iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 10 **Issue:** XI **Month of publication:** November 2022

DOI: https://doi.org/10.22214/ijraset.2022.47579

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.538
Volume 10 Issue XI Nov 2022- Available at www.ijraset.com

Copper-based MXenes: Synthesis, Properties and Applications

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Abstract: ***Great results are emerging subsequently from the isolation and characterization of graphene and have resulted in increasing interest in two-dimensional (2D) materials that are different from their three-dimensional (3D) analogues. Over the past decade, science-inclined researchers have invested in the synthesis of novel MXenes with combined transition metals forming a compound of the MAX phase family. MXenes, a derivative of MAX phase is a class of novel two-dimensional (2D) transition metal containing carbide/nitride with a $M_{n+1}AXn$ formula. Due to their unique physical, electronic, chemical, and structural properties, it has been utilized in the membrane, adsorption, and separation technique, respectively. Additionally, due to their surface reactivity, adsorption ability, and hydrophilicity, MXenes have revealed broad application prospects such as sensors, metal-ion batteries, environment, and catalysis. Although several works have been carried out and are still on-going in this area, copper-based MXenes are rare class of MXenes. In this review, we provide an overview of preparation, properties and applications of Copper-based MXenes reported in literature.***

Keywords: MXenes, MAX phase, synthesis, copper, two-dimensional materials

I. INTRODUCTION

In the context of MAX phase ternary compounds in material science, and subsequently, the isolation of graphene single layer in 2014 [1], the two-dimensional (2D) materials have increased tremendously due to their characteristic properties. The exfoliation of graphene and other layered nanosheets has attracted a tremendous amount of research in two-dimensional materials and unlocked the prospect for more discoveries. Currently, there are lots of new 2D materials such as transition metal oxides, clays, transition metal dichalcogenides, and hexagonal boron nitride, along with others [2]. Clearly shown is how the 2D ultrathin layered material introduction has allowed innovation in the performance of conventional devices, including energy conversion and storage appliances, chemical sensors, and gas [3-6]. However, research related to 2D ultrathin layered materials has fast developed and enabled the realization to possibly gain astonishing properties by turning the number of atomic layers of any layered material [7,8].

Since the foremost report on $Ti_3C_2T_x$ in early 2011, this class of two-dimensional transition metal carbides, nitrides, and carbonitrides (MXenes) has significantly grown with further interest to synthesize more comparable compounds that possess attractive properties including single and multi-element MXenes [9]. In general, the MXenes formula is represented as $M_{n+1}X_nT_y$, where M represents transition metals (such as Sc, Ta, Cr, Mo, Ti, Zr, Hf, V, Nb, etc.) and X is either carbon and/or nitrogen while T stands for surficial functional groups depending on method of synthesis and postsynthetic treatment. Basically, the term MXenes was specified to define the 2D material family and graphene comparisons and as well recognize the parent ternary carbide and nitrides, MAX phases where MXenes are synthesized [10]. On the other hand, the layered ternary, hexagonal carbides, and nitrides, MAX phases have a general formula: Mn+1 AXn, (MAX) where n = 1 to 3 and A represents the groups 12 and 14 of the periodic table [11].

MXenes have various characteristics property, for instance, it has maximum electrical conductivity (2 x 105 S/m) in par with that of comparatively larger specific surface distribution, multi-layered molecule graphene, enriched surface mechanism because of outstanding ability to function, easier to dispersive in water and some other solvents, and staggering electrochemical features which enhances conductive and useful for energy storage [12]. Another exciting aspect of MXenes is as an active component for building supercapacitors along with batteries such as Lithium, potassium, and metal-sulfur batteries. MXenes have been vastly applied including the use in conductive polymeric substances acting as polyaniline and polypyrrole and have equally been suggested for use as a negative electrode in establishing higher concentration gradients acidic solution electrolyte which leads to energy density augmentation [13].

