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MXenes – based systems as photocatalysts.
Sistemas basados en MXenes como fotocatalizadores.

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June 2021

Universitat de Barcelona

B:KC Barcelona Knowledge Campus
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Lo bueno de la ciencia es que es cierta,
independientemente de si crees o no en ella.

Neil deGrasse Tyson

Al hilo de la inspiradora frase de Neil deGrasse, la cual pretende claramente separar la opinión de los hechos, este trabajo me ha permitido ahondar con mayor profundidad en el mundo de los MXenes. Este mundo, aún muy virgen y con un interesante recorrido por delante, me ha brindado la posibilidad de acceder a numerosos artículos y, adquirir unos apasionantes conocimientos y espero también haber aportado mi pequeño granito de arena con mis conclusiones.

Agradezco a Pilar Ramírez de la Piscina la apuesta en mi persona, introduciéndome en un mundo muy específico y aún por desarrollar. Habiéndome inquietado en un principio el tema propuesto por lo novedoso y por tratarse de un área en plena ebullición científica, debo agradecer finalmente, la posibilidad que Pilar me ha ofrecido, perdiéndome en un tema, cuanto menos curioso y con una proyección futura que permitirá grandes avances tecnológicos.

Así mismo, agradezco a Francesc Illas, profesor de esta universidad y estudioso de la materia en cuestión (especialista en catálisis de los MXenes) quien me ha acabado de orientar y aclarar algunas dudas sobre el tema.

No debo olvidar a todos los que me rodean (familia y amigos), que han soportado mis momentos de tiniebla y estrés así como la ayuda moral que me han brindado incondicionalmente.

Estoy feliz de haber apostado por el mundo de la ciencia que, en este año 2021 más que nunca, ha empezado a tener el reconocimiento y posición que se merece a nivel social. La ciencia está aquí para avanzar, evolucionar y ayudarnos a todos, a vivir en un mundo más próspero y feliz.

REPORT

CONTENTS

1. SUMMARY

This bibliographic report summarizes the use of MXenes in photocatalysis based on the research of different papers published in the recent years. MXenes are two-dimensional materials formed by layers of carbides or nitrides, mostly carbides that have many applications in different fields. Due to their unique physicochemical properties, they are used in photocatalysis, electrocatalysis, lithium-ion batteries and biomedicine, among others. One of the most promising applications is photocatalysis. It has been analyzed that MXenes could have remarkable properties that allow a rapid separation of photogenerated charge carriers acting as photocatalysts. MXenes also have abundant superficial groups on the surface that allow them to have a high efficiency in photoconversion.

For these reasons, both theoretical and experimental studies have been carried out to demonstrate the potential of MXenes in different photocatalytic applications. This bibliographic study aims, on one hand, to relate the composition, structure and terminal groups to their photocatalytic behavior and, in addition, to acknowledge in which photocatalytic processes they have been applied and which are the most studied.

Keywords: MXenes, Photocatalysis

2. RESUM

Se trata de un trabajo bibliográfico en el que se ha resumido la utilización de los MXenes en la fotocatálisis a partir de la investigación de diferentes artículos en los últimos años. Los MXenes son unos materiales bidimensionales formados por capas de carburos o nitruros, mayoritariamente carburos que tienen muchas aplicaciones en diferentes ámbitos. Debido a sus propiedades fisicoquímicas únicas, estos tienen aplicaciones en fotocatálisis, en electrocatálisis, en baterías de iones de litio y en biomedicina entre otros. Una de las aplicaciones más interesantes es la fotocatálisis. Se ha analizado que el MXene podría tener unas propiedades destacables que permitan una rápida separación de portadores de carga fotogenerada actuando como fotocatalizadores. Estos también tienen abundantes grupos superficiales en la superficie que les permite la alta eficiencia en la fotoconversión.

Por estos motivos, se han realizado estudios tanto teóricos como experimentales que demuestran el potencial que tiene el MXene en diferentes aplicaciones fotocatalíticas. Este estudio bibliográfico pretende, por un lado, relacionar la composición, la estructura y los grupos terminales con su comportamiento fotocatalítico y, por otro lado, dar a conocer en qué procesos fotocatalíticos se han aplicado y cuáles son los más estudiados.

Palabras clave: MXenes, Fotocatálisis

3. INTRODUCTION

Photocatalysis refers to the chemical reactions that take place in the presence of light and a photocatalyst. The term is expressed as a combination of *photo* (derived from photon) and *catalyst* (substance that alters the reaction rate in its presence). The main role of photocatalyst is to accelerate the photoreaction by interacting with the substrate in its ground or excited state.[1]

The word catalyst was first used in the sixteenth century by a chemist called A.Libavius in his book *Alchymia*. The researcher Berzelius assigns that term to reactions that occur in the presence of compounds that are not directly involved in the chemical transformation. Shortly thereafter, Ostwald defined catalysis as a kinetic phenomenon in which the catalyst participates. The function of this catalyst is to change the rate of the reaction without changing the chemical equilibrium.[1]

3.1. PHOTOCATALYSIS

The electronic structure of the materials is essential to understand its photocatalytic properties. Depending on the distribution of the electronic states, there are three types of materials as depicted in figure 1.

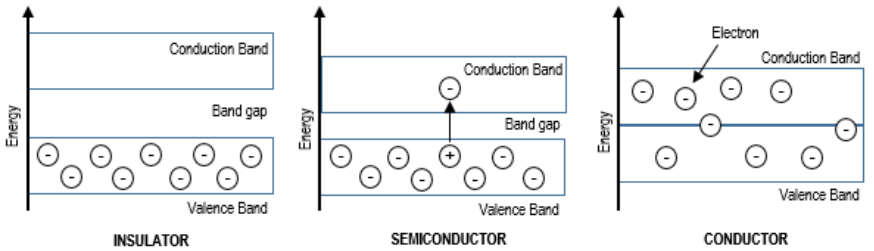


Figure 1: A diagram showing the different sizes of bands gaps for insulator, semiconductor and conductor.

