

NIOBIUM-BASED MAX (Nb_2AlC) AND MXENE (Nb_2CT_x) MATERIALS FOR THE HYDROGEN EVOLUTION REACTION

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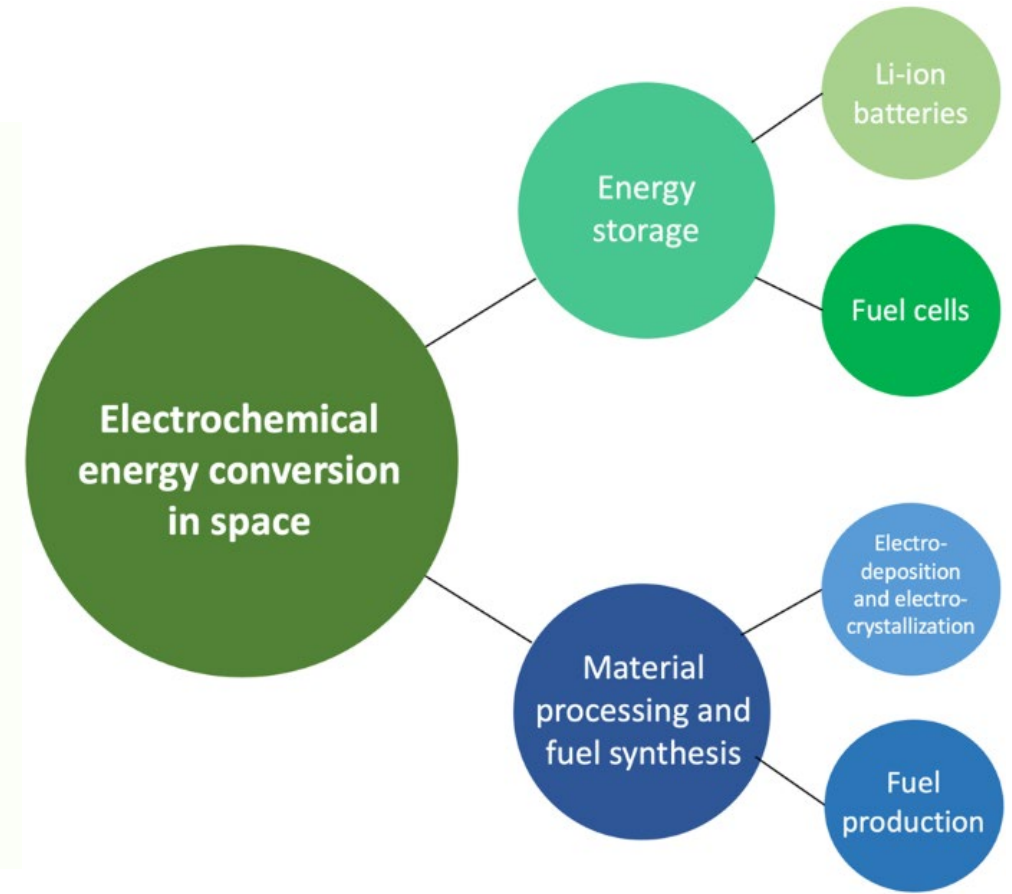
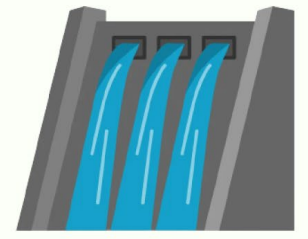
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Importance of Electrochemistry in Climatic and Sustainable Energy