Carbide-based MXenes can be gotten through selective etching of Si merged Al-C and Al-C sublayers established from $Zr_3Al_3C_5$ and $Hf_3[Al(Si)_4C_6]$.

During the etching process, the addition of Si improves ternary carbide layer etching via the lenient interfacial layer adhesive bonding of the Hf-C/Al(Si)–C sublayers [12]. Up to date, MXenes have been synthesized via wet-chemical etching in hydrofluoric acid (HF) or HF-containing or HF-forming etchants [14-16], which add surface functional groups that are extremely prevalent to chemical and physical features of MXene-based materials, which incline to influence environmental applications. Several functional groups such as oxygen (-O), fluorine (-F), and Hydroxyl (-OH), are represented by TX in this formula as $M_{n+1}XnTx$, thereby rendering their formation against the surfaces of MXenes. Ti_3C_2 MXene for example can have at least 3 dissimilar notations $Ti_3C_2O_2$, $Ti_3C_3(OH)_2$, and $Ti_3C_2F_2$, respectively [13].

Although not much experiment has been done in the past few years, a significant number of research in this research area and publications have been recorded, however, different factors are contributing to the speedy increase of MXenes. To date, more than 750 institutions from 50 countries are working in this area of research; the number of research institutions that are studying MXenes with many works in peer-views journal publications have also shown evidence of growth significantly [17]. Yuri and Babak 2019, reported that in May 2019, the 2nd International Conference on MXenes, held at the Beijing University of Chemical Technology in Beijing, China, attracted 450 attendees, which is estimated more than twice the number of participants of the first conference, organized at Jilin University in Changchun, China, in 2018. The second international conference on MXenes that was subsequently held discussed several aspects of the basic 2D material and applications of MXenes, including identification, synthesis, structure, and properties, together with its energy storage and conservation, environment, and catalysis, medicine, optics, separation membrane, and electronic applications. These topics cut across the major areas of expansion needed for the MXenes applications [18].

In this review, we explain general synthetic methods for MXenes and focus on the synthesis of copper MXenes with respect to their properties as well as their various applications.

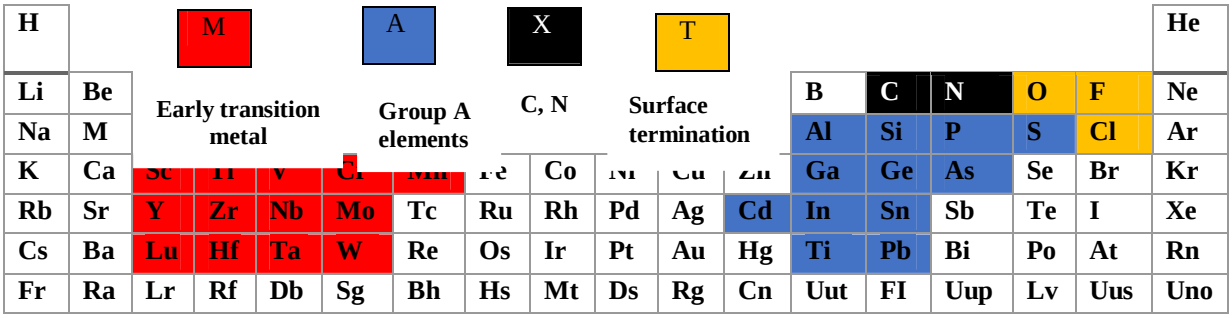

Fig. 1 Elements in the periodic table react together to form the remarkable MAX phases and their subsidiary MXenes. The red squares represent the M-elements; the blue squares are the A-elements; the black squares are X-elements, or C and/or N; the yellow squares T, represent termination elements.

TABLE 1
Synthesis, properties, and applications of MXenes.