Insulating materials are those that do not allow current to pass through because they have a very high energy band gap, which is the energy difference between the Most Occupied Molecular Orbital (HOMO) of the Valence Band (VB) and the Lowest Unoccupied Molecular Orbital (LUMO) of the Conduction Band (CB). Therefore, insulating materials under light-promoting conditions leave no room for an electron transfer process and therefore do not exhibit conductivity properties.[2,3]

Referring to the electrical and thermal conductivities of semiconductor materials, it can be seen that with increasing temperature, the thermal conductivity increases while the electrical conductivity decreases. They have no forbidden band, which means that electrons can freely ascend to the CB. Semiconductors are in between, because at very low temperatures they do not conduct electric current and therefore act as insulators, but as their temperature increases they acquire the properties of conduction and therefore increase their conductivity.[1]

Most primary light absorbers used in photocatalysis are semiconductors due to their light absorption properties.[1] The most commonly used in photocatalysis are semiconductors, which are constituted of a three-dimensional network where the atomic orbitals overlap. They have a relatively small band gap value and therefore the electron can move from the VB to the CB when there is incidence of light. Fundamentally, the VB is occupied by electrons that are in the last shell or energy level of the atoms, which are the ones who will shift to the CB and promote the conductivity of the material. Semiconductors can be type “p” or type “n”, depending on the predominating charges, positive or negative, respectively.

Photocatalysis’ basic principle consist on the excitation of one electron (e^-) from the VB to the CB by the action of a photon creating a hole (h^+) in the VB.[2] The initial stage of the process consists of the generation of an electron-hole pair in the semiconductor particles. When a photon with *hv* energy higher than the band gap of the material, an electron (e-) is boosted from the VB towards the CB, generating a gap (h^+) in the VB. In solid state physics, the VB and the CB are the ones closest to the Fermi level, which is defined as the thermodynamic work required to add an electron to the body.[2,3,4]

Figure 2 shows that there are two reactions at once, an oxidation reaction and a reduction reaction. The excited electrons work as a reducing agent and the holes generated work as oxidants.

In the figure 2 we have an example of a semiconductor in general:

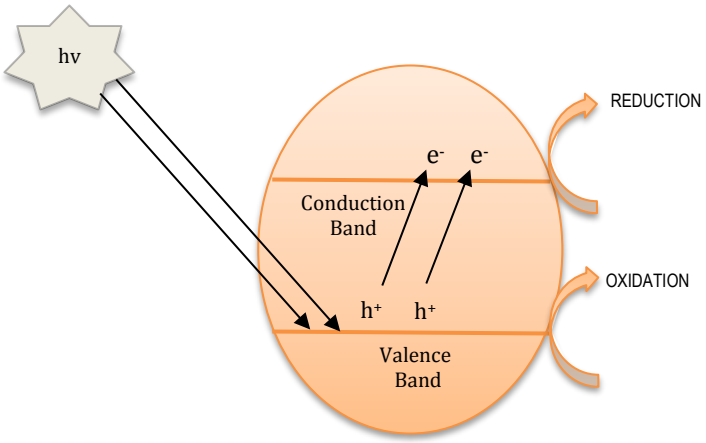


Figure 2: Photocatalysis reaction basic scheme.

Photocatalyst such as TiO_2, ZnO, CdS, WO_3, ZnS, iron oxides and Bi_2WO_6 are the most studied.[5,6] Normally these photocatalysts are used in heterogeneous photocatalysis. In recent years, TiO_2 has been the most studied photocatalyst due to its low cost, redox potential, environmental compatibility and good photostability.[7,8] Visible light cannot be used for TiO_2 because ultraviolet light is needed for the electron transition to take place and thus generate electron-hole pairs.[9,10,11,12] TiO_2 is a n-type semiconductor that has oxygen vacancies on the surface that correspond to unpaired electrons. Those results in a transference from a 2p oxygen orbital to the CB, which is formed by 3d orbitals of titanium.[13] However, TiO_2 has two disadvantages, which are its wide band gap and its high rate of photogenerated carrier recombination. Based on strategies that include metallic/non-metallic doping, cocatalyst loading and the construction of heterojunctions, solutions are being developed to expand the response range to light and improve the utilization rate of photogenerated carriers.[14]

Another photocatalyst used is graphene, which was the first 2D material. This nanomaterial is made up of a layer of hexagonally positioned carbon atoms linked by covalent bonds. Graphene has a high electron and hole mobility that prevents the pairs generated when lighting the catalyst from recombining and destroying each other before reaching the surface. These characteristics make graphene a good candidate for photocatalysis.[14]

Photocatalysis is applied to different areas, such as wastewater treatment, to minimize the impacts generated by industries in water sources, from water disinfection and contamination from titanium dioxide photocatalyst, in air pollutant degradation, nitrogen fixation and many others.[15,16]

According to its structure, there are several families of photocatalysts, being de MXenes one of the newest and most promising ones.

3.3. MXENES

Since 2011, a new two-dimensional material has a great relevance in photocatalytic processes, this newly discovered photocatalyst is called MXene. This material is formed by thick layers of carbides, nitrides or carbonitrides atoms; being carbides and nitrides the most typical ones. These materials are very new and are currently being studied for many applications since they have a high potential due to their good chemical properties.[17,18]

Figure 3 shows the composition of MXenes. They are composed of transition metal (M) layers such as (Ti, Sc, V, Mo and others) that are interspersed with n layers of carbon or nitrogen (X) and are terminated with a surface functional group (denoted as T_x) with a general formula of $M_{n+1}X_nT_x$, where n= 1-3. MXenes sheets surfaces may end with -OH, -O, -F, -S, -Cl, -Se, -Br, -Te, -I but these usually end with –OH, -O or -F.[17,18]

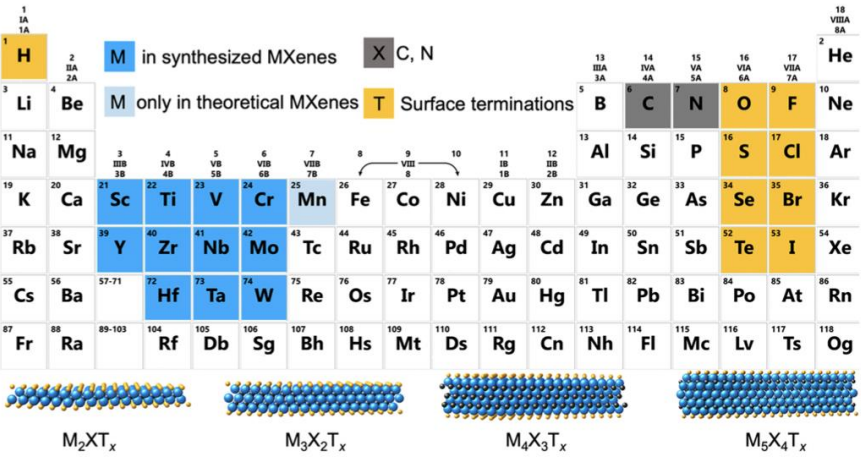


Figure 3: Periodic table showing the composition of MXenes. Adapted with permission from [18] Copyright 2021, ACS Nano.

