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Exploring mechanochemistry for fluoride-free MXene synthesis

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Transition metal carbides and nitrides, known as MXenes, have emerged as one of the fastest-growing groups of 2D materials with great potential for application in supercapacitors, micro-supercapacitors, batteries, fuel and solar cells, composite materials, photocatalysis, biosensors, photodetectors, etc. They are represented by the chemical formula $M_{n+1}X_nT_x$ (n=2-4), where M represents transition metals like Sc Ti, Zr, Hf, V, Nb, Ta, Cr and Mo, X is carbon and/or nitrogen, and T stands for surface termination groups (-OH, -F, -O or -Cl) [1]. To date, most MXenes have been prepared through a wet chemical etching method that requires: (1) preparation of precursors, known as MAX phases (chemical formula $M_{n+1}AX_n$, where A is an element from groups 13 or 14 of the periodic table, e.g., Al, Si, or Ga, (2) selective etching of the A layer from the MAX phase followed by delamination into multilayer MXene and (3) intercalation and delamination process to obtained monolayer MXene [2]. The etching process conventionally involves fluoride solutions such as HF or LiF/HCl due to their high efficacy and selectivity. However, fluoride-based solutions are highly hazardous and, their use is associated with considerable safety and handling concerns that are a major barrier to scaling up MXene production. Besides, -F terminal functional groups inevitably exist in these MXenes, detrimental to supercapacitor and battery performances. It is therefore desirable to develop simple, safe, reliable as well as sustainable synthetic routes for MXene preparation and practical application.

In this work, we explore mechanochemistry (MC) to prepare fluorine-free MXenes. This is a viable approach to promote reactions of solids quickly and quantitatively that can be easily scaled-up to manufacturing levels [3]. $Ti_3C_2T_x$ was prepared by mechanochemical ball-milling of Ti_3AlC_2 MAX phase with zinc chloride ($ZnCl_2$) at room temperature. Additionally, 20 µL of solvents (HCl or NaOH) were introduced to the MC reactions through liquid-assisted grinding (LAG). The obtained material was then treated in tetramethylammonium hydroxide (TMAOH) to complete the delamination process. The prepared MXene have been studied by cyclic voltammetry (CV), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible (UV/Vis) spectrophotometry, Raman (RAMAN) spectroscopy and low-energy ion scattering (LEIS) spectrometry.

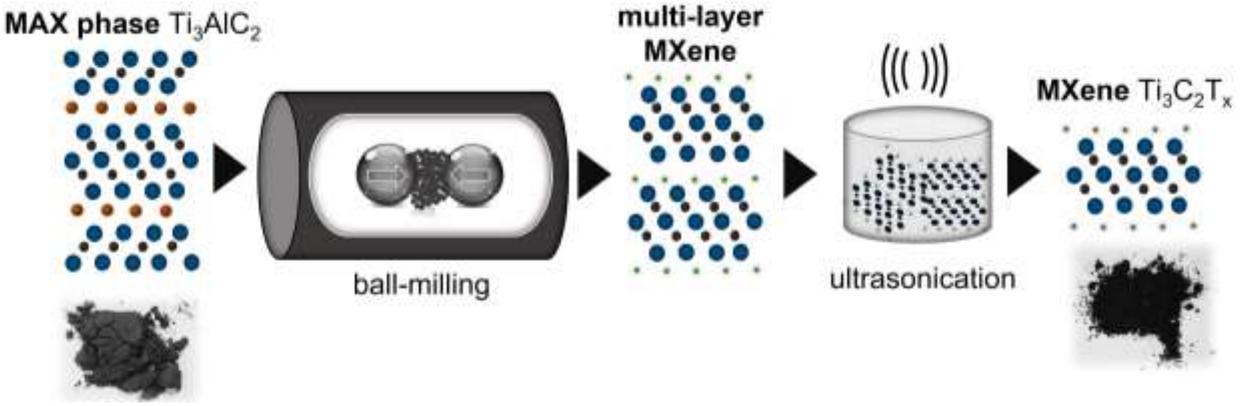

Figure 1. Schematic illustration of the synthesis procedure to obtain MXene using ball-milling and ultrasonication treatments [4].

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References

1. M. Hu, H. Zhang, T. Hu, B. Fan, X. Wang and Z. Li, *Chem. Soc. Rev.* **49** (2020) 6666-6693. https://doi.org/10.1039/D0CS00175A
2. K. R. G. Lim, M. Shekhirev, B. C. Wyatt, B. Anasori, Y. Gogotsi, Z. W. Seh, *Nat. Synt.* **1** (2022) 601-614. 10.1038/s44160-022-00104-6
3. M. Kralj, A. Supina, D. Čapeta, I. Sović, I. Halasz*, Materialia* **14** (2020) 100908. https://doi.org/10.1016/j.mtla.2020.100908
4. G. Ljubek, M. Kralj, M. Kraljić Roković, *Mater. Sci. Technol*. **39** (2023) 1645-1649. https://doi.org/10.1080/02670836.2023.2178173

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