions that occur when employing a single photocatalyst. MXene (2-D titanium carbide) has gained recognition as a promising co-catalyst material in the field of photocatalysis based on its distinctive physicochemical and mechanical characteristics that include a configurable bandgap, extensive surface area, strong conductivity, exceptional structural stability, facile functionalization, and hydrophilicity. The challenges associated with the utilization of an individual semiconductor photocatalyst could be effectively addressed by incorporating MXene as a co-catalyst, thus enhancing the photocatalytic degradation performance. One of the effective techniques for promoting photocatalytic activity and improving the electronic structure by utilizing MXene as a co-catalyst is the generation of Schottky junctions and heterostructures. The overall objective of this paper is to highlight MXene as a prospective co-catalyst for visible light photodegradation of persistent organic contaminants. The article critically focuses on the fundamental principles of photocatalysis, synthesis techniques, and recent advancements in MXene and MXene-based composite photocatalysts for efficient wastewater treatment. It is anticipated that this article will motivate additional research and pave the way for the development of novel, highly effective MXene-modified semiconductor photocatalysts, thereby expanding their potential applications.

Keywords: Co-Catalysts; Charge Separation; Composites; Exfoliation; Persistent Contaminants; Advanced Oxidation Strategies;

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1.0 INTRODUCTION

Development, commerce, urbanization, and industrialization have caused environmental problems. Therefore, clean energy and green water systems need to be developed more. Inadequate sewage management and treatment, especially industrial waste, pollutes our ecological systems from many sources [1]. Population growth has raised water use, lowering water quality. This loss of quality is caused by human activity and unsuitable water use [2]. Industrial waste and urbanization pollute the environment, harming humans and wildlife. Pharmaceutical solvents, endocrine disruptors, and harmful chemicals are regularly documented in urban wastewater, industrial byproducts, and tap water worldwide in several investigations. Contamination threatens human health and the marine ecosystem by reducing the supply of clean water [3]. Large amounts of these toxic substances and inefficient effluent removal have been observed in groundwater, tap water, and urban treatment plants for sewage. Wastewater contaminants can be treated before release in various ways. Sono-degradation, biological degradation, chlorination, separation by membranes, precipitation, adsorption, and solvent extraction are examples [4]. Considering its limitations, notably harmful byproducts, high cost, and low contaminant removal performance, photocatalysis is a potentially modern photodegradation technology. It turns solar energy into chemical energy, reducing energy shortages and risks to the environment. Cost efficiency, conservation of resources, reuse, and total degradation are advantages of this strategy [5].

Photocatalysts help destroy pollutants using light energy, enabling photocatalysis as an economically viable treatment alternative. The process of photocatalytic degradation usually has three phases: Absorption of incoming photons by the photocatalyst forms photoinduced charge carriers (e^-/h^+); the transfer of photoactive holes (h^+) and electrons (e^-) towards the outer layer; and redox processes that utilize photoexcited carriers [6]. The photoactivated e^-/h^+ reacts with oxygen, water, and hydroxyl molecules to form molecules of reactive oxygen with strong oxidation capabilities. Organic contaminants in wastewater decompose mostly due to reactive molecules of oxygen [7]. To treat wastewater efficiently and economically, researchers have studied semiconductor photocatalysts, including CuS, TiO₂, g-C₃N₄, Fe₂O₃, CdS, ZnO, WO₃, and ZnS [1, 8, 9]. Nevertheless, such photocatalysts have a wide band gap (E_g), minimal light utilization, and high photoexcited e^-/h^+ recombination. These challenges restrict this method to use for practical applications. An advanced E_g level demands more energy absorption to separate e^- and h^+ . Photoexcited e^-/h^+ can also recombine without participating in the photocatalytic activity [10]. The rapid progression of active charge recombination lowers the number of photoinduced molecules of reactive oxygen at the surface reaction sites of photocatalysts, reducing photodegradation performance. As a result, photocatalysis often functions at a much lower efficiency [3]. Consequently, it is essential that researchers accelerate the discovery of new materials with extraordinary photocatalytic activities.

Several scientists have modified photocatalysts to solve these issues. Despite employing expensive metals, graphene oxides, carbon nanotubes, and 2-D MXenes have been used to generate powerful and durable photocatalysts [11]. Composite materials of MXenes have generated interest in ecological

sustainability and clean energy because of their outstanding oxidation resistance, nontoxicity, resilient chemical composition, broad interlayer placement, unique thermal and electricity utilization, large surface area, high melting temperature, ecological versatility, and impressive biological stability. A co-catalyst adds a dipole moment to a semiconductor photocatalyst, changing the rate of electron transport [12]. This change reduces the band-gap energy by transferring electrons from the photocatalysts valence band (VB) to the conduction band (CB). A low E_g level signifies higher sunlight or visible-range light absorption [13]. A composite photocatalyst can be constructed from two catalytic materials with different chemical properties. This mechanism moves photoexcited e^- from the higher negative Fermi energy (FE) region in the CB to a lower-energy FE. The h^+ also changes from a higher positive FE in the VB to a lower positive FE at the interface [14]. This prevents photoactivated e^-/h^+ from recombining. Chemical composition, size of particles, morphology, and the microstructure of the material affect nanocomposite functionality. In addition to their unusual thermal and optical attributes, phenomenal dimension, valuable electrical conductivity, attainable chemical functions, high derivatives, hydrophilic properties, and normal plane micro-structures, 2-D MXene morphology has been extensively researched for the photodegradation of environmental contaminants [15]. The material's surface has enough hydrophilic functional groups, including fluorine (F), oxygen (O), and hydroxyl (-OH), to interact well with various semiconductor photocatalysts. F, O, and -OH terminal groups provide many reactive sites on the top layer. MXenes excellent electrical conductance traps photoexcited e^- , allowing charge carriers to migrate and separate quickly [16]. The advantages mentioned above are difficult to achieve with traditional 2-D nanomaterials such as bimetallic hydroxides, transition-layered metal dihalides, and graphene. Interfacial sorption and alteration, catalytic removal, and photodegradation have shown promise in removing environmental pollutants. Systematically, MXene has a structure that survives change in the environment [17].

