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The Future of MXenes

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We are entering the era of new materials: materials that can be assembled from nanoscale building blocks, unlike all previous material generations from the Stone Age to the Silicon Age. Two-dimensional (2D) materials provide nanometer and subnanometer-thin "bricks" for such assembly. If needed, organic molecules and polymers can serve as mortar, but van der Waals (vdW) or electrostatic forces can also provide a strong bonding between the 2D layers. To make this vision real and start assembling materials, structures, and devices from nanoparticles, we need many building blocks with a large variety of physical and chemical properties.

The separation of single layers of graphene and demonstration of unique physics in this atomically thin sp^2 carbon layer attracted attention to other 2D materials. Initially, known vdW-bonded materials such as MoS_2 and boron nitride (BN) were explored, but later 2D layers were created from elements like Si, Ge, or B and compounds that do not have weakly bonded layered precursors. MXenes belong to the latter group.[1] They are carbides, nitrides, oxycarbides, and carbonitrides of early transition metals, such as Ti, Nb, Mo, etc. (Figure 1). However, they occupy a special place in the large class of 2D materials for several reasons. First, they come in a large variety of structures with 2−5 layers of early transitional metal atoms (M elements) connected by 1−4 layers of nonmetal atoms (X = C, N, O). Moreover, multiple M metals can be combined in one structure, forming in-plane and out-of-plane ordered MXenes or random solid solutions, including high-entropy MXenes with 3−5 metals (Figure 2). The hexagonal structure of MXene is a (111) slice of the cubic NaCl structure of bulk cubic carbide/nitride. The surface of MXenes can be terminated with oxygen, OH, amines, halogens, and chalcogens; antimony and phosphorus were added to this group recently.[2] Considering a dozen transition metals, carbon and nitrogen, four archetypical MXene structures, and the known monatomic surface terminations, at least a thousand stoichiometric compositions may be possible. With solid solutions on M and X sites and mixed surface terminations, an infinite number of 2D materials can be created in this system.[3]

Thus, MXenes are taking us into the era of atomistic design and chemical assembly of new 2D materials. This was only possible in the world of organic molecules in the past, including covalent organic frameworks (COF) and metal−organic frameworks (MOFs). More than 50 MXenes have been reported to date. Considering solid solutions with various ratios of elements and distinct surface terminations defining MXene properties, the number of experimentally created MXenes probably approaches a hundred. Advances in computational materials science, machine learning, and artificial intelligence should allow us to predict properties and synthesis conditions for numerous other MXenes that have not been made in a lab yet.

The fact that so many new materials can be produced in this system is astonishing and attracts attention. The interest in the MXene family has been increasing with every new composition discovered (Figure 2). However, with dozens of dichalcogenides and quite a few other 2D materials, it is not the number of new compositions but the properties they offer that matter. While numerous semiconductors and dielectrics have been made and semimetals have been demonstrated, good 2D metallic conductors are rare. Graphene, which is praised for its conductivity, is a zero band gap semiconductor that needs doping or defects to acquire carriers, and its conductivity decreases by many orders of magnitude when graphene is terminated with oxygen or hydroxyl, forming graphene oxide (GO). All MXenes in a bare (nonterminated) state are predicted to be metals with a high density of states at the Fermi level and a high concentration of carriers. The first MXene reported in 2011, $Ti_3C_2T_x$ (T stands for surface terminations), showed metallic conductivity,[1] which stayed stable in a very broad temperature range. Chemically tunable superconductivity has been reported for Nb MXenes.[5] The electrical breakdown current measured on single-layer MXene flakes is much higher than copper and is similar to that of graphene.[6] Moreover, the currently reported values for multilayer films of this MXene exceed 20 000 S/cm, much higher than reduced graphene oxide (rGO).[7] Important is that those values are achieved on O/OH terminated MXene, which is dispersible in water like GO due to a high negative (below −30 mV) zeta potential and, just after drying, becomes more conductive than rGO after high-temperature reduction. This makes MXenes highly attractive for conductive coating and 2D/3D printing applications. Thus, MXenes combine metallic properties with the hydrophilicity of clays, layered double hydroxides, or rGO - an unusual and very useful combination of properties. One can call MXenes "metallic clays" or "water-dispersible metals". Their slurries actually behave like clay rheologically. While MXene pottery is possible to make, the shear-thinning and liquid-crystalline behavior of MXenes

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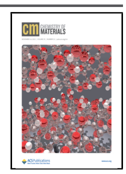