SUSTAINABLE ENERGY EXAMPLES

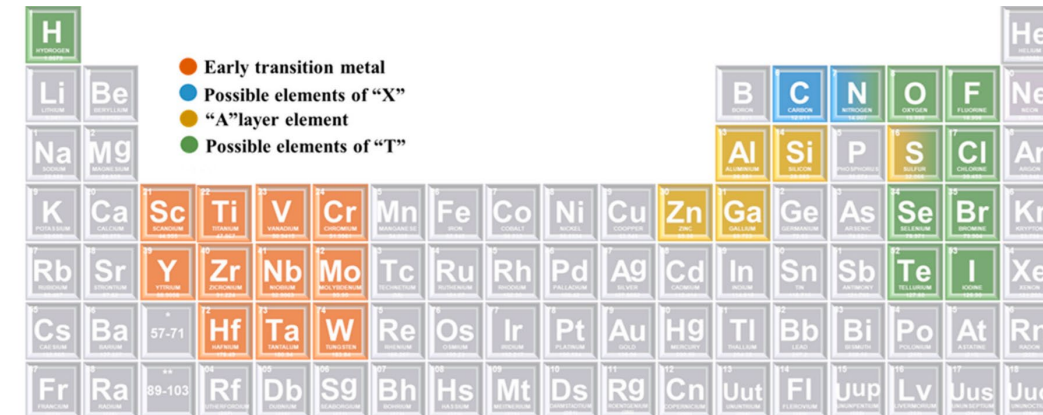
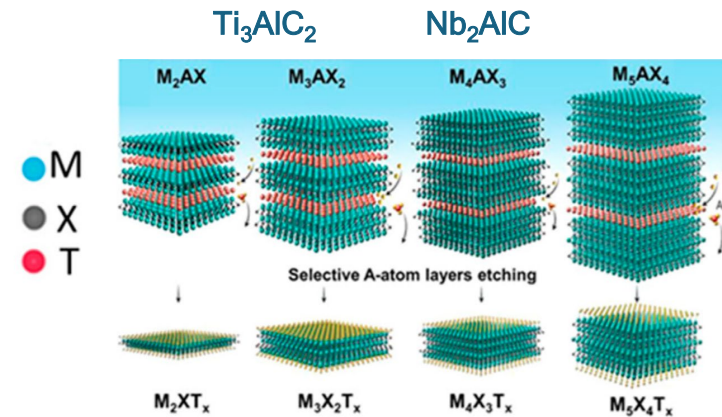


- Cleaner energy generation
- Efficient resources recovery
- Effective pollutant removal

- Wastewater treatment
- Recycling and material recovery
- Electrochemical sensors

History of MXene and motivation towards electroch

- Discovered in 2011
- by Prof. Yury Gogotsi & Michel Barsoum



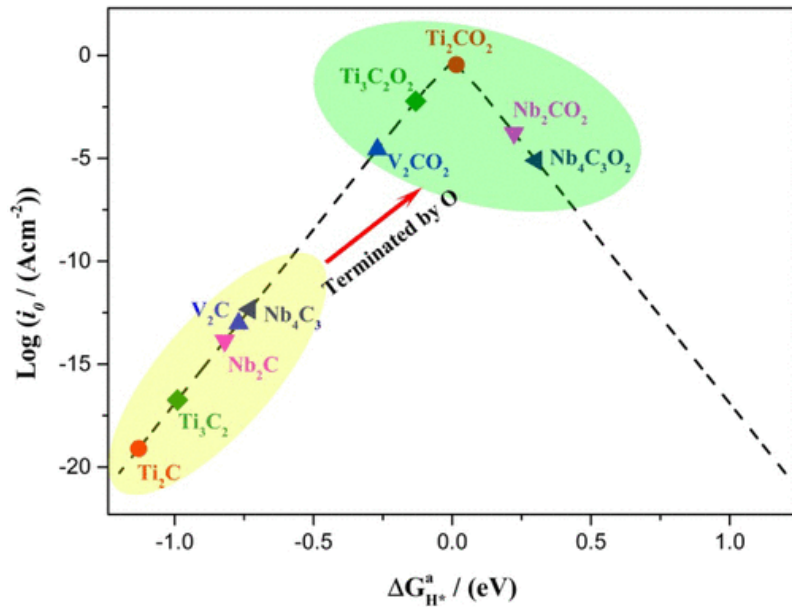
Why Nb₂CT_x over other MXene materials:

- Superior electronic conductivity and electrochemical performance
- Less explored than other MXenes
- Nb-based materials are stable in acid medium - suitable to be used as electrode materials in proton exchange membrane water electrolyzers
- Canada has the second reserved of Nb in the world.

Why MXenes are preferred for electrochemistry?

