COMMENTARY

Evolving MXene species

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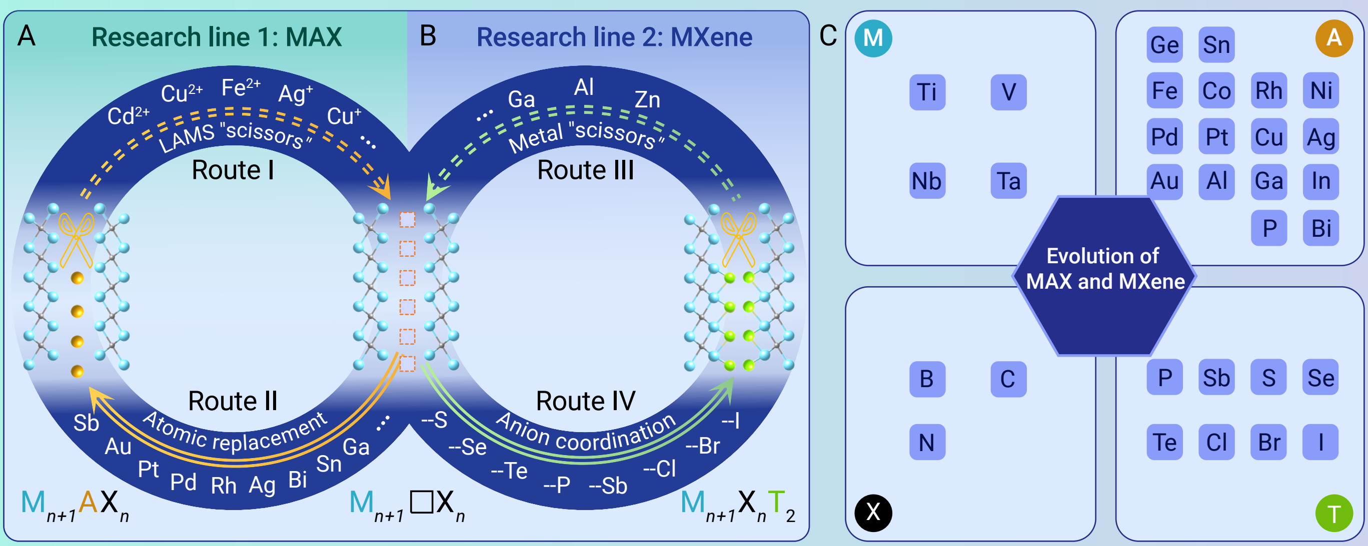
Received: August 15, 2023; Accepted: September 15, 2023; Published Online: September 15, 2023; https://doi.org/10.59717/j.xinn-mater.2023.100027

Citation: Pang J., Zhang S., Rümmeli M., et al., (2023). Evolving MXene species. The Innovation Materials **1(2)**, 100027.

The transition metal carbide or nitride (recently expanded to boride), with a chemical formula of $M_{n+1}X_nT_x$, termed MXene, has shown vast application potentials in energy conversion and storage, environmental remediation, electromagnetic interference shielding, and human healthcare.[1] However, the number of MXene family members has been long confined by combining M (Ti, Nb, V, and Mo, etc.), X (C, N, B), and T (OH, F, O). Then, chasing the new ligand coordination onto the metal centers such as Ti becomes a significant frontier scientific problem. First, Lewis acidic molten salts (LAMS) were employed as mediators to form the MAX phase (with A of Zn or Ga) and eventually transformed into $Ti_3C_2Cl_2$. Here, the Cl element was added to the library of T ligands. Second, $CdBr_2$ for selective etching MAX led to Br-terminated MXenes, which further broadened the choices of T ligands through the



D	Research line 1: MAX	Research line 2: MXene
Parent	Ti_3AlC_2	Nb_2AlC
Step 1	$2\ Ti_3AlC_2 + 3\ Cu^{2+} \rightarrow 2\ Ti_3C_2 + 2\ Al^{3+} + 3\ Cu$	$Nb_2AlC + 3\ Cu^{+} \rightarrow Nb_2C + Al^{3+} + 3\ Cu$
Step 2	$Ti_3C_2 + Ga \rightarrow Ti_3GaC_2$	$Nb_2C \rightarrow [Nb^{2+}]_2C + 2e^-$; $[Nb^{2+}]_2C + x\ Te^{2-} \rightarrow Nb_2CTe_x$
Product	Ti_3GaC_2	Nb_2CTe_x
	Empowering MAX with more A choices (other than Al and Si)	Empowering MXene with more T ligands (beyond the OH, F, and O)

Figure 1. Chemical scissors approach for empowering the MAX and MXene families (A) Development of MAX species by Lewis acidic molten salt scissors and atomic substitution of more A elements, including Ga, Sn, and others. LAMS denotes the Lewis acidic molten salt. (B) Enriching the MXene with more terminational types by metal scissors and anion coordination. (C) Highlighting the newly explored A elements and T ligands that have been applied for composing new MAX and MXene phases. (D) Reaction pathway for empowering more species of MAX and MXene phases. (A, B) Reprinted (and adapted) with permission from Ref. [3] Copyright 2023, AAAS.

substitution of Br with anions such as O, S, Se, Te, NH, and vacancies.[2] The library of MXene is still urged to expand, driven by the bright future of multiple applications. Indeed, the evolution of MXene species could be empowered by coordinating more types of ligands after one knockout A from MAX by chemical scissors.