Properties	Synthesis	Application
Structural	Etching	Catalysis
Thermal	Top-down	Therapy
Electrical	Top-up	Sensing
Optical		Energy
		N_2-fixation

II. SYNTHESIS OF MXENES

MXenes are produced from the MAX phase. The synthesis pathway had an imperative impact on their physiochemical features, electrical characteristics, and an extensive array of applications. Generally, three different types of MXene synthesis techniques are identified and being used to date: Etching, top-down, and bottom-up [**Table 1**]. In the etching synthesis process, the "**A**" element of the MAX phase is more reactive chemically than the MX, therefore, can be able to etch the elements of group **A**. Basically, the top-down strategy is the mostly used method of MXene synthesis and a larger number of precursor materials is essential for the top-down fabrication approach.

On the contrary, the bottom-up synthesis fabrication approach requires few inorganic or organic molecules or atoms during their structure construction. But due to divergence reasons in the etching process, there is a tendency that the numerous atoms of the transition metals could bond to different end groups, which will result in surface-free Gibbs energy reduction thereby completing their coordination spheres [19]. From the initial state of the parent three-dimensional (3D) layered structure (MAX phase), a crystal growth method is preferably used to assemble the precursors into a definite 2D order which constitutes the structure of MXenes.
Different methods of MXene preparation including the hydrofluoric acid (HF) etching method, modified acid etching methods, electrochemical etching method, non-fluoride etching method, In-situ HF etching, Lewis acid etching method and the like have been reportedly used to prepare MXene compounds.

A. Hydrofluoric Acid (HF) Etching

The first MXene compound discovered Ti_3C_2Tx was produced via a wet etching chemical process from a MAX phase. In the hydrofluoric acid (HF) etching synthesis process, the "**A**" element of the MAX phase is more reactive chemically than the M-X bond, therefore, can be able to etch the elements of group **A.** After the etching, deionized water is used
Michael *et al.* [20] in their work proposed that the reaction between HF with Ti_3AlC_2 as follows:

$$Ti_3AlC_2 + 3HF = AlF_3 + 3/2H_2 + Ti_3C_2 \quad (a)$$
$$Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2 \quad (b)$$
$$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2 \quad (c)$$

The reaction of (a) is important and followed by (b) and (c). In reaction (a), HF reacts with Ti_3AlC_2, F and Al then forms AlF_3 and is removed when washed with deionized water. In reactions (b) and (c), Al in Ti_3AlC_2 can be replaced by O, OH, or F, respectively, which are denoted as surface-terminating functional groups [21,22]. This termination can be assigned to the strong M-A bonding which has higher potential energy when the atomic number of M is highly sufficient. Interestingly, the surface terminating functional groups, morphology, particle size, yielding percentage, and defection concentration having high similarity with MXene-based compounds, possess similar features crucial for the etching method.

B. Lewis Acid Etching

Compared with the commonly used HF etching process method, the etching effect of Lewis acid in molten salts offers safe and clean chemistry. The aqueous solution containing fluoride such as fluoride salt, HCl/LiF mixture, and HF ions is used to remove **Al** layered element in the MAX phase. Therefore, MXenes are better found from the Al MAX phase percussor due to the high reactivity level of Al transversely to the aqueous solutions of fluorides. There is a restriction on the MAX phase precursor towards the **A** original elements of group XIII-XVI. The transition metal halide in reaction forms the supposed Lewis acid in its molten state. The molten salts can produce robust electron-accepting ligands which could react with the **A** elements of the MAX phase thermodynamically. Also, the 2D atomic plane and bond with the unsaturated Mn+1Xn sheet can be formed when certain types of atoms or ions diffuse, thereby forming a corresponding MXenes or MAX phase [23].