- High electric and metallic conductivities
- Redox-active surface
- Ability to intercalate cations between 2D sheets
- High surface area
- Tunable surface chemistry
 - OH, -O, -F, and -Cl

Literature survey of hydrogen evolution reaction studies of Nb₂CT_x



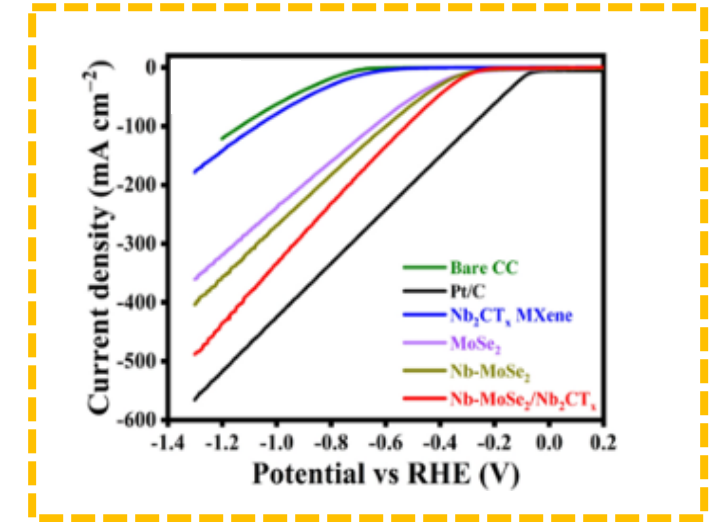
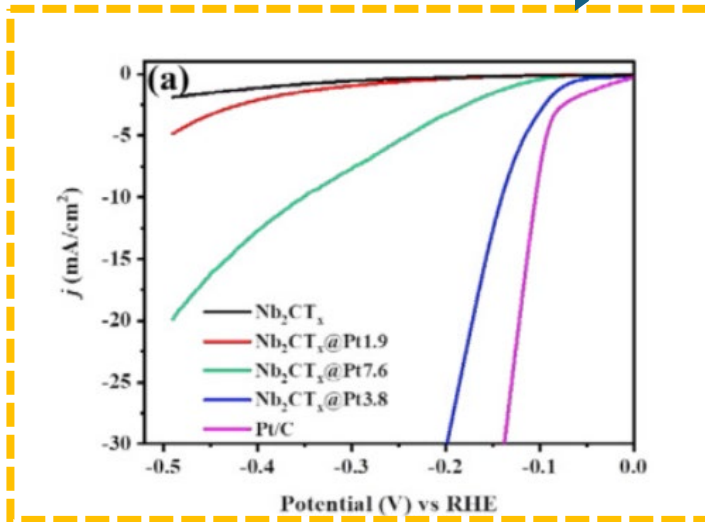
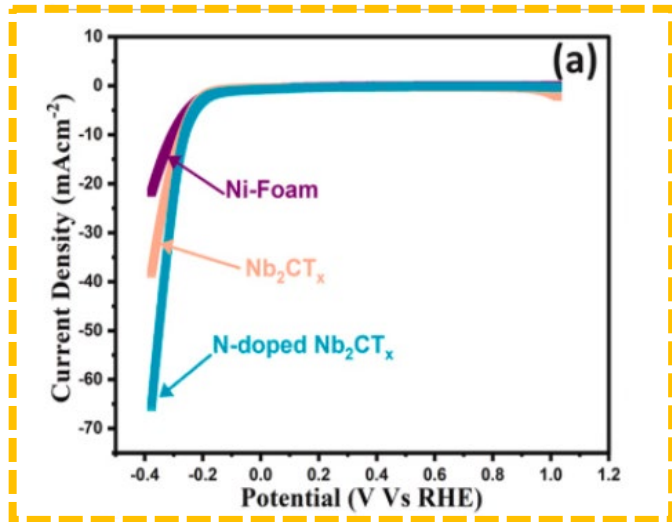
- Gibbs free energy plot is used to determine whether materials have activity for HER
- MXenes carry mixed terminations (-F, -OH, -O) which are heterogeneous active sites
- **Activity is termination dependent (-OH > -O > -F)**