As shown in figure 4, the 'M' atoms are organized in a compact hexagonal structure, in which the octahedral sites are filled with the 'X' atoms.[19] Several studies have evaluated that the most stable configuration occurs when the atoms of the "T" terminations are placed in different positions than the "M" and "X" atoms. Although, in some compounds, "T" atoms are above the "X" ones, in order to enhance their electronic interaction.[14]

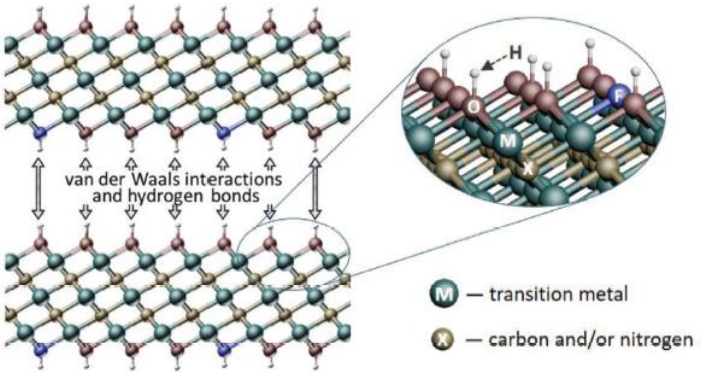


Figure 4: Schematic illustrations of the Surface of MXenes with general formula of $M_{n+1}X_nT_x$. Adapted with permission from [24] Copyright 2020, Advanced Functional Materials.

M atoms are arranged in a close-packed structure and X atoms fill the octahedral interstitial sites. The M-X bonds are less chemically active and more stronger than the M-A bonds, therefore A layers can be selectively removed by a strong acid (e.g. HF or HCl) etching to produce $M_{n+1}X_n$ layers than can be further separated by sonication.[20,21] Since the first MXene discovered in 2011 (Ti_3C_2); which is the most studied one; more than twenty types of MXenes have been obtained, such as $SrTiO_3$, Ti_3CN, TiNbC, Mo_2C, Nb_2C, V_2C and Y_2CF_2.[14,20,22,23] All of these have not been comprehensively studied yet.

MXenes can be found in different structures as: mono-M elements (e.g. Ti_2C, Nb_4C_3); solid solutions (e.g. $(Ti,V)_3C_2$, $(Cr,V)_3C_2$; ordered out-of-plane double-M elements, in which one transition metal occupies the external layers (e.g. Mo and Cr), while the central ones are filled by another metal (e.g. Ta and Nb), for example Mo_2TiC_2 and $Mo_2Ti_2C_3$; ordered in-plane double-M elements, in which the different M elements are ordered in the basal plane (e.g. $(Mo_{2/3}Y_{1/3})_2AlC$; vacancies ordered (e.g. $Mo_{1.33}CTx$) and vacancies randomly distributed (e.g. $Nb_{1.33}CTx$).[14]. The different structures mentioned are observed in figure 5.

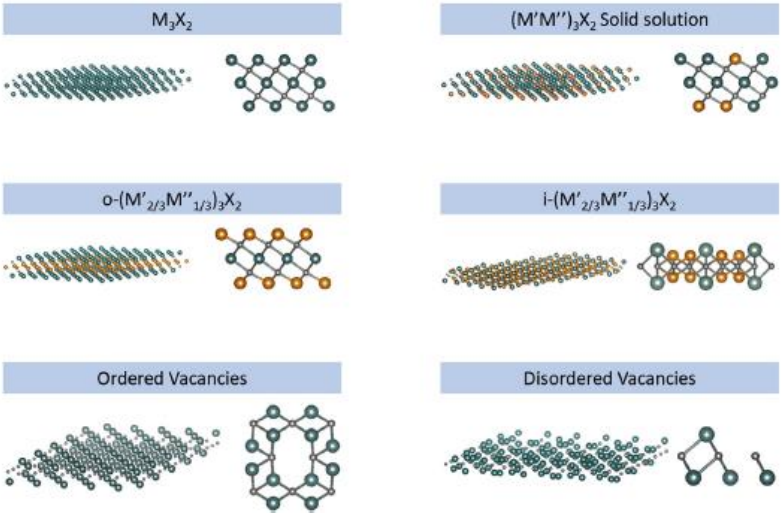


Figure 5: Different MXenes structure. Adapted with permission from [19] Copyright 2019, Ceramics International.

In figure 6 is observed the structure of this material, based in nanolayers. This allows increasing the active surface of the material resulting in enhanced catalysis rate.

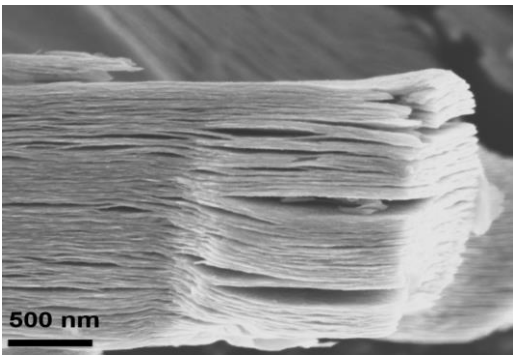


Figure 6: Image obtained by scanning electron microscope of Ti_3AlC_2. Adapted with permission from Creative Commons.

Referring to stability of MXenes, they are not stable in the presence of oxygen or water. However, they are relatively stable in dry air or in oxygen-free degassed water. In addition, when these are exposed to light, the oxidation process of the colloidal solutions of the MXenes can be accelerated. In consequence, it is recommended to store MXene colloids in a dark environment without oxygen.

Different applications of MXenes in several areas can be found. They participate in reactions as photocatalysts, in biomedicine for the detection of cancer biomarkers, in lithium-ion batteries they act as accelerators in the charge period, reducing it to just few seconds. Numerous theoretical and experimental studies are currently underway to demonstrate the great potential that MXenes can have when used as a photocatalyst in photocatalysis systems.[25]

A further analysis of MXenes' properties, their synthesis and their applications in photocatalysis systems will be carried out in the results and discussion section.[17]

4. OBJECTIVES

The main objective of this bibliographic research project summarizes the current use of MXenes as photocatalysts.

In this context special attention will be pay to:

- The relation between the composition and structure of MXene to its catalytic behaviour.
- Determine which MXenes are most commonly used.
- To define which MXenes terminations show the best photocatalytic behaviour.
- Analyse in which processes MXenes have been studied.

5. METHODS

Bibliographic research on this project was subjected to an exhaustive research on MXenes and their based systems as photocatalyst from two main data bases including Science Direct® and Scifinder® available on the CRAI of the Universitat de Barcelona. The search criteria were based on keyword (e.g. MXenes, photocatalysis, etc.), type of document (e.g. review, article, journal, etc.) and year of published.