CHEMICAL SCISSORS EDITING MECHANISMS

In the MXene-related material species, their structures can be readily edited by the Lewis acid molten salt strategy, termed chemical scissors with cations as oxidizers to ionize the A elements. In March 2023, Huang, Gogotsi, and collaborators reported a chemical scissors-mediated intercalation approach for pushing forward the product types of MAX and MXene species.[3] In research line 1 (Route I and Route II in Figure 1A), the types of newly developed MAX species have been expanded with more A elements such as Sb, Au, Pt, Pd, Rh, Ag, Bi, Sn, and Ga. Then, Lewis acids are $CdCl_2$, $CuCl_2$, $FeCl_2$, AgCl and CuCl.

Another research line has promoted the types of MXene with different terminating groups. In research line 2 (Route III and Route IV in Figure 1B), the terminational ligands can be etched by metal scissors and cured by new coordinating radicals such as elements in group 16 (chalcogen: S, Se, Te), group 15 (nitrogen: P, Sb), and group 17 (halogen: Cl, Br, I). Here, the diversity of MXene can be empowered by the newly developed terminating groups (Figure 1C). Combining these two lines has dramatically expanded the family numbers of the MAX and MXene phases (Figure 1D). This discovery may shed light on single-atom catalysis and sensing with large-area homogeneity and mass production compatibility.

HURDLES TO OVERCOME

The fluidized bed reactor method leads to the continuous production of MXene nanosheets. This is an advantage. But, the challenges of such a delicate strategy should be addressed prior to mass production. First, the size and thickness distribution should be statistically recorded and narrowed down because the MXene nanosheets could be synthesized in an uncontrolled manner. Indeed, the same concerns occurred during the carbon nanotube production and sorting of the same diameter and chirality. Inspired by the cloning of carbon nanotubes via a designed chirality cap, one may consider incorporating the seeding nanosheets or nanodots of MXene to provide the reacting edges or surfaces for hosting MXene growth. Maybe a single crystal of MXene could be prepared in such a bottom-up growth fashion. Second, the MXene species could have evolved except for the production of Ti_2CCl_2, i.e., their family expanded to include the other metals and halogens. Here, the thermodynamics and kinetics should be calculated to provide the reaction pathway for the synthesis of MXene other than the by-product. Third, the collection of unreacted precursors could be taken care of for cost reduction and sustainability. In addition, the try-and-error experimental synthesis modes could be assisted and promoted by the simulation of molecular dynamics and big-data trained prediction of reaction parameters for the production of MXene.

EMERGING TRENDS

During the course of the commentary preparation, we noticed that Huang's team and collaborators had applied the chemical-scissor mediated method to incorporate six kinds of metal atoms into the interlayer spacing of transition metal dichalcogenides including TaS_2 and $NbSe_2$ (preprint at arXiv:2304.14036). Here, Cu powder mixed with salt was blended into powders of transition metal dichalcogenides (TMDC) nanosheets, and subsequently, after LiCl-KCl molten salt treatment (at 360 °C), Cu was successfully intercalated into TaS_2 2D layered structure. Furthermore, Mn, Fe, Co, Ni, and Ag atoms were individually intercalated inside 2D materials such as $TiSe_2$ and $TaSe_2$, which may facilitate the in-depth investigation of magnetic and catalytic applications at the single atom level. To date, these single-atom terminals over MXene may provide an ideal platform for examining the concepts of spin-related nanomagnet[1] or even single-atom magnets (if existing).

In another research line, they updated the MAX family by empowering more elements on the A layers other than conventional Al or Si elements (preprint at arXiv:2307.09091). Indeed, the Lewis acid molten salt mediates the knockout of conventional Al or Si in MAX, which follows the reaction of substitutions by foreign elements in the composition of the molten salts. To date, the A layer has been broadened into the categories of 28 elements, including Mn, Fe, Ni, Pt, Pd, and Rh. Yet, the high-cost Tc, Ru, Re, and Os elements and liquid Hg, remain unexplored but hold promises in this line.

FUTURE OPPORTUNITIES

After seeing the success of chemically editing TMDC intercalations, we may foresee the application of chemical scissors in the intercalation of van der Waals materials, including carbides, nitrides, oxides, chalcogenides, and halides. For instance, how to immobilize single atom or dimer Pt or Pd atoms over the hosting matrix remains an unsolved problem for electrochemical catalysis for hydrogen energy production.[4] Another example is the high-throughput screening of composite aerosols composed of MXene nanosheets and others.[5] Therefore, we expect more exciting results coming out from the structural editing of MXene species via mild Lewis acid molten salt chemical scissors and metal scissors.

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ACKNOWLEDGMENTS

The authors thanks the Natural Science Foundation of Shandong Province for Excellent Young Scholars (ZR2022YQ41), and the fund (No. SKT2203) from the State Key Laboratories of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences for support. The Project was supported by the Foundation (No. GZKF202107) of State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences.

DECLARATION OF INTERESTS

The authors declare no competing interests.