Routes to improve the activity

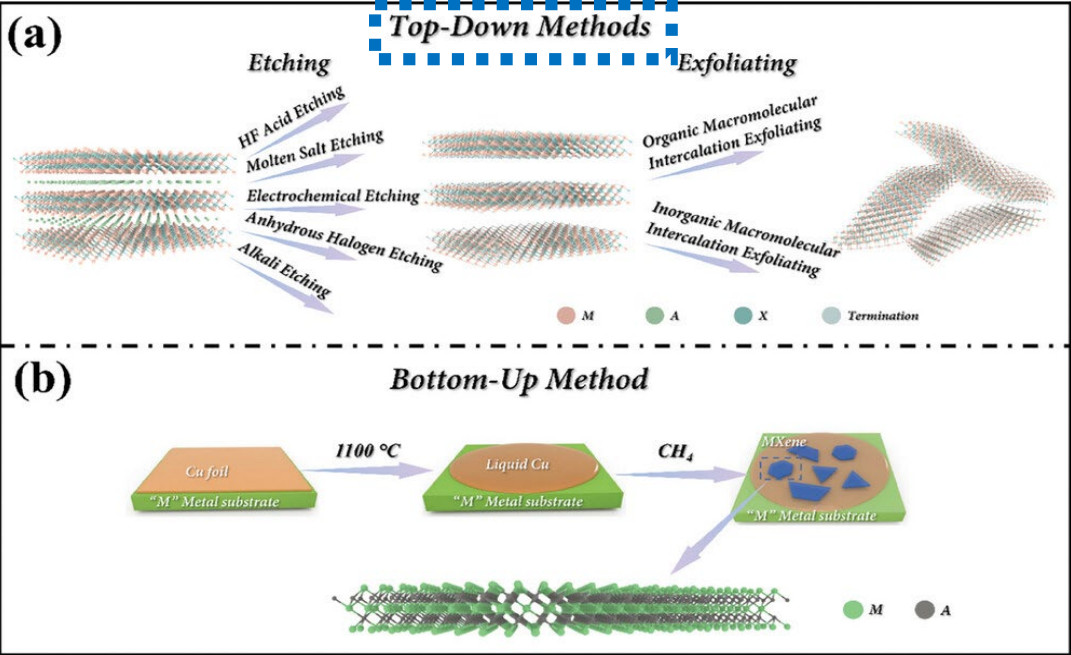
Nitrogen doping

Platinum

Composite formation



Synthesis methods, challenges and objectives of this work



MILD method:

Summary for the synthesis of Nb₂CT_x MXene using in-situ/MILD HF solution.

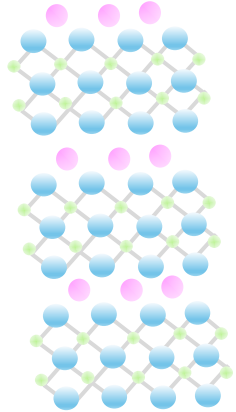
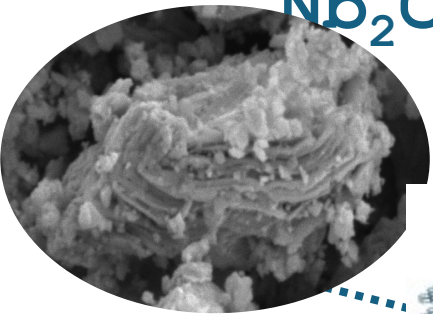
Raw materials	MAX phase	Etchant	Concentration (%)	Time (Hrs)	Temperature (°C)	pH	Intercalant	MXene
Nb:Al:C	Nb ₂ AlC	LiF:HCl	1.6 g:9 M	24	45	6	-	Nb ₂ C
Nb:Al:C	Nb ₂ AlC	LiF:HCl	1 g:6 M	45	40	7	-	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	3 g:12 M	24	180	7	-	Nb ₂ C
Nb:Al:C	Nb ₂ AlC	LiF:HCl	1 g:9 M	24	90	-	-	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	2.5 g:9 M	120	75	-	-	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	1.6 g:9 M	24	45	6	-	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	2 g:9 M	90	60	-	-	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	1 g:1.7 M	24	200	~6	-	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	3 g:12 M	3	55	-	Li	Nb ₂ CT _x
Nb:Al:C	Nb ₂ AlC	LiF:HCl	2 g:9 M	24-120	55-70	~7	-	Nb ₂ CT _z
Nb:Al:C	Nb ₂ AlC	LiF:HCl	2 g:9 M	120	55	~7	-	Nb ₂ CT _x

- Vast majority of the reports: Nb₂AlC MAX powders immersed into 47-51% HF at room temp for 160 h
- MILD method using LiF:HCl less hazardous alternative route but different reaction condition with variation in time and temperature particularly.
- Objectives of this work:
 - To optimize the standard conditions of time and temperature for transition of MAX to MXene phase
 - Time-dependent study of reaction from Nb₂AlC to Nb₂CT_x
 - Evaluate the activity of Nb₂CT materials for HER.

