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HIGHLIGHT

General synthesis of MXene by green etching chemistry of fluoride-free Lewis acidic melts

Lu-Yang Xiu, Zhi-Yu Wang*, Jie-Shan Qiu*

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The MXene has emerged as a rising star on the horizon of material science due to widespread applications ranging from energy and catalysis to biomedicine [1, 2]. These two-dimensional (2D) transition metal carbides/nitrides well collect a variety of attractive properties such as rich surface chemistry, high hydrophily, and metallic conductivity that are difficultly attained for all in conventional 2D atomic crystals [3, 4]. The state-of-the-art strategies for making MXene mainly rely on the selective etching of the layered structure consisting of A elements in the MAX phase by fluoride-involved chemistry [5]. Although dozens of MAX phases are commercially available, this way is mostly work for the Al-containing MAX phase with high reactivity with fluoride ions [1–5]. Meanwhile, the use of aqueous fluoridated etchants further makes the process highly hazardous with the fatal risk of toxicity and corrosivity, hindering the extensive studies and use of MXene. These agents also show a negative impact on the specific capacitance of etched MXene in supercapacitors by introducing a high concentration of fluoride groups. Electrochemical etching route has been developed for etching MAX precursors to fluoride-free MXene [6, 7]. Nevertheless, the high effectiveness is still limited to a handful of MXene from the Al-containing MAX phase. The development of safer and efficient strategies for yielding high-quality MXene from the expended family of the MAX phases is imperatively necessary to full exploitation of the potential of MXene.

Recently, Huang. et al. proposed a generic Lewis acid etching route for preparing various MXene from a large family of MAX phases with different A elements (such as Al, Zn, Si, Ga, etc.) [8]. Selectively etching these MAX phases is realized in terms of the oxidation of the A elements by the cation of fluorine-free Lewis acid molten salts with a higher electrochemical redox potential (e.g., $ZnCl_2$, $FeCl_2$, $CuCl_2$, AgCl). Remarkably, the redox coupling between the A elements in MAX phase and the cation of the Lewis acid Cl melts can be predicted by a Gibbs free energy mapping according to the redox potentials of A elements in MAX phases and the cations in molten salt melts (Fig. 1a). It guides the rational selection of appropriate Lewis acid melts for MXene synthesis, and demonstrates the generalization of this route to a wide range of MAX precursors (Fig. 1b–g). By this way, the MXene with surficial groups like –Cl, –O could be yielded to deliver high reactivity and constant pseudocapacitive properties for electrochemical Li storage. Coverage of –OH or –F groups on MXene surface is avoided to optimize the interaction between Li and surficial groups on MXene. It leads to the highest capacitance among reported Ti_3C_2 MXene in non-aqueous electrolytes with an excellent high-rate response and lower operating potential, highlighting the great promise in electrochemical energy storage.

General synthesis of MXene by manipulating the diversity and green chemistry of MXene and Lewis acid in the molten salt system offers a safer and highly efficient way for the preparation of MXene. Expanding the range of parent MAX phases provides an extra room for tuning the

L.-Y. Xiu, Z.-Y. Wang*, J.-S. Qiu*
State Key Laboratory of Fine Chemicals, Liaoning Key Laboratory for Energy Materials and Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
e-mail: zywang@dlut.edu.cn

J.-S. Qiu
e-mail: jqiu@dlut.edu.cn

J.-S. Qiu
College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

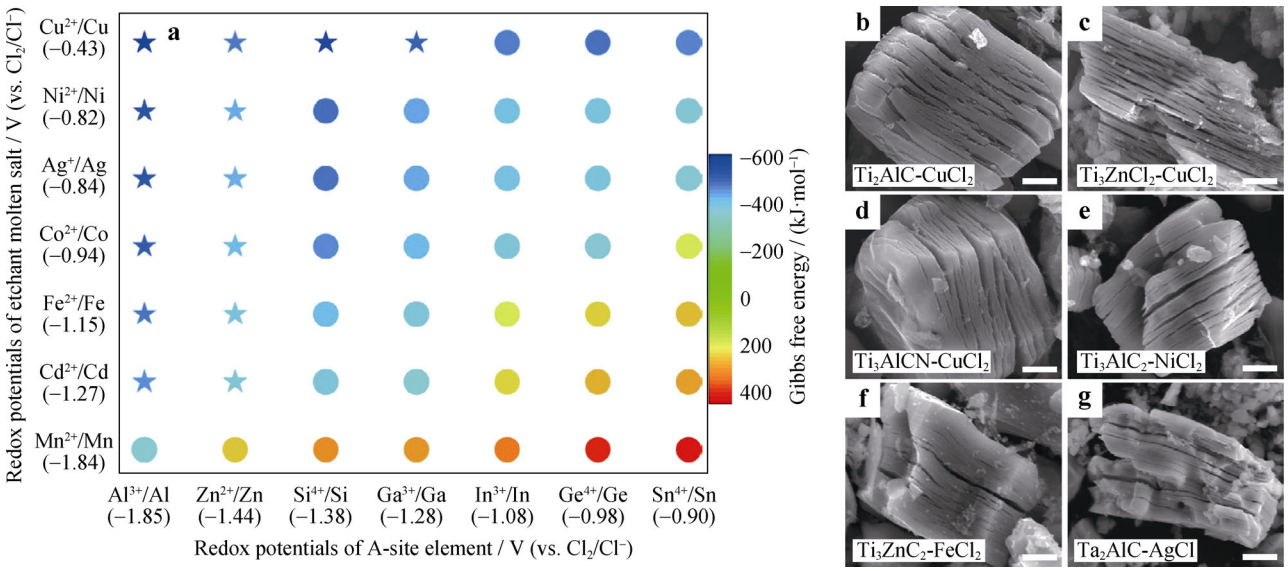

Fig. 1 Generalization of the Lewis acid etching route to a large family of MAX phases: **a** Gibbs free energy mapping (700 °C) guiding selection of Lewis acid Cl salts according to electrochemical redox potentials of A-site elements in MAX phases (*x* axis) and molten salt cations (*y* axis) in Cl melts, where stars mark corresponding MXenes demonstrated in current study, while spot symbols remain theoretical prediction; SEM images revealing typical accordion morphology of MXenes from different MAX phases etched by various Lewis acid Cl salts, such as **b** Ti_2AlC by $CuCl_2$, **c** Ti_3ZnC_2 by $CuCl_2$, **d** Ti_3AlCN by $CuCl_2$, **e** Ti_3AlC_2 by $NiCl_2$, **f** Ti_3ZnC_2 by $FeCl_2$ and **g** Ta_2AlC by AgCl with scale bars, 2 μm. (Reproduced from Ref. [8] Copyright 2020 Springer Nature)

functionalities and properties of MXene. More importantly, it enables the production of new MXenes that are hardly obtained via existing methods. Undoubtedly, this general approach may hold great promise in the scalable production of MXene with a wide chemical and structural variety if the energy consumption could be further reduced.

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