For the last 20 years, there have been published more than 16,700 documents about MXenes. This research report is focused on articles based on MXenes in photocatalysis systems. For the last 9 years there have been more than 1,200 documents about Mxenes in photocatalysis systems publicated. However, the exponential increase of these publications has been in the last 5 years, being the 2020 the highest peak, as shows Figure 7. If one takes a close look and compares the individual years with the total amount of documents, will see that around 40% of the documents corresponds to the year 2020. This shows that MXenes generated a great impact and interest in many research fields such as industries, universities, etc. If you look at this year 2021, publications are increasing in proportion to the other years. This means that this field is very interesting and that there is still a lot of research to be done.

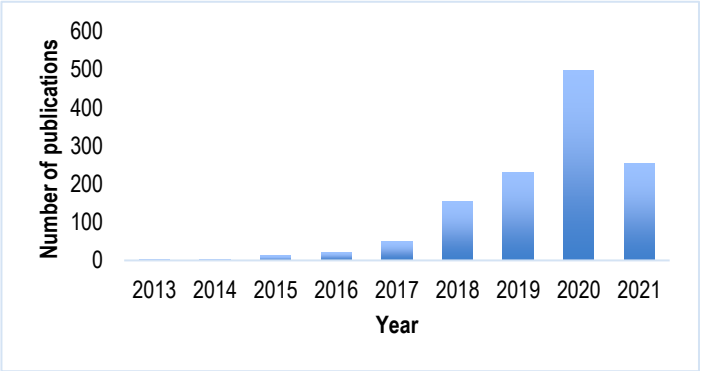


Figure 7: Published MXenes base on photocatalysis systems from 2013-2021.

The work on this project has been focused on the search of different articles. Many articles associated to photocatalysis, to MXenes and MXenes based on photocatalysis systems have been studied. In general, the report is focused on the last 5 years, between 2016-2021.

Based on this bibliographic research, it has been discovered that there are 4 main research groups which are in China, Philadelphia, Missouri and the University of Barcelona. All of them were contacted and the following questions were asked:

- How long have you been researching MXenes?
- How do MXenes work in photocatalysis?
- What are the advantages of MXenes in comparison to other catalytic elements?
- What reactions do they cause in the photocatalysis? Are they involved in these four reactions: Photocatalytic water splitting, Photocatalytic CO_2 reduction, Photocatalytic pollutant degradation, Photocatalytic N_2 fixation?
- What applications do you see coming in the future?
- What are the most important things about MXenes you found in your research?
- Do you have enough researchers to continue with your research?

As of now, the replies received were from one of the main discoverers of MXenes, the Philadelphia author Gogotsi, who explained that he is not studying MXenes in photocatalytic systems because he and his team are researching the MXene nanomaterial which allows gas separation for the use of hydrogen fuel. This author enclosed some of his articles on MXenes, some of which, have been useful for this work.

In addition, Francesc Illas a professor from University of Barcelona has been really helpful explaining his MXenes research work. His research is focused on the application of this material on catalysis reactions.

6. RESULTS AND DISCUSSION

Based on the collected information during the research, we can sum up all the applications that MXenes have in the photocatalysis process.

The main role of a MXene is that it acts as a photogenerated electron acceptor for light-gathering materials in a photocatalysis process, due to its Fermi level, which is lower than most semiconductors studied in this process. MXenes have a layered structure that contain more than one element. The density functional theory (DFT) suggested the first structure of these 2D materials, the Ti_3C_2. This structure is composed of several layers of titanium bonded to carbons and with OH terminations.[26]

MXenes have different properties, which include: electrical, electronic, mechanical, thermal, magnetic and optical. Two of the main properties of this materials are electrical and electronic, which are related with their stoichiometry, the alteration of functional groups or the formation of a solid compound. Experimentally, the electrical conductivities of MXenes are similar to the ones that graphene has, but greater than carbon nanotubes and graphene oxide materials.[19,27] This shows that MXenes are good conductors of electricity.

Mechanical properties also have a huge interest because MXenes are composed of strong M-C and M-N bonds. Thanks to these bonds, these materials have a better interaction with the polymeric matrices than graphene has. Other studies have validated that the Young modulus of carbides and nitrides of MXenes decrease when the number of layers increase.[19] The presence of terminations reduces the values of the elastic constant in the following order: O > F > OH, but increases its critical deformations. An example found in the articles [27] demonstrated that the Ti_2C can be deformed up to 9.5, 18 and 17% at biaxial tensions. However, the Ti_2CO_2 can reach deformations up to 20, 28 and 26,5%.

Among the thermal properties, as has been demonstrated in the study [28,29], we can find that the thermal expansion coefficients of MXenes are low and their thermal conductivities higher than other semiconductors such as phosphorene or the MoS_2 monolayer. Experimentally, just the

thermal conductivity of $Ti_3C_2T_x$ has been studied, which means there is not enough information about these properties, and therefore it should be proved with other compounds.

To determine the magnetic properties of MXenes, an individual analysis of each one of them and their functional groups must be performed. Studies have shown that Ti_3CNT_x and $Ti_4C_3T_x$ attached to functional groups become non-magnetic; however, compounds such as Cr_2CT_x and Cr_2NT_x become ferromagnetic at room temperature bound to OH and F groups. Nevertheless, these studies have not yet been demonstrated experimentally since the synthesis of MXene compounds is limited.[19]

Optical properties are very important for photocatalysts. First of all, it's important to highlight the absorption bands that are between 300-500 nm, as this is the range in which the catalyst must be irradiated in order to have a photocatalytic effect. It should be noted that these optical properties may be affected by the presence of functional groups such as OH or F.[19]

MXenes are made from a bulk crystal called MAX (M denotes a transition metal, A represents an element from the 13th or 14th group of the periodic table such as aluminum or gallium and X is either carbon or nitrogen).[7,14,26,30,31]

The MXene's manufacturing process is very complex due to the need of acids and strong oxidants in large amounts. This generates an elevated cost that limits the possible applications in different areas.[32]

MXenes can be synthesized trough different methods. Among those, we can find HF etching using a mixture of HCl and LiF, hydrothermal/solvothermal treatment, calcination method, electrochemical method and molten salts.

The most common method is HF etching using a mixture of HCl and LiF, even though it is also possible to etch with HCl. This method consists of a selective elimination of the "A" elements from the MAX phases in the presence of HF at room temperature. MXene's surface is negatively charged due to the presence of surface functional groups, which allows them to adsorb the metal cations from an electrostatic attraction and enables the formation of the semiconductors on their surface.[32] In this case, the etching solution contains traces of HF. In order to avoid the use of HF, there are 3 ways to synthesize MXenes:

1. Hydrothermal method in an aqueous NaOH solution, which is carried out in a closed container under high pressure and high temperature conditions. This is beneficial for the production of composites with highly crystalline and controlled morphologies.[14] This

method is particularly used to prepare MXene-based compounds with a 2D/2D structure. For example, Cao et al.[33] applied an electrostatic attraction and a thermal strategy to Ti_3C_2 / Bi_2WO_6 compounds, which indicated the formation of a 2D/2D heterojunction.