The literature review found many reviews on MXene applications and synthesis methods, but few on MXene-based nanocomposites for visible-range photocatalytic environmental remediation. This review covers the current research and analyses the recent developments in using MXene and MXene-based nanomaterials to remove persistent contaminants (PCs) from sewage. This review covers the fundamental basics of photocatalysis, MXene-based composite material advances, and the role of MXene in enhancing composite material photoactivity. MXenes have not been extensively studied as co-catalysts in nanocomposites to absorb sunlight or visible-range light and induce photocatalytic degradation processes. To maximize reaction efficiency, MXenes and MXene-based materials with photocatalytic activity must be scientifically improved. The study finishes with MXene-based photocatalyst findings and the potential for sunlight photodegradation.

2.0 FUNDAMENTAL PRINCIPLES OF PHOTOCATALYSIS

2.1 Photoexcitation Mechanism

Photocatalysts absorb photon energy ($h\nu$) to start photo-redox reactions and transform hazardous organic contaminants into CO_2 and H_2O . The photoinitiated redox mechanism depends on semiconductor photocatalyst energy band arrangement, mobility of electrons, and active e^-/h^+ transfer efficiency [18]. Photocatalyst band-gap energy level affects the absorption of light, transfer rate of charges, redox activity, and photodegradation performance. Figure 1 illustrates the photocatalytic degradation mechanisms of organic pollutants and various applications of photo-redox reactions. These applications encompass the generation of hydrogen through water splitting, photoinduced green synthesis, photocatalytic degradation, and the reduction of carbon dioxide [8]. Light irradiation can excite semiconductor electrons when the striking photon energy is equivalent to or greater compared to their band-gap energy levels, transferring electrons from VB to CB and generating holes (h^+) in the photocatalyst VB. The band-gap/position of the photocatalyst is located between CB and VB [19]. The photocatalysis reduction step utilizes the photoactive e^- and generates superoxide radicals ($\bullet\text{O}_2^-$), whereas the oxidation step requires h^+ and forms hydroxyl radicals ($\bullet\text{OH}$). The contaminated solution undergoes a redox reaction when electrons are photoactivated. After photocatalysts absorb photons, they form photo-generated charge carriers. This produces photoinduced h^+ and e^- , which compete to recombine. Following recombination, the energy that was captured is released as either heat or light [20]. The photoactivated e^- must transfer to the catalyst surface and react with water-absorbed species as receptors or electron donors during photocatalysis. However, the photocatalytic reaction has three essential phases. First, photocatalysts capture energy ($h\nu$) to create e^-/h^+ pairs. Second, photogenerated e^-/h^+ pairs are separated from one another and moved to the surface of the material. At last, activated e^-/h^+ pairs participate in photocatalyst surface reduction and oxidation (redox) processes [21]. The photocatalysts VB and CB limits and reactants energy absorption during the reaction determine the photoactivity viability. Highly reactive photoinduced oxygen and radical species aided the photo-redox conversion of harmful pollutants into CO_2 and H_2O , reducing additional contamination. According to a 2019 study by Michael and colleagues, an elevated E_g value requires more energy consumption to segregate photoactivated charge carriers [22]. Photoexcited h^+ and e^- can recombine independently of the photocatalytic action. The photocatalytic degradation mechanism is limited by rapid recombination, resulting in decreased production of photoinduced oxygen and radical species. Thus, photocatalytic quantum activity is greatly reduced [23]. Sustaining thermodynamic excitation for photodegradation requires excellent redox ability and a relatively narrow band-gap. Photocatalysts with a noticeable band-gap can absorb a restricted range of solar radiation wavelengths, but their redox capabilities decrease [24]. Thus, observing a semiconductor photocatalysts total photocatalytic degradation activity is difficult.

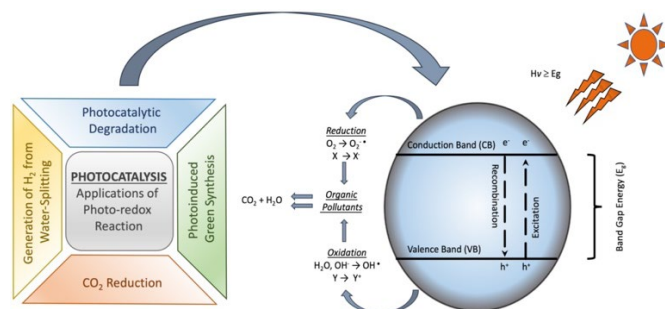


Figure 1 Depicts the mechanism of photocatalytic degradation and the applications of photo-redox reactions

