On the Structural Stability of MXene and the Role of Transition Metal Adatoms

Supporting Information

Justinas Palisaitis*, Ingemar Persson, Joseph Halim, Johanna Rosen and Per O.Å. Persson

Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

*Corresponding author: justinas.palisaitis@liu.se

S1. MXene synthesis details.

Nb₂AlC MAX phase powders were synthetized by pressureless sintering of elemental powders of Nb (99.8%, 325 mesh, Alfa Aesar, Kandel, Germany), Al (99.5%, 325 mesh, Alfa Aesar, Kandel, Germany) and C (99.9995%, 200 mesh, Alfa Aesar, Karlsruhe, Germany) as reported in.¹ The elemental powders were mixed in an agate mortar with a molar ratio of 2:1.1:1 and mixed together afterwards the mixture was poured in a Teflon jar and hand shaken for 5 min. The mixture was heated at a rate of 5 °C/min to 1600 °C in an alumina crucible under 5 sccm Ar flow and held at 1600 °C for 2 h. After furnace cooling, the lightly sintered sample was crushed using agate mortar and pestle and sieved through a 450 mesh sieve. To produce Nb₂C from Nb₂AlC, 2 grams of Nb₂AlC powder were immersed slowly in a Teflon bottle containing 20 ml of 48% aqueous hydrofluoric acid (HF). The bottle containing the mixture was placed on a stir plate at room temperature and the mixture was stirred using a Teflon coated magnet for 100 h. The resulting suspension was washed with deionized (DI) water for several cycles till the mixture reached a pH of \approx 6. In each, washing cycles of 40 ml of DI water were added to the mixture in a centrifuge tube and the tube was hand-shaken for 1 min before centrifuging at 5000 rpm for 1 min. One gram of the settled powder was added to a 5 ml of an aqueous solution of 54-56 wt.% TBAOH, (C₄H₉)₄NOH. The mixture was hand-shaken for 5 min then washed 3 times by 40 ml DI water each time. Then 50 ml of DI water were added to the settled powder and sonicated using an ultrasonic bath for 1 h. The sonication was performed while N₂ gas was bubbled in the solution. Finally, the mixture was centrifuged for 1h at 5000 rpm and the supernatant was collected for TEM investigation.

S2. STEM, EELS and STEM image simulation details.

TEM characterization was performed using the Linköping double Cs corrected FEI Titan³ 60-300 equipped with a high-brightness gun (XFEG), monochromator, efficient high solid angle Super-X EDX detector and ultrafast Gatan GIF Quantum ERS post-column imaging filter. Prior to investigation, the sample was *in situ* heated inside the TEM employing a furnace type double tilt heating holder (Gatan Model 652) at 150 °C for 1h, for eliminating carbon contamination.

High-resolution STEM high-angle annular dark-field imaging was performed at 300 kV using an optimized 25 mrad beam convergence semi-angle, ~10 pA beam current, 80-250 mrad HAADF detector collection angle. Single layer MXene sheet identification was performed through STEM image intensity analysis. The elemental constituents of the MXene sheets was identified by EELS. EELS spectrum images of 50 px \times 50 px were recorded with 0.5 eV/channel energy dispersion, a collection semi-angle of 29 mrad and 0.3 s pixel dwell time. Single spectra were extracted by averaging the as-recorded spectrum images to improve signal-to-noise ratio, followed by background subtraction using a power law model.

STEM image simulations were performed using the Dr Probe software² employing microscope experimental parameters as listed above. Multi-slice scan image calculations with 25 frozen phonon modes adopting a Lorentzian probe with 0.7 Å FWHM was carried out on Nb₂CT_xNb_n (n=0, 1, 2 and T_x=2O) single sheet supercells that were defined using CrystalMaker.³

S3. Model Nb₂C MXene.



Fig. S3 Plan-view crystal structure projection (left) and corresponding STEM image simulation for the bare Nb₂C MXene (right).

S4. MXene sheet 5 days after synthesis.



Fig. S4 Nb_2CT_x sheet 5 days after synthesis and after being stored in vacuum.

S5. MXene sheet 6 days after synthesis.





S6. EELS data.



Fig. S6 Core-loss EELS spectra showing from the fresh Nb_2CT_x sheet showing absence of F after synthesis.

S7. STEM image simulations of Nb₂C surfaces terminated with O.

STEM image simulations were performed considering fully O terminated Nb₂C surfaces. Theoretical calculations predict two potential sites for O surface terminations which could be positioned either over Nb (A-sites) or over C (B-sites) while A-sites are more favourable.⁴ STEM image simulations as shown in Fig. S7 shows that either case will have a minor effect on the STEM intensity by increasing intensity locally over C sites or Nb sites as shown in line profiles. Considering the noise level in the experimental STEM images, resolving such minor intensity changes are not feasible given the current experimental setup.



Fig. S7 STEM image simulations with O terminating Nb₂C surfaces.

References:

- 2 J. Barthel, Dr. Probe High-resolution (S)TEM image simulation software, 2017.
- 3 CrystalMaker Software Ltd, Oxford, England.

4 Y. Xie, M. Naguib, V. N. Mochalin, M. W. Barsoum, Y. Gogotsi, X. Yu, K.-W. Nam, X.-Q: Yang, A. I. Kolesnikov and P. R. C. Kent, *J. Am. Chem. Soc.*, 2014, **136**, 6385-6394.

¹ M. Naguib, J. Halim, J. Lu, K. M. Cook, L. Hultman, Y. Gogotsi and M. W. Barsoum, *J. Am. Chem. Soc.*, 2013, **135**, 15966-15969.