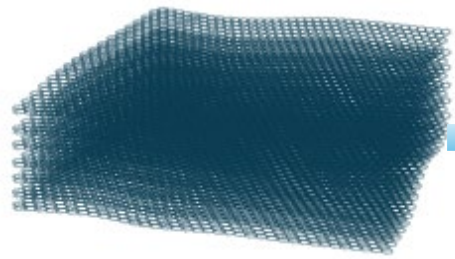


Methodology

Schematic Presentation for Nb₂AlC to Nb₂CT_x - MILD

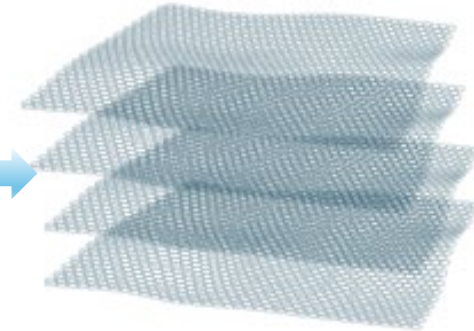


MAX (Nb₂AlC)

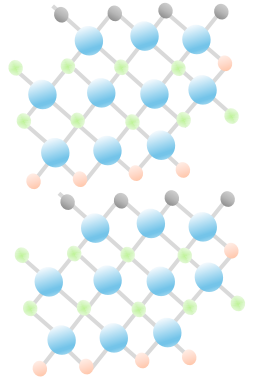
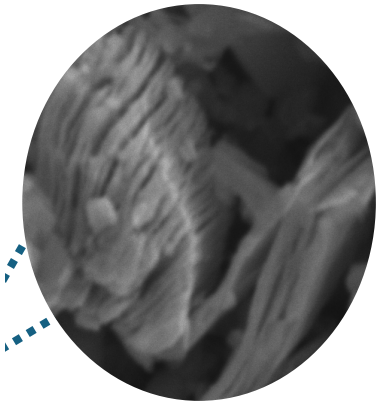


Etching
LiF-HCl/ 24-90 h
48-50°C

Washing & Purification
Centrifugation Cycles
pH (5-6)



MXene (Nb₂CT_x) multilayer



(F/OH)



Bulk sample
(taken from sediment)