2.2 Mass Transfer Procedure

Active transfer of mass enhances the photodegradation of harmful organic contaminants. Photocatalytic contamination treatment has two major phases. First, photoexcitation occurs when the outermost surface of the photocatalytic material absorbs photons, creating active sites. Second, contaminants begin to move from the water solution to be absorbed by the catalyst surface through mass transfer [25]. The photocatalytic materials ability to interact with contaminants is enhanced when it receives light irradiation, potentially improving results [26]. The effective transfer of mass in photocatalytic reactions is usually determined by assessing the catalyst's active sites and reactor size. Organic contaminants are adsorbed by transferring mass from the solution to the catalyst surface [7]. The following stages explain this phenomenon:

- Organic contaminants move from the solution to the catalyst surface in bulk.
- Contaminant diffusion in photocatalyst pore space (catalyst internal surface movement).
- Photoexcited catalysts adsorb contaminants at active sites.
- Reacting with contaminants on catalyst-active sites.
- Converted substance desorption occurs from the inner layers of the photocatalyst.
- Converted substances diffuse through catalyst pore spaces from the inner to the exterior surfaces.
- Transfer of mass from the outermost layer of the catalyst to the treated water solution back.

Technically, the photocatalytic reaction mass transfer variables should be optimized to avoid mass transfer restrictions. The unit surface area of the material, pH of the solution, photoreactor configuration, stirring/turbulence, pressure gradient, and solution temperature affect the process of mass transfer [27]. By choosing the right configuration of the reactor and an effective photocatalyst, these system drawbacks can be reduced. Enhancing the concentration of the contaminants inside the solution has the potential for greater mass transfer. It has been observed that when photoreactors are overloaded with photocatalyst materials, their performance suffers [28]. Overloading occurs when there is more catalyst suspension than necessary, which hinders the absorption of irradiation light and the mass transfer mechanism inside the catalyst particles. The transfer of contaminants to the photocatalyst surface follows catalytic concentration optimization [29]. Steps I through VII of the exterior surface diffusion process are shown in Figure 2. Due to limited reactant absorption and fluid velocity in the bulk solution, these steps

may progress slowly. Augmentation of turbulence for adsorption rate amplification resolves the issue. Continuous solution stirring increases turbulence in the solution. Thus, the direct photocatalyst domain will have the same contaminant concentration as the bulk solution [26]. Steps II and VI in Figure 2 show the contaminants entering and leaving the catalyst pore space, respectively. Since the photocatalyst particles are bigger, it takes longer for contaminants to move across the surface and only reach the top layer for chemical reactions. This means that both steps are equally important. Reducing photocatalyst particle size for internal contaminant diffusion solves the problem [30]. Steps III to V of Figure 2 describe the action of adsorption and desorption of contaminants inside and outside of the photocatalyst surface. These steps are crucial because they limit contaminant-to-product conversion. The active portions of the reaction, which can be exploited to degrade organic contaminants, are revealed in steps III through V. Photocatalytic reactions produce byproducts, the nature of which is determined by the characteristics of the catalyst [31]. As all the molecules in the solution must be moved to the photoexcited site in order to be transformed into the product of desire, the procedure for transferring mass can be improved by persistent desorption and expulsion steps following the photocatalytic conversion procedure [32]. Optimal photon energy, active transfer of mass, sufficient active site availability, active adsorption and desorption of contaminants, and by-product elimination must be achieved in photoreactors for effective photodegradation performance.

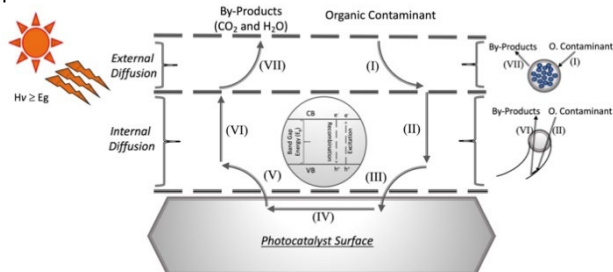


Figure 2 Schematic illustration of the mass transfer mechanism in the photocatalysis process

3.0 RECENT ADVANCEMENTS IN MXENE

Ongoing research on 2-D element family members enables photocatalyst development. Carbide, transition metal nitride, and carbonitride (MXene) are innovative 2-D compounds that have become attractive photocatalytic materials. It is widely recognized for its favorable electronic structure, affordability, non-toxicity, optical features, and effective stimulated e^-/h^+ mobility [33]. In recent years, MXenes have received considerable attention as a promising material for applications across multiple disciplines. It is studied for photocatalysis (H_2 generation, decontamination, N_2 fixation, H_2O_2 production, and CO_2 conversion), optical (lasers and optoelectronic devices), biomedical (chemotherapy treatment, neural electrodes, biosensors, dialysis), energy (Mg, Li, Al, Na ions, capacitors, power sources, batteries), electromagnetic devices, surface insulators, and sensors [34]. In 2011, Naguib and his colleagues conducted a study where they selectively removed certain layers of 'A' elements out of the MAX state of compounds utilized for the exfoliation of MXene, a form of

transition metal carbide [35]. It has exceptional features such as ease of functionalization, a negatively charged surface, a customizable band gap, a greater surface area, biocompatibility, hydrophilicity, high metallic conductivity, hydroxide sites, and plasmonic features. Additionally, it has high chemical durability and visible light-reactive characteristics [36]. MXene has tremendous photocatalytic potential, but it lacks the key characteristics of a semiconductor photocatalyst, hence limiting its application as a single active photocatalyst. The utilization of this substance as a co-catalyst demonstrates a high level of effectiveness in facilitating a synergistic interaction among the composite materials [37]. This interaction serves to boost the efficient transfer and separation of photoexcited carriers as well as the formation of reactive oxygen species. Consequently, the overall photodegradation activity is significantly improved [38]. Typically, the activation of electrons in MXene materials is accomplished by harnessing visible light, as it has a comparatively lower fermi level than most of the semiconductor photocatalysts. The catalytic enhancement provided by MXene extends beyond the reception of photoinduced electrons, despite its notable features, including abundant surface functional groups and a large surface area [39]. By harnessing visible light energy, absorbing contaminants, separating photoinduced carriers, offering strong support, limiting particle size, having a large surface area, and offering a lot of active sites, MXene can speed up photodegradation activity [40]. Figure 3 demonstrates various photocatalytic functions and prospective applications of MXenes.