2. Molten salt method to produce 2D nitrides. This synthesis has only been used for the production of Ti_4N_3 and it requires the use of fluoride salts and a high temperature.[25]
3. Electrochemical method at room temperature in HCl or ammonium chloride electrolytes.[25]

The previously discussed etching process is followed by an exfoliation, where the dissolved atomic layers are replaced by several terminations linked by hydrogen bridges or van der Waals forces resulting in MXenes. The individual layers can be delaminated in aqueous colloidal suspensions in order to obtain other 2D materials. These layers can be exfoliated by intercalation with large organic molecules or with cations, by agitation or by sonication. Finally, it is also worth mentioning that, for the synthesis of some ultra-fine MXenes, this exfoliation process is not necessary to obtain MXenes with one or a few layers. [25]

Furthermore, the calcination method has also been explored for the synthesis of MXene-based photocatalysts. This method consists of a heat treatment procedure under controlled temperature and atmosphere whose purpose is to eliminate the present volatile components. MXenes have been studied to be easily oxidized at high temperatures and either oxygen or air atmospheres. Yang et al.[34] used the calcination method to synthesize Ti_3C_2/g-C_3N_4 from a mixture of Ti_3C_2 and urea, where urea releases NH_3 gas to exfoliate the multilayer of Ti_3C_2 in nanofilms and generate g-C_3N_4 on the surface. Using calcination, the yield of Ti_3C_2 is improved.

Ti 2D-based MXenes have been considered excellent candidates for TiO_2 synthesis and TiO_2-based photocatalysts.[14] In their article, Yuan et al. [35] studied a 2D carbon / TiO_2 layered compounds that were obtained from the oxidation of CO_2 with Ti_3C_2. They improved the synthesis method by intercalating sulfur layers in Ti_3C_2, which resulted in TiO_2 based compounds doped with carbon and sulfur. With this study, it was stated that the layer intercalation could improve the separation of photogenerated carriers and, subsequently, more active sites would be formed.

In short, Ti_3C_2 is the most widely used photocatalyst in photocatalysis. This is because the MAX phase naturally exists and its synthesis protocol is well established.

The etching different methods used to obtain MXenes are done with different components at specific temperatures, as shown in table 1.

Table 1: Distinct etching methods used to get MXenes.[25]

Type of method	Etchent	Temperature
Acid with fluorine	HF	Room temperature
	H_2O_2 + HF	40
	HCl + LiF	35-55
	HCl + (Na, K or NH_4F)	30-60
	NH_4HF_2	Room temperature
Molten salts	LiF + NaF + KF	550
Hydrothermal	NaOH	270
	$NaBF_4$, HCl	180
Electrochemical	NH_4Cl/TMAOH	Room temperature
	HCl	Room temperature

6.1 MXENES IN PHOTOCATALYSIS

As we previously stated, due to MXenes conductivity, they can be used as photocatalysts. In this process, the photogenerated electrons are excited to the CB, generating holes in the VB.[32]

The different terminal groups are important for the catalytic behavior of MXenes, due to the high availability of active sites for the adsorption of atoms and their low ΔG^o. For example, the presence of terminal groups such as -O, have turned out to be beneficial for hydrogen production.[24]

Figure 8 shows the mechanism of the MXenes in a photocatalyst system. This mechanism is the same as the one described in the introduction. The only difference between them is that in this case, a MXene is used as a photocatalyst instead of another type such as TiO_2.

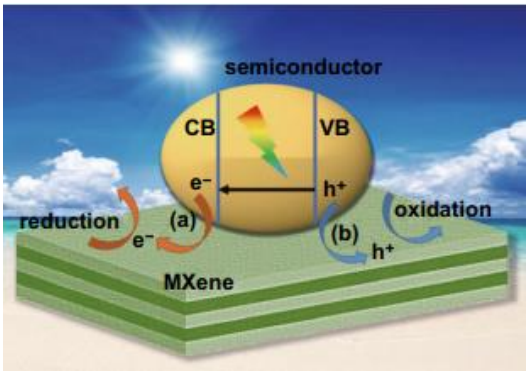


Figure 8: Mechanism of MXenes applied in photocatalysis. Adapted with permission from [32] Copyright 2019, Nano-Micro Letters.

MXenes play different roles in the improvement of the photocatalytic activity, which are their action as a deposit of electrons, as active sites and as adsorbents among others. These are briefly detailed below.[32]

MXenes have a high electrical conductivity and a favorable structure that allows them to act as a reservoir of electrons to trap and transport photoelectrons from semiconductors. This promotes the separation of charge carriers and improves the photoactivity of MXene-based compounds.[32]

MXenes can also act as absorbents or as active sites. This last one is because the surfaces that have functional groups terminated in –OH, -O or –F serve as active sites for different photocatalytic applications, such as the hydrogen evolution reaction. The Gogotsi group has reported in an article [38] the use of $Ti_3C_2T_x$, a MXene that is used as an absorbent for dyes. In order to investigate the degradation of $Ti_3C_2T_x$, they chose two colorants; a cationic methylene blue (MB) and an anionic acid blue 80 (AB80). In the presence of the MXene $Ti_3C_2T_x$ for more than 20 hours, no change in AB80 concentration was observed. On the contrary, under the same conditions but within 8 hours instead of 20, a decrease in the concentration of MB was observed. These results demonstrate that $Ti_3C_2T_x$ has a preference for adsorbing the cationic MB dye and not the anionic AB80. This is due to favorable electrostatic interactions between negatively charged $Ti_3C_2T_x$ surfaces and cationic MB molecules. In short, these results show that MXenes have great potential as adsorbents for 2D materials and it is expected that, in the future, they will

contribute to photoactivity for specific reactions, such as the degradation of cationic dyes. All these functionalities are also applied to graphene.