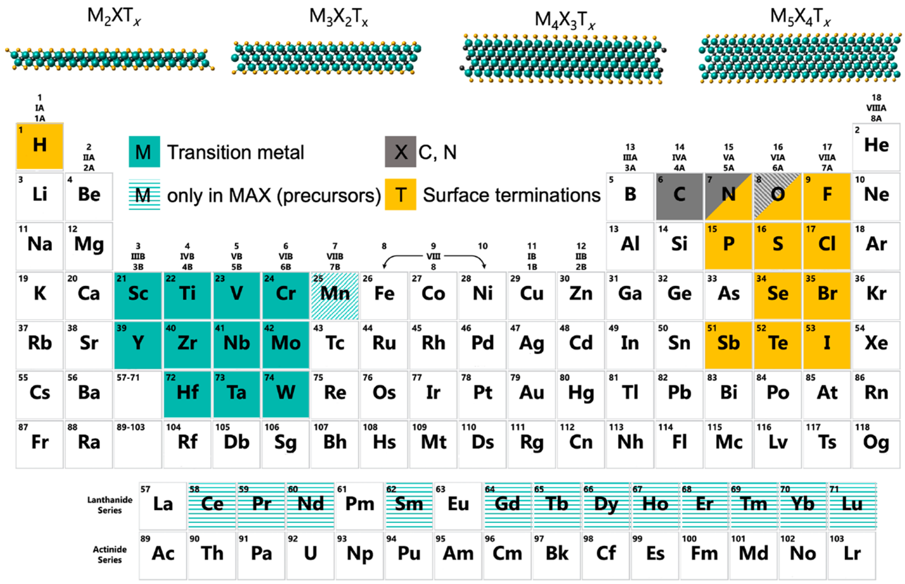

Figure 1. Periodic table showing elements used to build MXenes. The striped background shows elements that can be components of MAX structures, substituting main elements. Modified from ref 4. Copyright 2022 Springer Nature.

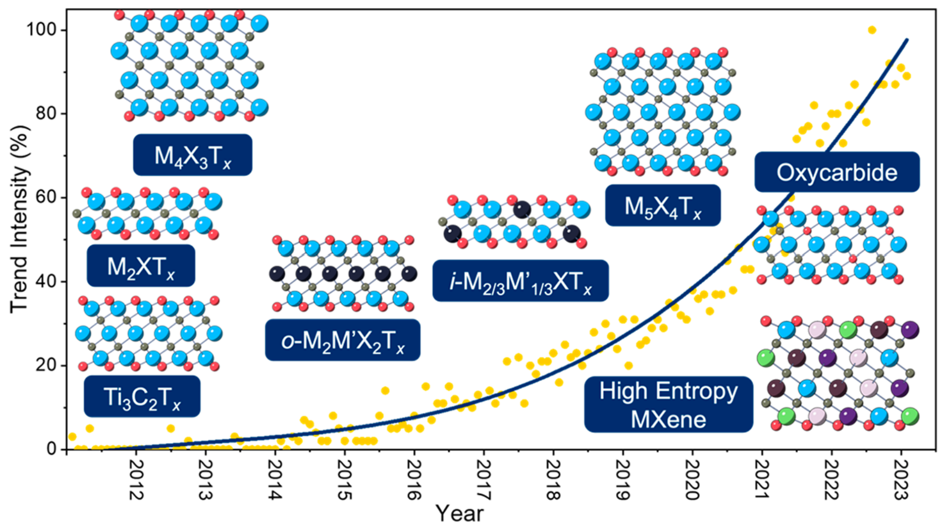

Figure 2. Trends in "MXene" Google searches (August 20, 2023). The interest increases with new materials being added to the family and new exciting properties of MXenes resealed. Asian countries confidently lead in this statistic. *i*-MXene stands for in-plane ordering, and *o*-MXene stands for out-of-plane ordering.

dispersed in water is useful in manufacturing films, drawing fibers, and 3D printing.[8]

The same O/OH terminations that make MXenes hydrophilic allow their use in electrochemistry due to the possibility of reversible surface redox reactions. These properties are useful in energy storage and conversion applications. The mechanical properties of MXenes are also outstanding, although this is not surprising, as they are inherited from bulk carbides and nitrides. Single-layer Ti_3C_2 and Nb_4C_3 have higher mechanical properties compared to other solution-processed 2D materials, such as oxides, GO, or dichalcogenides.[9] This is important in manufacturing MXene-reinforced composites, but MXene strength also allows us to make very thin free-standing films and produce large single flakes from solution.