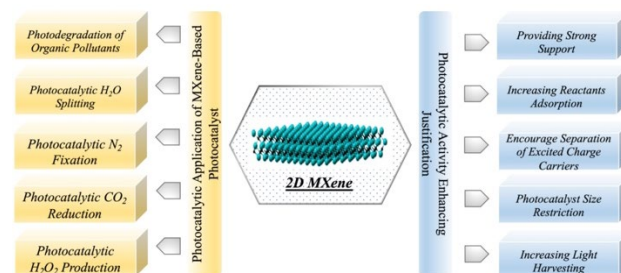
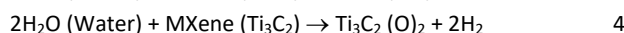
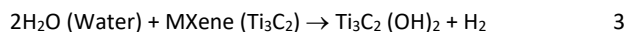
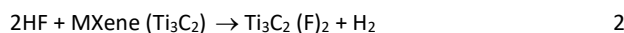


Figure 3 Illustration of MXene functional characteristics for various photoactivities and potential applications

The structure of MXene is characterized by the composition $M_{n+1}X_nT_x$, wherein 'M' symbolizes initial transition metals like Sc, Cr, Ti, V, Mn, Mo, Nb, Zr, Hf, and Ta. The variable 'X' demonstrates the presence of N or C elements, while the symbol 'T' signifies the existence of functional groups that include -F, -OH, and -O located on the outermost surface of the material [41]. MXenes typical structures, $M_2X_1T_x$, $M_3X_2T_x$, and $M_4X_3T_x$, have 'n' values from 1 to 3 as a result of variations in layers by atom numbers within the structural component cell [42]. To date, 150 variations of the MAX phase have been identified, including 14 initial transition metals and 16 group 'A' elements. The MAX phase hexagonal atoms of 'X' layers are molded with the metal atoms of the 'M' layer organized in octahedrons, and layers of group 'A' elements alternate with MX layers [43]. The structure of a 2-D MXene is illustrated in Figure 4. The metallic link between the 'M' and 'A' layer elements and the covalent connection between the 'M' and 'X' layer elements provide the MAX phase with excellent strength in mechanics and chemical durability. Compared to the X-M

connection, the A-M link has a relatively low level of strength [44]. The binding between 'A' and 'M' elements is easier to break than the link between 'X' and 'M' elements. Therefore, hydrofluoric acid (HF) etching effectively removes the elements of the 'A' layer from the MAX phase [45]. The MXene preparation procedure involves adding 2 g of Ti_3AlC_2 MAX phase precursor material to a 50 mL solution containing 40 wt% HF. The mixture is stirred continuously at ambient conditions for 24 hours, and then the suspension is centrifuged to collect the small particles, which are rinsed multiple times with DI water until their pH reading is close to 7, followed by being dried out in the oven for 18 hours at 60°C [46]. The chemical bond between the metals experienced destabilization, resulting in the etching of layers of Al atoms, leading to the exfoliation of MXene (Ti_3C_2) layers. The functional groups that are appropriate substitutes for broken Ti-Al bonds are the hydroxyl (-OH) and fluorine (-F) groups [47]. Equations 1-4 delineate the experimental reactions pertaining to the synthesis of 2-D MXene ($Ti_3C_2T_x$) in an aqueous solution.



The practical application of semiconductor photocatalysts in chemical processes is limited by two major factors: a lack of active sites and the rapid recombination of photoactivated carriers. Various techniques have been employed to improve the formation of surface-active sites and facilitate e^-/h^+ pair separation in the synthesis of novel materials [48]. The techniques include metal and nonmetal component doping [49, 50], surface alteration [51], Z-scheme structure utilization [52], interface/crystal engineering [40, 53], and Type-II heterostructure [54] utilization. In the photocatalytic technique, heterojunctions gained interest for their improved charge carrier transfer and separation, increased active sites, and enhanced capacity to absorb light for photoactivity [38].