Table 2: Comparison of the different functionalities of MXenes and graphene for photocatalysis.[40]

Functionalities		**Contributing factors**		**Competitive of MXenes**
		MXenes	**Grapehene**	
For photocatalysts fabrication	Growing platform	Surface functional groups such as -OH, -O and –F	Surfactants; Surface functional groups of graphene oxide precursors	High
	Semiconductor precursor	Metastable transition metal atoms	N.A.	High
For photoactivity improvement	Electrons reservoir	High electrical conductivity and favourable energy structure	High electrical conductivity and favourable energy structure	High
	Active sites	Versatile transition metal atoms	N.A.	High
	Adsorbent	Electrostatic interactions	π – π interactions	Moderate
For photostability enhancement	Prohibiting photoreduction	Shutting photogenerated electrons	Shuttling photogenerated electrons	Moderate
	Alleviating cations leaching	Local cations confinement	N.A.	High

A comparison between the functionalities of MXenes and graphene, as shown in table 2, leads to the conclusion that MXenes have a polar surface that allows interfacial charge transfer in order to improve catalytic efficiency. In contrast, graphene possesses surfactants that deteriorate its properties and complicate processing. Another point to note is that MXenes can be used as semiconductor precursors; a feature that graphene does not have. As summarized in table 2, MXenes can attract multiple factors to drive the activity of photocatalysts. Among these, MXenes have a high conductivity. Although graphene also has a high conductivity, they require materials for their construction in which reduction processes are generated resulting in a partial recovery of conductivity. In particular, it has also been found that MXenes can be used as active sites for photocatalytic applications, which have not been reported in graphene. MXenes and graphene share similar characteristics as adsorbents of reagents by electrostatic interactions or π - π interactions.[40]

Some considerations to take into account when using MXenes in photocatalytic applications are their morphological control, the problem of their stability and the mutability of their electronic structure.[24]

When MXenes are used for semiconductor growth, some semiconductors are grown on the open edge of MXenes rather than in their basal plane. This reduces the functions of the MXenes as a growth platform and charge carriers since the interfacial interaction between the semiconductors and the MXene is reduced. In addition, it was reported that the resistivity of MXenes increases as their thickness also increases, generating a multilayer stack of MXenes. This results in a conductivity decrease and, consequently, affects the performance of MXenes when they have to transport and accept charge carriers. In order to avoid these problems, it is necessary to effectively etch the MAX phase and then intercalate multilayered MXenes into single or few-layered nanosheets.[24]

Due to the high amount of metal atoms exposed on the surface of MXenes, they are vulnerable to oxidation. It has been shown that the use of organic solvents, inert atmosphere and low temperature can decrease the oxidation rate and increase the stability of MXenes.[24]

One of the most attractive properties of these materials is their high electrical conductivity to accept and transport photogenerated electrons and thus be able to improve the activity of the photocatalyst. Studies have shown that the Fermi level of MXenes depends on the surface

terminal groups. An example is the terminal group – O that, due to its high electronegativity, increases the work function compared to MXenes that do not have it.[24]

Due to the high metallic conductivity of MXenes, large surface area, abundant functional groups, excellent light absorption capacity and strong interactions with metals, they can be applied in different reactions; which are photocatalytic water splitting, photocatalytic CO_2 reduction, photocatalytic pollutant degradation and photocatalytic N_2 fixation, which will be detailed below.[25]

6.2 PHOTOCATALYTIC REACTIONS

6.2.1. Photocatalytic water splitting

This reaction consists of the photocatalytic splitting of water for the production of H_2.[26] It is used as an alternative energy source to fossil fuels and can provide solutions to environmental problems. This has been considered a good method for converting solar energy into chemical energy by splitting water into hydrogen (H_2) and oxygen (O_2).[37]

In this reaction, photocatalysts participate in the migration of electrons through the absorption of solar energy and holes are generated on the semiconductors surface. Then we obtain the redox reaction of water, which creates H_2 and O_2 on the surface.

In order to achieve water splitting, it is necessary for the photocatalyst to have four characteristics which are:[38]

- The ability to absorb light.
- Stability in extreme environments
- Excited electrons and holes must migrate from the surface of catalysts with a low possibility of recombination.
- The CB edge must be higher than the hydrogen reduction potential (H^+/H_2) and the VB edge must be lower than the water oxidation potential (H_2O/O_2).

Referring to the last feature, it has been studied that the band gap of a semiconductor must be between 1.24-3.0 eV in order to make the reaction efficient as shown in figure 9.[38]

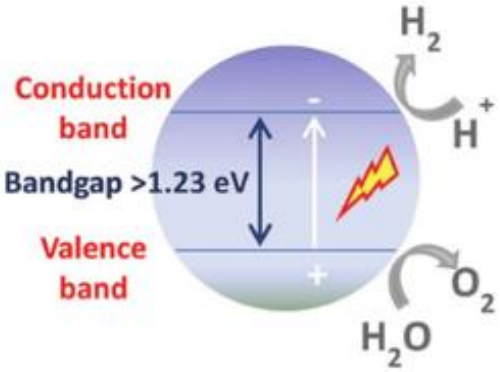


Figure 9: Band gap necessary for the water splitting reaction to take place. Adapted with permission from Creative Commons.

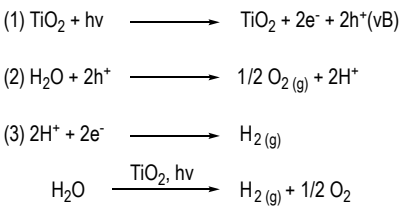
TiO_2 is the most investigated photocatalyst for the water splitting reaction, since it fulfills some of the characteristics mentioned above such as stability, its ability to absorb light and the compatible band edge level to produce water splitting. However, it has a drawback which is that has a fast recombination of photogenerated electrons and holes [37].

One of the possible solutions to improve the photocatalytic water splitting activity is the use of MXenes which can guide the flow of photogenerated charge carriers in semiconductors.[26] These MXenes meet the above characteristics and currently many studies are being done applying this new 2D material as a semiconductor in the water splitting reaction. However, there are some MXenes that perform better than others depending on their forbidden bands.