Last but not least is the strong interaction of MXenes with the entire electromagnetic spectrum from ultraviolet (UV) to microwaves. Interband transitions and/or surface plasmons give MXenes colors in solution and in smooth films. For example, Ti_2C absorbs at around 550 nm, like Au nanoparticles.[10] As a result, the dilute solution of Ti_2C has a red color in transmission, and a Ti_2C film is green in reflection. This is the combination of colors of the famous Roman Lycurgus Cup from the fourth century, which is often given as the first known example of man-made nanotechnology. Adding a Ti−C layer to Ti_2C produces Ti_3C_2 and shifts the absorption peak to 780 nm, making this MXene look green in solution.[10] This MXene, as well as Nb-MXenes that absorb in the infrared (IR) range, is useful for the photothermal therapy of cancer. It is possible to obtain any color by making various MXenes and to tune it finely by changing the ratio of elements in a solid solution. Similarly, MXenes show a broad range of emissivity values in the IR range. Ti_3C_2 has the reflectivity of polished metal (good for thermal insulation, IR stealth, and clothes that

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keep us warm by preventing the loss of body heat), but Nb_4C_3 is an excellent emitter of IR radiation (great for space heaters).[11] In a similar way, a very broad range of other optoelectronic, physical and chemical properties has been demonstrated by members of this family.

So, what's next for MXenes? There is no doubt that the synthesis of new 2D materials in this system will continue. The recently added $M_5C_4T_x$ family should be expanded to nitrides. One can expect some extreme properties from the bulkiest members of the 2D family (11 atomic layers, if surface terminations are taken into account).[12] However, the compositional and structural variety of MXenes and related materials is not limited by the basic structures and chemistries described above. Note that oxycarbide MXenes reported to date have less than 50% oxygen in the lattice, but this may not necessarily be a limit and 2D oxides may be considered as an extreme case of oxycarbides.[13] Oxynitride MXenes have not yet been made, but it is probably just a matter of time, as bulk oxynitrides and oxycarbonitrides of transition metals are well-known. 2D borides (MBenes or boridenes) have been reported, but stand as a separate group due to a different crystal structure.[14] They further expand the family of nonoxide 2D materials. Properties of all those materials should be evaluated computationally and tested experimentally.

What will be the "killer application" for MXenes? Ti_3C_2 has demonstrated its ability to compete with gold and silver in printed electronics, outperform indium−tin-oxide (ITO) in flexible and foldable transparent devices,[15] and perform at the level of copper and aluminum in EMI shielding, but allow the use of much thinner than metal foils films.[16] It also outperforms both gold and graphene in epidermal and implantable electronics due to a lower impedance in contact with skin and tissue.[17] Note also its room-temperature deposition from solution, which does not require vacuum sputtering or high-temperature deposition and post-treatment. The high breakdown current makes Ti_3C_2 also promising for nanometer-thin interconnects. In battery current collectors, micrometers-thick Ti_3C_2 not only can replace 10−20 μm thick Al and Cu, making the devices thinner and lighter, but it also operates in chloride electrolytes that those metals cannot tolerate, thus opening the road to new battery chemistries.[18] Dendrite suppression on MXene current collectors has been demonstrated not only for Li but also for K, Na, and Zn, enabling pure metal battery anodes.[19] Of course, MXenes can also be used as active materials in a variety of batteries and supercapacitors.[20] Optoelectronic applications are emerging, with Ti_2C offering the same colors as colloidal gold particles due to an optical absorption peak at 550 nm, and $Ti_3C_2T_x$ with the near-IR absorption is promising for photothermal therapy. Engineering of the thermal behavior (reflectivity/emissivity in IR and highly anisotropic thermal conductivity) is extremely attractive and only requires the use of very thin, sub-micrometer coatings.[11] For thermal management, MXenes offer a unique combination of low emissivity of polished metals with low thermal conductivity of porous insulators. Applications of MXenes are being explored by thousands of researchers worldwide in structural and multifunctional composites; healthcare; water desalination and purification; chemical catalysis and electrocatalysis; energy storage and conversion; communication (antennas, etc.); gas, pressure, electrochemical, and other sensors; and many other fields.[21] Joint efforts of academic and industrial communities will be required to translate excellent research done in a lab into industrial products and future technologies. The advancement of MXenes toward industrial use would require the development of scalable, low-cost, safe, and environmentally friendly synthesis processes,[22,23] as well as extensive and thorough studies of their toxicity and fate in the environment. All new materials follow this path. Based on the unique and tunable properties of MXenes as well as their enormous compositional diversity and tunability of properties, we are confident that the field of MXenes has a bright and exciting future.

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Notes

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