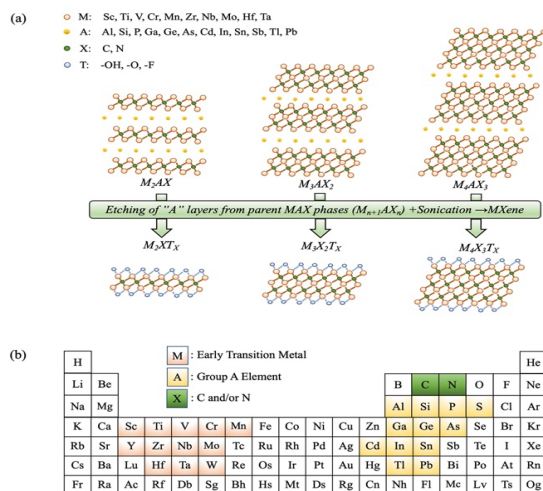


Figure 4 (a) depicts the crystal structure of both MAX phase and MXene materials, and (b) the chemical composition of MXene is represented in the periodic table of elements

Noble metals are commonly substituted as co-catalysts in the fabrication of MXene-based composites to improve their charge separation capability. The most commonly used fabrication methods for preparing composite materials are in-situ oxidation, mechanical integration, and self-assembly [55]. The simplest technique for developing composites is mechanical integration, wherein numerous elements are combined in pulverized powders or a solution. The integration of negatively charged MXenes and positively charged photocatalysts enables the creation of composite photocatalysts with self-developed functionalities because of their electrostatic attraction [56]. The in-situ oxidation strategy entails directly developing different elements on the MXene surface, as compared to self-assembly and mechanical integration processes. Thus, the use of in-situ synthesized materials with durable chemical bonding, such as MXenes, could provide significant benefits to certain design applications [57].

The discipline of energetic photo-thermal conversion has witnessed a growing interest in MXenes, primarily due to their wide spectrum of light absorption functions spanning from infrared to ultraviolet wavelengths. Hence, it is imperative to explore their potential applications in the photodegradation of toxic contaminants [58]. Numerous recent studies have been performed to explore the application of different composites based on MXene materials. These composites include $Ti_2C-ZnCo_2O_4$ [59], $ZnO/Ti_3C_2T_x$ [60], $AgNPs/TiO_2/Ti_3C_2T_x$ [61], TiO_2/Ti_3C_2 [62], $NiFe-LDH/Ti_3C_2T_x$ [63], $g-C_3N_4/Ti_3C_2$ [64], and Bi_2WO_6/Nb_2CT_x [65]. The purpose of these investigations is to assess the effectiveness of these composites in the process of photodegradation, specifically targeting the elimination of harmful contaminants. Multiple techniques have been employed to improve the photocatalytic efficiency of the material, including both covalent and non-covalent adjustments [66]. Non-covalent modification is accomplished by the collective action of three different forces, namely van der Waals forces, electrostatic attraction, and the bonding of hydrogen [67, 68]. According to Chen et al. (2018), there are three main chemical strategies for the purpose of covalent interface modification [69].

- I. Oxygen-containing groups on 2-D materials form covalent bonds with extremely small molecules such as acid halide, acid anhydride, or organic amines.
- II. To produce multipurpose composite materials, the "grafting onto" approach is used to covalently graft polymers onto 2-D materials with terminating functional groups.
- III. Selective polymerization using the "grafting from" approach is a common technique for the surface modification of 2-D materials.

The long-term viability of 2-D materials can be greatly enhanced through polymer modification. The incorporation of polymers, nanoparticles, and surface-active agents can lead to covalent modifications on the topmost layer of the material, facilitated by the presence of multiple oxygen groups at active locations [70]. The intrinsic features of MXene can be greatly altered by increasing the presence of surface functional groups by chemically modifying them. Heterogeneous composites incorporating MXene and semiconductor elements are not expected to exhibit extensive lattice mismatch at the interface. However, it is possible for structural faults to develop during the synthesis process [71]. The impact of interface lattice

mismatch on the faulty structure of composite materials requires thorough investigation. The lattice divergence problems are caused by the atomic structural features of the MAX phase and the synthesis procedures employed for MXene. The occurrence of surface defects in materials is attributed to the process of synthesis [72]. Faulty structures have no major impact on the activity of MXene-based photocatalysts. In fact, these structures can provide multiple active sites and regions with monoatomic doping, thereby enhancing the photoactivity of the composites [73]. The increased photocatalytic efficiency of MXenes is traced to their considerable electrical conductivity and hydrophilic influence, which enable them to effectively connect with semiconductor materials to promote photoinduced charge separation [74]. The exceptional conductivity of MXenes across their surface and interface enables them to effectively capture and retain photoelectrons (e^-) while preventing photoactivated carrier recombination through the formation of a Schottky junction [38].

Table 1 summarizes the photoactivity of numerous MXene-based composite materials for the degradation of harmful contaminants under an extensive spectrum of light illumination. Several composites based on MXenes have demonstrated substantial prospects for the photodegradation of persistent organic contaminants. In the overall context, MXenes have demonstrated excellent co-catalysts that improve photoactivity by facilitating photoexcited carrier transfer and separation. Additionally, they have been employed as photosensitizers to augment the light energy consumption rate by synergistically interacting with large band-gap energy materials. As a result, it enhances the number of chemically active sites and improves the absorption of visible light in composites. MXene-based composites have exhibited exceptional degrading efficacy towards various contaminants, as shown in Table, which includes acetaminophen, ibuprofen, methylene blue, rhodamine B, 2,4-dinitrophenol, Cr (VI), ciprofloxacin, ranitidine, azo dyes, and tetracycline hydrochloride.