The synthesized MXenes usually end with -O, -OH and -F groups such as Ti_3C_2, Sc_2C, Mo_2CF_2, among others. Results from a study indicate that MXenes Sc_2C and Mo_2CF_2 have forbidden bands of 0.74 eV and 0.84 eV respectively, which are too small to provide sufficient energy for water splitting.[38] However MXenes Zr_2CO_2 and Hf_2CO_2 have a band gap greater than 1.55 eV which is higher than water's reduction potential of (1.23 eV), implying that these two are potential photocatalysts to drive the water splitting reaction. These two exhibit large size absorption of visible and ultraviolet light, which ensures high efficiency in harnessing solar energy. The mobility carrier is highly anisotropic, i.e., electrons have a tendency to migrate in the y-direction while holes have a tendency to move in the x-direction. This movement facilitates the migration and separation of photogenerated electron-hole pairs to obtain good photocatalytic

water splitting. Thus, it is found that the adsorption of water and the formation of hydrogen in the MXene are energetically favorable for the photocatalytic production of hydrogen gas.[38]

Another study used the hydrothermal method for photocatalytic water splitting from a $TiO_2/Ti_3C_2T_x$ composite. With X-Ray Diffraction (XRD) characterization, it was observed that $Ti_3C_2T_x$ can reduce the crystalline size of TiO_2 and avoid the aggregation of TiO_2 nanoparticles. Next, the photocatalytic activity of the different samples prepared from the photocatalytic separation of water was studied in order to produce hydrogen. It was observed that the photocatalytic activity of $TiO_2/Ti_3C_2T_x$ was approximately 4 times higher than that of pure TiO_2 due to the formation of the Schottky barrier between TiO_2 and MXene $Ti_3C_2T_x$, whose function is to guide the transfer of photogenerated electrons from TiO_2 to $Ti_3C_2T_x$ in order to enhance the separation of photogenerated electrons and holes in TiO_2.[26] The photocatalytic activity of $TiO_2/Ti_3C_2T_x$ was found to be approximately 4 times higher than that of pure TiO_2 due to the formation of the Schottky barrier between TiO_2 and MXene $Ti_3C_2T_x$. TiO_2 can react with H_2O to produce O_2. The reactions of this process are shown in reaction 1 as follows:



Reaction 1: Use of TiO_2 semiconductor in water splitting reaction.

Therefore, electron-hole pairs can be separated and transferred in the presence of the $TiO_2/Ti_3C_2T_x$ catalyst.

It is important to note that surface functional groups (T_x) allow to determine the surface active sites in a photocatalytic system and allow to create a close contact between the MXene and the photocatalyst. Xiang [39] demonstrated this fact in his study, based on the solvothermal method. He used plasma treated $Ti_3C_2T_x$ with abundant oxygen groups on its surface which allowed the $Ti_3C_2T_x/CdS$ bonding. It was determined that the $Ti_3C_2T_x/CdS$ hybrid had a higher hydrogen production rate than pure TiO_2 nanoparticles due to the oxygen-containing groups on the $Ti_3C_2T_x$

surface and the intimate contact between $Ti_3C_2T_x$ and CdS nanoparticles, which suppressed electron-hole recombination. Ultimately, using MXene $Ti_3C_2T_x$, H_2 production was obtained by modifying the Ti_3C_2 surface with plasma technology.

6.2.2. Photocatalytic CO_2 reduction

The constant increase in the concentration of carbon dioxide (CO_2) in the atmosphere is one of the main causes of global warming and the greenhouse effect. This increase is due to different activities related to combustion. In order to reduce the amount of CO_2 in the atmosphere, photocatalytic CO_2 reduction has been performed. As a way to enhance the photocatalytic activity, MXene has been used to improve the separation of photogenerated charge carriers.[26] Photocatalytic reduction of CO_2 is a method to obtain chemical energy from solar energy storage. During the past few years, a variety of semiconductors such as metal sulfides, metal oxides, etc. have been applied in the reactions of photocatalytic CO_2 reduction. Due to the characteristics of MXenes, a Ti_3C_2 compound was prepared from the calcination method, which was used in the photocatalytic reduction of CO_2 to CH_4. From the direct oxidation method, the Ti atoms on the surface of Ti_3C_2 can be oxidized to TiO_2 and form an interface between TiO_2 and Ti_3C_2 that generates a benefit for electron and hole separation.[40] TiO_2/Ti_3C_2 provided a large amount of surface active sites that favored the photocatalytic reaction. In this compound, in the presence of light, the photocurrent density increased because electron-hole pair separation was achieved from the migration of electrons from TiO_2 to Ti_3C_2 before reaching the cathode. Then, when the light was turned off this density decreased, a process that indicates the electron deposition behavior of Ti_3C_2.[26] The CO_2 reduction reaction that took place is shown in reaction 2.

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$$

Reaction 2: CO_2 reduction reaction.

In this experiment, it was observed that the CO_2 reduction photocatalytic activity of TiO_2/Ti_3C_2 was higher than that of pure TiO_2, which shows that MXene gives enhanced CO_2 reduction activity.[26]

Another researcher studied a 2D/2D heterojunction composed of Ti_3C_2/ g-C_3N_4 from the direct calcination method. Tests of CO_2 photoreduction show that pure g-C_3N_4 has very weak photoactivity, however when Ti_3C_2 is coupled with g-C_3N_4 the photocatalytic performance is increased. This improvement in CO_2 reduction photoactivity is due to the Ti_3C_2 / g-C_3N_4 heterojunction, which allows for intimate contact and faster electron transfer that promotes good separation of the photoexcited charge carriers. The compounds are shown to have a strong chemisorption effect, thereby increasing the adsorption capacity of CO_2 and leading to CO_2 activation.[34]

6.2.3. Photocatalytic pollutant degradation

Nowadays, water pollution caused by organic pollutants has attracted more and more attention in society. Among these organic pollutants, dyes and antibiotics (belonging to the group of pharmaceutical compounds) represent a growing group of organic pollutants in wastewater.

Another group of reactions that can be catalyzed by MXenes are the degradations of organic compounds. These aim to transform organic pollutants into simple and inert molecules in a process analogous to combustion, where the necessary energy is provided by photons.

A study indicating the capabilities of MXenes as photocatalysts to remove pollutants is investigated by Z.Miao [41] et al. In this study, Bisphenol A (BPA) “as can been seen in figure 10” is used as a pollutant and the degradation of BPA is compared in catalyst-free experiments with TiO_2 and with a TiO_2 / Ti_3C_2-derived MXene.

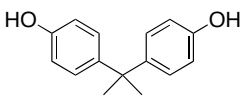


Figure 10: BPA.

$$C_{15}H_{16}O_{2\,(g)} \longrightarrow 15\,CO_2 + 8H_2O$$

Reaction 3: Pollutant degradation reaction.

As can be seen in the reaction 3 above, the initial product is a complex organic molecule, which is reduced to CO_2 and water, inert products that do not pose a problem for living beings.

As mentioned in the article, it can be seen that in the experiments carried out in the presence of MXene, the % of BPA degraded over a period of time is significantly higher than in the other experiments.

Another study by M.Abdullah[42] "as can been seen in figure 11 and 12" uses Congo red and acetophenone as a contaminant, in this case the MXene acting as a catalyst is $BiFeO_3$ / Ti_3C_2.

