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MXenes

In 2011, the Professor Gogotsi and Professor Barsum reported the use of MAX phase Ti₃AlC₂ as a precursor to prepare two-dimensional structured Ti₃C₂T_x MXenes (T_x, various functional groups including O, F and OH, etc.), and applied them to lithium-ion batteries [1]. In the past 12 years, researchers have developed a large family of MXenes by using hydrofluoric acid etching [1,2] and Lewis acidic molten salt [3,4] to match a large family of MAX. MXenes were also synthesized through the chemical vapour deposition method and direct preparation method without using MAX phase materials [5]. Due to the unique properties of MXenes, such as metallic conductivity, hydrological nature, large interlayer spacing, and rich surface chemistry, researchers have used MXenes for energy storage, energy harvesting, energy production, catalysis, sensing, electromagnetic interference, biomedicine, health care, and environment [2]. MXenes have demonstrated a vigorous upward trend in recent years (see Fig. 1). To highlight the recent developments on Mxenes, we organize this special issue in the Journal of Materiomics (JMAT).

MAX phases and its derived two-dimensional Mxenes have attracted considerable interest because of their rich structural chemistry and multifunctional applications. Lewis acid molten salt route provides an opportunity for structure design and performance manipulation of new MAX phases and Mxenes, Although a series of new MAX phases and Mxenes were successfully prepared via Lewis acid molten route [6] in recent years, few work is explored on nitride MAX phases and Mxenes. A new copper-based 413-type Ti₄CuN₃ MAX phase was synthesized through isomorphous replacement reaction using Ti₄AlN₃ MAX phase precursor in molten CuCl₂ [7]. MXene nanosheets are considered advantageous for functional materials, but current delamination methods to prepare MXene nanosheets have many limitations including high cost, small production scale, low efficiency, and deteriorated structure integrity of obtained nanosheets. A scalable shear stress-induced delamination (SSID) strategy to boost the production of single-/ few-layered $Ti_3C_2T_x$ MXene nanosheets is described [8].

MXenes have captured extensive attention in various fields by virtue of unique hydrophilicity, high conductivity and tunable surface terminations. In the review [9], the progresses of designing functional MXenes have been summarized. Firstly, the synthesis methods of MXenes are classified into HF etching, *in-situ* HF etching and fluoride-free etching approaches based on the effect on the surface chemistry of MXenes. Secondly, the factors that affect the surface termination groups are discussed, including synthesis methods, heat treatment temperature and atmosphere. Thirdly, the synthetic routes of functional MXenes including termination modification by synthesis methods and heat treatment, heteroatom (N, S, or P) doping, cation and organic molecule intercalation and

hybridization with polymer, which inhibit restacking and increase active sites for intrinsically enhancing the inherent physical and chemical properties of MXenes. Finally, the applications with respect to energy storage and conversion, catalysis, sensors, electromagnetic interference shielding and microwave absorption of functional MXenes are introduced.

To respond the recent experimental advances, the phase stability, mechanical properties, phonon as well as infrared- and Raman-active modes, thermal expansion and heat capacity were investigated by density functional theory for the S-containing MAX carbides and borides (M from III B to VIII B), of importance, well consistent with the available experimental results. After examining the thermodynamic competition with all the competing phases and intrinsic stability by their lattice dynamics, 18 MAX phases were screened out from 138 ones [10]. Reminded by the well-known MAX phases, several an atomic layers are inserted into the binary borides to form ternary transition-metal borides named MAB phases for this problem of binary borides, where M, A and B represent the early transition-metal element, IIIA-VIA group element, and boron element, respectively. Similar to the MAX phases, the MAB phases have an interesting combination of metal and ceramics-like properties, such as low hardness, good electrical conductivities, high toughness, and oxidation resistance, rendering them potential applications in many aspects such as wear-resistant coatings, electrocatalysts, magnetic refrigeration, etc. A 314-type MAB phase V₃PB₄ with hexagonal crystal structure is synthesized by self-propagating high temperature combustion synthesis (SHS) [11].

The valley index is a promising degree of freedom for information processing in electronic devices. However, the researches on valley polarization are mainly focused on ferromagnetic order, which breaks the time reversal symmetry simultaneously. A example for achieving stacking order modulated anomalous valley Hall (AVH) effect is proposed in antiferromagnetic monolayers [12]. The example involves the introduction and reversal of nonuniform potentials by modulating the position of substrate, to break the combined symmetry of spatial inversion and time reversal (PT symmetry) and achieve stacking-dependent valley spin splitting.

MXenes have potential applications in energy conversation such as water splitting and solar cells, as well as in energy storage such as Li-ion batteries, supercapacitors, and hydrogen energy are comprehensively elaborated [13]. The escalating demand for micro/nano-sized devices, such as micro/nano-robots, intelligent portable wearable microsystems, and implantable medical microdevices, necessitates the expeditious development of integrated microsystems incorporating energy conversion, storage, and consumption. Critical bottlenecks in microscale energy storage/sensors and their integrated systems are being addressed by exploring new technologies and new materials, *e.g.*, MXenes, holding great





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Fig. 1. Publication number of MXenes by year (Web of Science, 2023.12.05).

potential for developing lightweight and deformable integrated microdevices. These reviews summarize the latest progress and milestones in the realization of MXenes-based micro-supercapacitors (MSCs) [14,15] and sensor arrays [14], and thus discusses the design fundamentals and key advancements of MXenes-based energy conversion-storage consumption integrated microsystems.

With the rapid growth in renewable energy, researchers worldwide are trying to expand energy storage technologies. The development of beyond-lithium battery technologies has accelerated in recent years, amid concerns regarding the sustainability of battery materials. However, the absence of suitable high-performance materials has hampered the development of the next-generation battery systems. The extraordinary electronic conductivity, compositional diversity, expandable crystal structure, superior hydrophilicity, and rich surface chemistries make MXenes promising materials for electrode and other components in rechargeable batteries. This report especially focuses on the recent MXenes applications as novel electrode materials and functional separator modifiers in rechargeable batteries beyond lithium [16]. Three-dimensional crosslinked nanoarchitectonics of CoP@NC anchored on $Ti_3C_2T_x$ with high ionic diffusion has been enhanced sodium storage performance [17].

Precise assembly of active component with sophisticated confinement in electrocatalyst are promising to increase the active site exposure for enhanced hydrogen evolution reaction (HER). Here, PCN-333 films with mesopores are firstly assembled on titanium carbide MXenes with the assistance of atomic layer deposited oxide nanomembrane. With the whereafter pyrolysis process, the composite is converted to N-doped porous carbon multi-layer containing Fe nanoparticles. The strong confinement of Fe active particle in carbon as well as great contact between metal and carbon effectively enhance active site exposure [18]. Heterostructure engineering of MoS₂/Mo₂CT_x nanoarray *via* molten salt synthesis has been enhanced hydrogen evolution reaction [19]. MXenes exhibited a highly efficient adsorption capability as hemoperfusion absorbent towards middle-molecular mass and protein bound uremic toxins in the end stage of renal disease treatment [20].

We thank all the authors for their contributions to this special issue on the development of MXenes. Many aspects of MXenes are still unknown. This includes the number of family members and the large-scale preparation and environmentally friendly synthesis methods for preparing stable products. Accurate control of structure and surface chemical treatment. Theoretical predictions and experimental proofs of physical and chemical properties such as topological insulation and ferromagnetic MXenes. Applied on printable and wearable self-powered electronic instruments. With all these questions in mind, we hope this special issue stimulates new ideas crossing the traditional disciplines in this increasingly prominent research area.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Journal of Materiomics 10 (2024) 520-522



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