4.0 ROLE OF MXENE IN ENHANCING COMPOSITE MATERIALS PHOTOACTIVITY

2-D MXenes has gained significant recognition and is highly regarded for its remarkable properties. It has demonstrated exceptional performance in diverse areas of research. MXene is primarily recognized for its function as an acceptor of photoactivated e^- in light-harvesting photocatalytic materials [84]. This is attributed to the semiconductors investigated in the field of photocatalysis. MXenes have become progressively popular for their special 2-D layered structure, high specific surface area, configurable chemical properties on the surface, exceptional metal conductivity, multiple surface functional groups, and incredible photoelectronic properties [85]. MXene plays multiple roles in enhancing photoactivity beyond serving as a photoexcited e^- acceptor. The addition of MXene as a co-catalyst significantly enhances the visible light absorption, photoexcited e^- transfer and lifetime, stability, and postponed recombination of the h^+/e^- pair in composite materials [38]. The following part examines the factors that enhance the photodegradation performance of composite materials.

4.1 Enhance Light Energy Harvesting

MXenes demonstrate a high degree of visible light absorption owing to their narrow band gap and distinctive structural features. The incorporation of MXene in the composite materials leads to a notable enhancement in both chemical stability and photocatalytic activity when exposed to visible light, hence facilitating the degradation of organic contaminants [86]. The findings of the literature study demonstrate that the utilization of MXene in conjunction with semiconductor photocatalysts yields a synergistic outcome, consequently enhancing the overall efficiency of photocatalysis [87]. The incorporation of MXene as a co-catalyst enhances the stability of composite materials, facilitates the transfer of photoexcited electrons, and prolongs the lifespan of photoactivated charge carriers. The synergistic impact of this phenomenon greatly improved the photoactivity within the spectrum of visible light [17]. The efficacy of $\text{CuFe}_2\text{O}_4/\text{MXene}$ in the photocatalytic degradation of sulfamethazine under visible light was examined by Cao and colleagues in 2020 through the synthesis of the material utilizing the sol hydrothermal technique. The reduction of sulfamethazine displayed a notable catalytic efficiency (70%) when employing $\text{CuFe}_2\text{O}_4/\text{MXene}$, which can be attributed to the synergistic effects arising from the integration of these two produced components [88]. Another study conducted by Zhuge et al. (2021) reported the utilization of $\text{CaIn}_2\text{S}_4/\text{MXene}$ for the purpose of photodegrading tetracycline hydrochloride. The synthesis of this compound was achieved by the hydrothermal method. The addition of MXene resulted in the inhibition of charge carrier recombination and an increase in visible light absorption (96%), therefore enhancing the photoactivity of CaIn_2S_4 . The study identified that positive holes (h^+) and superoxide radicals are the main elements that are responsible for the photodegradation process of tetracycline hydrochloride [89]. Significantly, these recyclable and durable photocatalysts possess the capability to enhance the absorption of visible light while facilitating the photodegradation of hazardous organic contaminants.

4.2 Optimize The Ability To Absorb Contaminants

The incorporation of MXene into composite materials is an innovative strategy for enhancing the adsorption efficiency of organic contaminants from effluent. The process of reactant adsorption plays a crucial role as it determines the level of photoactivity [90]. The adsorption capacity for contaminants is improved in photoactive materials as a result of their high specific surface area and the presence of numerous functional groups on their outermost layer [14]. The substantial presence of functional groups on the surface of MXene material offers the potential to boost the adsorption ability of contaminants in photocatalysis, hence benefiting a wide range of applications involving photocatalytic processes. Functional groups, including oxygen (-O), fluorine (-F), and hydroxyl (-OH), frequently emerge on MXene surfaces during various etching synthetic methods [91]. As an example, MXene's negatively charged surface facilitates the effective adsorption of reactants with a positive charge.

Table 1 Photodegradation of various contaminants utilizing MXene-based composites

Composite Photocatalyst	Preparation Technique	Pollutants	Performance	Remarks	Ref.
Zn/Ti-LDH/Ti ₃ C ₂	Hydrothermal Technique	Acetaminophen, Ibuprofen	100%-40 min, 99.7%-60 min	High photoactivity was due to MXenes e^-/h^+ separation	[75]
AgNPs/TiO ₂ /Ti ₃ C ₂ T _x	Hydrothermal Technique	Methylene blue, Rhodamine B	96%-120 min, 88%-120 min	Shows a low recombination rate under visible light irradiation	[76]
MXene/g-C ₃ N ₄	Wet Impregnation Technique	Methylene blue	Improved-180 min	Rapid photocarrier transfer and high reactive site availability	[77]
CeO ₂ /Ti ₃ C ₂	Hydrothermal Technique	Rhodamine B	75%-90 min	Higher solar energy utilization improves photoactivity	[78]
BiOBr/Ti ₃ C ₂	Self-assembly Technique	Rhodamine B, 2,4-Dinitrophenol, & Cr (VI)	99.4%-24 min, 45%-60 min, 47.5%-40 min	Formation of Schottky junctions and high carrier separation boost photoactivity	[79]
BiOCl/Ti ₃ C ₂ T _x	Self-assembly Technique	Ciprofloxacin	90%-30 min	Light absorption and e^-/h^+ pair separation improved	[80]
Ti ₃ C ₂ /MoS ₂	Hydrothermal Technique	Ranitidine	88.4%-60 min	Heterojunction facilitated charge separation and transfer smoother	[81]
ZnS/CuFe ₂ O ₄ /MXene	Solvothermal Technique	Azo dyes	100%-30 min	MXene accelerates e^-/h^+ separation under visible light irradiation	[82]
g-C ₃ N ₄ /MXene /Ag ₃ PO ₄	Self-assembly Technique	Tetracycline Hydrochloride	88.40%-60 min	S-scheme heterojunctions promote charge transfer and separation	[83]
TiO ₂ /Ti ₃ C ₂	In situ Technique	Tetracycline	97.6%-90 min	Heterojunctions enhance photocarrier lifespan and light absorption range	[62]