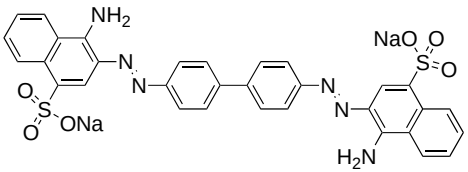


Figure 11: Congo Red

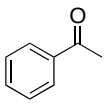


Figure 12: Acetophenone

Congo Red is a dye, therefore, to study its degradation, the color change of the solution can be observed. UV-Vis spectrometry can be used to determine the contaminant remaining in the solution. The presence of light and the photocatalyst allows the contaminant to be completely eliminated from the water in a remarkably short time. On the other hand, the experiments carried out with acetophenone, which is colorless, as a contaminant are also successful, also managing to eliminate the presence of this one from the water.[42]

This type of reaction is mainly used for the removal of dyes, widely used in the textile industry, but it is not only limited to colored compounds since, as we have seen, it can also be useful for colorless molecules.

6.2.4. Photocatalytic N_2 fixation

At present, the synthesis of ammonia at industrial level is carried out by means of the Haber-Bosch process from N_2 and H_2. This process currently allows large-scale production with a higher yield, but as it requires very high temperature and pressure conditions, it has a high energy cost, which makes the process more expensive and causes a high environmental impact due to CO_2 emissions. It is estimated that the Haber-Bosch process consumes between 1 and 2% of the world's energy. On the other hand, it is a necessary process due to the high demand for ammonia derivatives, mainly fertilizers, which are necessary to maintain current food production.[43]

This is why it is of great interest to search for other ways of fixing nitrogen, in order to reduce energy expenditure and that can serve both to reduce costs and to be more sustainable.

Among many other avenues of research, one of them is photocatalysis. This technique was first described in 1977 by Schrauzer et al.[44] who used TiO_2 as a photocatalyst to synthesize ammonia. In this case, the light energy allowed hydrolyzing water which then together with nitrogen formed the desired compound in a process analogous to photosynthesis.

In this process, the limiting step is the breaking of the triple bond of molecular nitrogen, a very strong bond, which can be broken by light energy. Once the nitrogen is dissociated, it is easily hydrogenated under non-extreme conditions with H_2 at moderate temperature. The reaction of this above mentioned process can be seen in reaction 4.

$$3H_{2\,(g)} + N_{2(g)} \longrightarrow 2NH_3$$

Reaction 4: Nitrogen fixation.

In recent years, interest in the development of catalysts that allow the production of ammonia from water and nitrogen has been increasing. This has made it possible to synthesize several catalysts that are capable of fixing nitrogen at ambient temperature and pressure. Despite the advances, it has not yet been possible to achieve sufficiently high yields to allow production at an industrial level. This is mainly due to the nature of N_2. The very stable triple bond makes it a very inert gas and makes nitrogen reduction very difficult.

Currently, new materials called MXenes that can act as photocatalysts in the nitrogen fixation reaction are being studied. Liu and co-workers [45] prepared an $AgInS_2$ / Ti_3C_2 based MXene composite from the hydrothermal method and found that the coupling of Ti_3C_2 with $AgInS_2$ created a direct heterojunction in order to maximize the photoxidation and photoreduction capabilities of

the photocatalytic system. As it is commonly known, the N_2 molecule should be chemisorbed on the surface of a photocatalyst in order to perform the nitrogen fixation reaction. This $AgInS_2$ / Ti_3C_2 compound has a high adsorption capacity which makes it a good candidate for this reaction.

In the work of J.D.Gouveia[46] up to 18 different MXenes are compared in this reaction. One of these is W_2C, in which the reaction is carried out at 800 K and low pressure. Moreover, it presents energetic values comparable to those of the catalysts currently used in the Haber-Bosch process, suggesting that they are a field of great interest due to their potential, although there is still much to be investigated.

Ultimately, the use of a MXene-based photocatalyst represents a viable way to achieve photocatalytic N_2 fixation in order to produce NH_3. However, to this day many questions remain as to how MXenes act in this reaction since it is not known how the N_2 molecule is adsorbed on Ti_3C_2. Therefore, much research and future studies are needed to determine the N_2 adsorption capacity of MXene-based photocatalysts, in particular Ti_3C_2.

In addition to the applications mentioned above, MXenes can be used for the production of hydrogen peroxide due to the excellent electrical conductivity and two-dimensional structure of MXenes. These materials are also being applied in organic synthesis. Using bioethanol as an example, which is a material widely used in this type of synthesis, a study was carried out where it was concluded that, when used with the aid of a photocatalyst and under visible light the material, it could be converted into fine chemical raw material. This demonstrates that the use of the photocatalyst favors the reaction. Another current application is that these can be used for disinfection and sterilization. With the global outbreak of COVID-19 there has been increasing attention on this application. One researcher, prepared a single-layer $TiO_2/Ti_3C_2T_x$ photocatalyst and coated it with polyurethane (PU) foam. With this experiment, it was shown that the efficiency of MXene-based photocatalyst to kill airborne bacteria under UV irradiation was better than that of pure TiO_2.[47]

7. CONCLUSIONS

One of the main goals of this bibliographic project was to research the different applications of MXenes in photocatalysis. Taking this into account, the following conclusions can be extracted.

MXenes are newly discovered 2D materials. As mentioned in the report, all applications of these materials are still to discover. This project covers the photocatalytic applications of MXenes, which represent a small fraction of all applications this substance can have. That is why information is limited and it is still under massive research.

Related to the first objective of this project, the relation between the composition and the structure of MXenes to its catalytic behavior has been analyzed. The interest of this material in catalysis is due to the fact that MXenes have a really small band gap. This characteristic makes this material more prone to have the electron exited when exposed to visible light wavelength. That is why they are more interesting than semiconductors such as TiO_2, $SrTiO_3$, etc.

There are a lot of MXenes that are being studied, but not a lot are synthesized. The MXene that is most commonly used is Ti_3C_2 because it was discovered in its MAX phase in a natural form and the synthesis protocol is formally known.

Talking about which MXenes terminations show the best photocatalytic behavior, this is a still under research topic. Although no conclusion is being extracted yet about which is the best termination. Some groups are better suited for some applications and some for others. For example, the groups -O have been proved to be very beneficial for hydrogen production.

One of the last objectives of this project was to analyze in which processes MXenes have been studied. As mentioned on the report, there are 4 major processes that are very important for the development of a sustainable society which are photocatalytic water splitting, photocatalytic CO_2 reduction, photocatalytic pollutant degradation and photocatalytic N_2 fixation. Finally, it is worth to mention that this is a really new material that is now on the exponential growth on properties discovery. In the next year more information and more application will be known around the scientific world.

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12. ACRONYMS

HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
VB	Valence Band
CB	Conduction Band
DFT	Density Functional Theory
MB	Methylene Blue
AB80	Acid Blue 80
XRD	X-Ray Diffraction
PU	Polyurethane