C. Modified Acid Etching Method

Investigations and several trials have been made to avoid hydrofluoric acid direct etching. Interestingly, the aluminum layer extracted from the MAX phase because of the toxic and corrosive properties of fluorides contained in acid solution has been tried out. Initially, the advanced HF method is used for MXene synthesis, the traditional hydrofluoric acid etching method, a form of wet etching. Practically, combined fluoride salts with other bonding elements/atoms such as FeF3, NaF, and NH_4F_2, are exchanged with hydrofluoric acid, HF [24,25]

III. COPPER MXENES SYNTHESIS, PROPERTIES AND APPLICATIONS

Copper-based MXenes are one of the interesting compounds in the MXenes family. Copper-based MXenes have been added up to the structures of 2D materials for various uses in ion-based batteries, heterogeneous catalysis and as biomedical agents. Catalysis, sensors and others [26]. Different methods have been employed in the synthesis of Cu-based MXenes.
Ponce-Pérez *et al.* predicted using Vienna Ab initio Simulation Package (VASP) first-principles calculations a new family of MXenes based such as Cu_2N, Cu_2C, and Cu_2O on copper for the aforementioned applications. These Copper-based MXenes through their Cu-3d orbitals display non-magnetic metallic characteristics. When functionalized with Cl, F, O and OH groups, the copper-based MXenes also display non-magnetic metallic properties similar to the respective MXenes. Because of its great electric conduction, Cu is an effective current collector [27].

Elemental copper has pleiotropic applications because of its electromigration characteristics; it's often used to construct integrated circuits. Guerrero and coworkers reported that Cu thin films in large areas and on solid surfaces can be realized through atomic layer deposition. In a ligand-exchange reaction process, Cu-based organometallic molecules chemically interact with the solid surface to make growth [28]. Cu_2O, a type of semiconductor and synthetic compound of MXenes with unique optical and electrical properties was reported by Yupeng *et al.* Their work describes Cu_2O and MXene-Cu_2O as showing an outstanding catalytic effect on the thermal decomposition of Ammonium perchlorate (NH_4ClO_4 or AP) [29].

The group of Huang Pang reported MXene-Copper/Cobalt hybrids synthesized by acidic molten salts etching method. Their findings adder insights into the molten salt mechanism and Copper-based MXenes application in electrochemical energy storage. Specifically, their synthtic method involves the use of molten salts of $CuCl_2$ or $CoCl_2$ to etch MAX phase Ti_3AlC_2 leading to Ti_3C_2-Cu and Ti_3C_2-Co, respectively. Mixture of the two salts were also used to obtain bimetallic hybrids Ti_3C_2-Cu_1Co_2, Ti_3C_2-Cu_1Co_4, and Ti_3C_2-Cu_1Co_8 with the Cu/Co ratio of 1:2, 1:4, and 1:8. Their results demonstrated synergistic interaction between Ti_3C_2 and Cu which contributed to the high electrochemical performances as supercapacitor electrode [30].

Asides native MXenes, composites/nanocomposites and hydrogens of copper-based MXenes are also been explored. For example, flexible MXene/copper/cellulose nanofiber heat spreader films had been reported. Copper particles possesing high thermal conductivities and Ti_3C_2 MXene sheets were mixed by high-speeding shear mixing with cellulose nanofibers (CNFs) to fabricate polymer composite films after the vacuum filtration. This led to composites possessing improved thermal conductivity. The com film possess a basic skeleton formed by dehydration and esterification of hydroxyl groups in MXene and carboxyl groups in CNF [31].

The group of Zhang also reported MXene-supported copper oxide nanocomposites (MCNs) for promoting the decomposition of ammonium perchlorate (AP). The MCNs were prepared through a simple ice-crystal templating method without the use of chemical modifiers. The elevated catalytic activity of MCNs for AP thermal decomposition was adduced to synergistic effect of MXene nanosheets and CuO nanoparticles [32]

Similarly, Li *et al.* synthesized through a simple and benign method copper/MXene/polyacrylamide hydrogel which served as catalyst for reduction of 4-nitrophenol. The hydrogel catalyst was synthesized by in-situ polymerization and self-reduction with copper as as catalytic species, two-dimensional transition metal carbides (MXene) as electron transfer medium, and porous polyacrylamide (PAM) as adsorbent which enhanced the electron transfer and adsorption capacity through synergistic effects of Cu/MXene/PAM. The non-noble foam-like hydrogel catalyst can be easily separated and reused many times and possesses properties that make it suitable for industrial catalysis [33].