The increase in surface area of composite materials results in a corresponding increase in the number of active sites, which facilitates the efficient adsorption of reactants. The photocatalytic degradation performance of composite materials based on MXene is found to be superior to that of pure MXene [71]. This can be primarily due to the absence of a porous structure and active sites in pure MXene. The presence of functional groups that are active on a materials surface can form a composite with other semiconductor materials and improve the band gap energy of the material in question by adding suitable porous material and changing its characteristics, morphology, and effectiveness [51]. In 2022, Nasri and colleagues investigated the utilization of MXene-based composite material (MXene/g-C₃N₄) in the visible light photodegradation of methylene blue. The study compared the performance of the composite heterostructure to that of pure g-C₃N₄ over a duration of 180 minutes. The composite of MXene exhibited superior degradation performance compared to pure g-C₃N₄. The observed improvement in photoactivity was attributed to the increased surface area of the MXene/g-C₃N₄ composite heterostructure [77]. This higher surface area allows for greater adsorption of the reactants and provides more reactive sites, ultimately enhancing the photocatalytic performance.

4.3 Improve The Separation Of Photoactivated Charges

MXene-based photocatalysts demonstrate superior photocatalyst performance compared to traditional photocatalysts due to their ability to efficiently separate photoactivated carriers. The rapid recombination of active charge carriers significantly impacts the efficiency of photocatalysis [13]. The separation performance of the e^-/h^+ pairs in an individual semiconductor photocatalyst is limited by the recombination of photoactivated charges. The utilization of co-catalysts is imperative in order to augment photoactivity through the facilitation of e^-/h^+ pair separation generated by

light [92]. When MXene is employed as a co-catalyst, Schottky junctions are formed, which accelerate the separation of photoactivated e^-/h^+ pairs on the surface of semiconductor photocatalysts. In addition to its higher fermi energy level than semiconductors, MXene makes photoexcited charged electrons easy to flow between them [93]. In 2020, Cui and colleagues conducted a study on the synthesis of nanosheets of the Bi₂WO₆/Nb₂CT_x composite using a hydrothermal process. The purpose of this study was to investigate the photodegradation performance of methylene blue using these composite nanosheets. The researchers found that the addition of Nb₂CT_x (MXene) to Bi₂WO₆ resulted in modified photocatalytic characteristics. Bi₂WO₆/Nb₂CT_x photocatalysts exhibited superior photoactivity efficiency for MB, achieving a remarkable performance of 92.7% in comparison to Bi₂WO₆. The addition of MXene as a co-catalyst with Bi₂WO₆ enhances the efficiency of photoinduced e^-/h^+ pair separation [65]. A separate study conducted hydrothermal synthesis to create a composite material consisting of MXene-Ti₃C₂ and MoS₂. The MXene/MoS₂ composite exhibited strong visible light photoactivity towards ranitidine. MoS₂ exhibits a relatively small band gap of 1.8 eV, rendering it a photocatalyst responsive to visible light. However, its catalytic activity is limited by its rapid recombination of photoactivated e^-/h^+ and low light absorption efficiency. The introduction of MXene enhanced charge separation and minimized recombination, thereby improving photocatalytic activity [81]. Furthermore, MXenes have the capability of exceptional electrical conductivity, which renders them highly effective in trapping electrons, facilitating the capture of photoactivated electrons, and enhancing the transfer and separation of photoinduced carriers. Obtaining this advantage is challenging in traditional 2-D atomic crystals, including bimetal hydroxides, layered metal dihalides, and graphene [94]. These features make them highly suitable for environmental restoration functions.

4.4 Enable Significant Surface Area And Active Sites

Two-dimensional (2-D) MXene nanomaterials possess significant advantages over semiconductor photocatalysts, specifically due to their extensive surface area and large number of active sites available for efficient adsorption of organic contaminants [95]. MXenes exhibit the ability to transform the adsorbed reacting agent and the interaction pathway through their diverse composition and functional groups on the surface. The particle size of a photocatalyst plays a major part in determining the amount of photocatalytic activity it produces. However, photocatalysts have a tendency to aggregate and form larger particles as a result of their significant surface energy [95]. Consequently, this aggregation leads to a reduction in the contact area between the photocatalyst and the reactant, thus limiting the overall efficiency of the photocatalytic process. Semiconductor photocatalyst particle size plays an essential role in photoactivity as it affects the contact area and the number of surface-active sites available for reacting agents. In chemical reactions, nanoparticles normally aggregate, leading to their deactivation as a result of their elevated energy at the surface [96]. The composite materials based on MXene as a co-catalyst, often synthesized through the etching technique, possess numerous functional groups on the surface. This characteristic makes them highly appropriate as substrates for growth to control the particle size of photocatalysts, potentially providing higher performance. The negatively charged surface has the capacity to absorb metal cations, facilitating the corresponding unified growth of catalytic materials [41]. Hence, MXene-based nanomaterials can attain a substantial specific surface area, hence offering an extensive number of surface-active sites to enhance the photocatalytic efficiency of composite materials. MXenes can serve as effective supporting materials for certain photocatalytic reaction mechanisms due to their valuable surface area. This property enables them to reduce the particle size and prevent the aggregation of nanoparticle-sized semiconductor materials [97]. In a study, $\text{TiO}_2/\text{Ti}_3\text{C}_2$ composite photocatalysts were produced by electrostatic self-assembly techniques and tested for methyl orange degradation under visible light. The composite degraded methylene blue faster than pure mesoporous TiO_2 under visible light irradiation. The $\text{TiO}_2/\text{Ti}_3\text{C}_2$ photocatalysts increased surface area, and interfacial contact boosted photocatalytic performance. These features promote reactant adsorption and reactive sites, increasing photoactivity. This study provides evidence for the potential application of MXene family compounds as effective co-catalysts in the field of photocatalysis without the need for noble metals [98]. In another investigation, electrostatic self-assembly generated a $\text{BiOCl}/\text{MXene}$ composite material that photodegrades (~90%) ciprofloxacin in 30 minutes under sunlight exposure. Due to its extensive surface area, strong electrical conductivity, and accessible active sites, MXene is used to construct good heterostructures with BiOCl . The MXene-based composite improves photocatalytic degradation by increasing visible light absorption and reactant adsorption [80].

4.5 Functioning As A Strong Form Of Support

MXene exhibits enhanced chemical, thermal, structural, and mechanical stability when compared to alternative two-dimensional materials such as reduced graphene. These

features significantly influence the photoactivity of MXene-based composite photocatalysts [99]. MXene is a suitable support material for semiconductor-based composite materials, facilitating uniform development and effective scattering of photocatalytic nanosized particles including $g\text{-C}_3\text{N}_4$ [100], TiO_2 [101], ZnO [102], CdS [103], and ZnS [104]. This enables the creation of Schottky heterojunctions and a large number of surface-active sites, enhancing the mechanical support between the materials. The long-term stability of Ti_3C_2 is an essential factor for its potential industrial applications. The energy of the lattice is an essential variable in determining the stability of a crystal. Greater energy from the lattice makes crystal stability more challenging [104]. In 2012, Shein and Ivanovskii conducted first-principles calculations to ascertain the energy density of the lattice of MXene. Their findings revealed a negative value. This finding implies that MXene exhibits stability when subjected to typical conditions of pressure and temperature [105]. Fang and colleagues in 2019 produced an $\text{Ag}_2\text{WO}_4/\text{Ti}_3\text{C}_2$ composite material. The inclusion of MXene greatly enhanced the photodegradation efficiency, stability, and resistance to corrosion of Ag_2WO_4 . The Schottky heterojunction of composite photocatalyst ($\text{Ag}_2\text{WO}_4/\text{MXene}$) material achieved a photocatalytic removal rate of 88.6% for sulfamethazine and 62.9% for tetracycline hydrochloride [106]. The close contact and Schottky heterojunction can enhance the migration and separation of photoactivated carriers, leading to increased photodegradation performance. Moreover, MXene-based photocatalysts induced by the chemical substances typically exhibit a structure with pores, leading to a significant enhancement in their specific area of contact [40].

Figure 5 demonstrates the substantial role of MXene as a composite co-catalyst in improving the efficiency of photodegradation for persistent organic contaminants. The functionality of nanocomposites is influenced by factors such as chemical composition, particle size, morphology, and the microstructure of the material. A composite photocatalyst can be synthesized by combining two catalytic materials with distinct chemical properties. In heterojunctions, the mechanism facilitates the transfer of photoexcited e^- from the higher negative Fermi energy state in the conduction band to a region with a lower negative Fermi state. The positively charged h^+ particle also undergoes a transition from a higher positive Fermi energy state within the valence band to a lower positive Fermi energy state near the interface. This mechanism inhibits the recombination of photoactivated electrons and holes. In addition, MXene-based composites exhibit enhanced light energy harvesting, contaminant absorption, charge separation, high surface area, and active sites and serve as a strong form of support, as illustrated in the figure. Consequently, the composites demonstrated an overall enhancement in their photocatalytic activity.

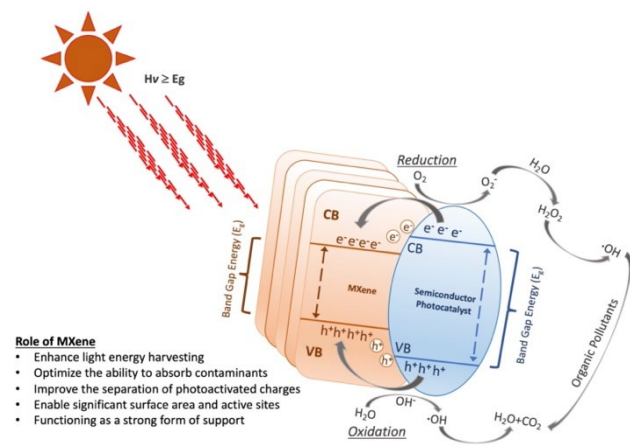


Figure 5 Illustrates a schematic representation of the role of MXene in composite materials as a co-catalyst

5.0 CONCLUSION

As a co-catalyst in composite materials, MXene photodegrades persistent organic contaminants in the aqueous medium. MXene is employed as charge transfer bridges that enhance carrier separation by the metallic conductivity, or Schottky junction, and also as a photosensitizer to increase photon utilization rate by combining with large bandgap semiconductor photocatalysts. MXenes could also increase chemical active sites and composite visible light absorption. MXene research is still in the stages of development compared to other 2-D photocatalytic materials. Researchers anticipate numerous challenges and prospects as they study MXene's immense potential in multiple fields. This review should help rationally design MXene-based photocatalysts for practical applications that are efficient and stable.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper

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