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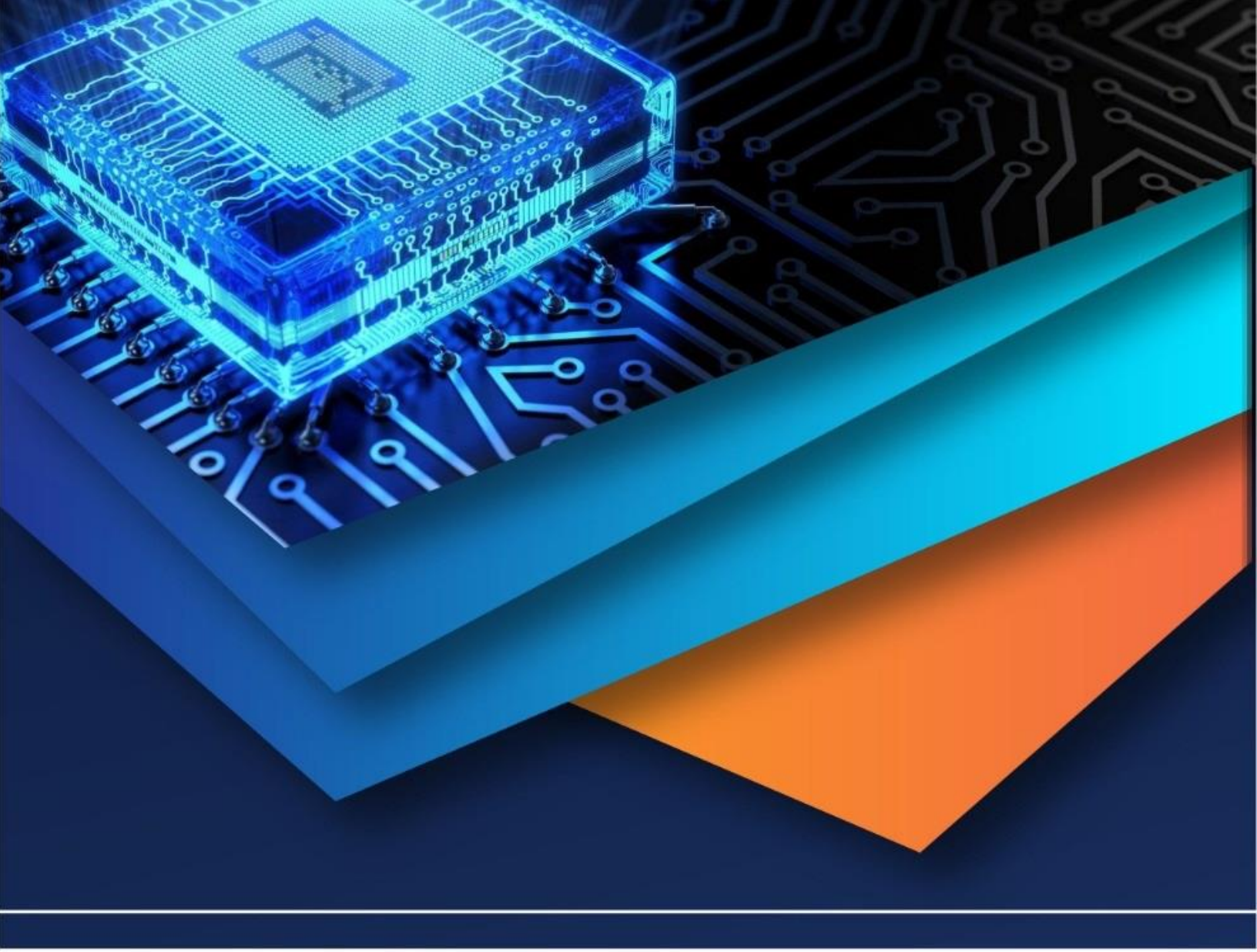

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