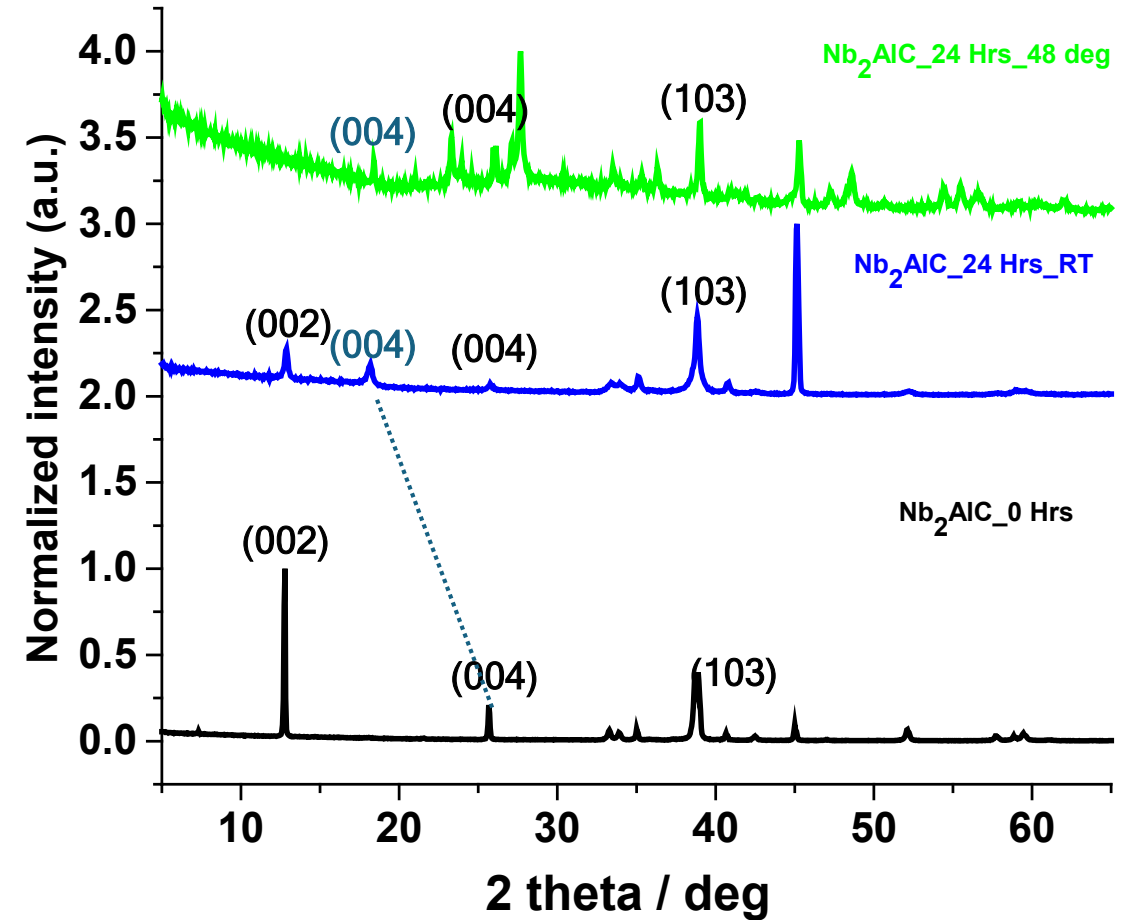
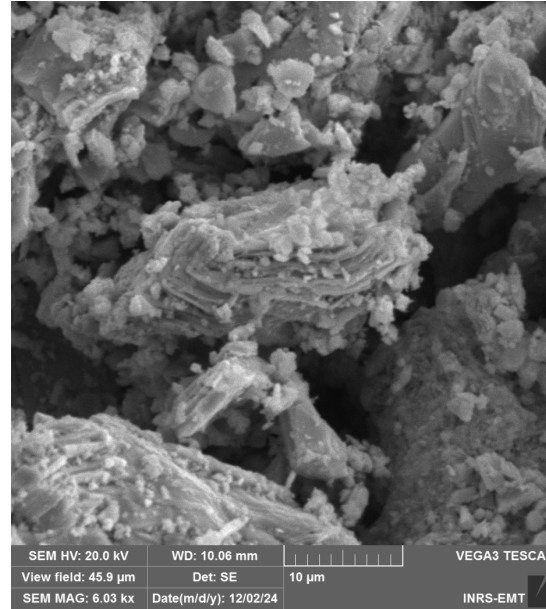
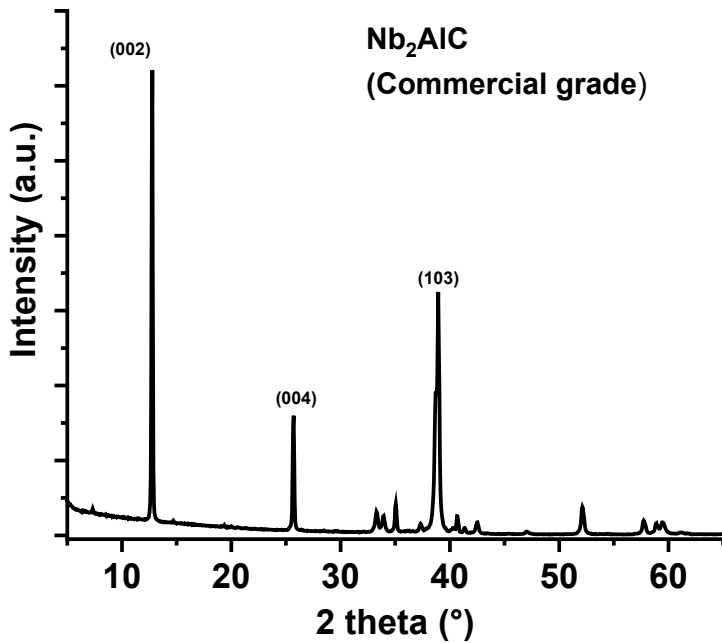


Supernatant

XRD and SEM



X-ray diffraction and Scanning Electron Microscopy images

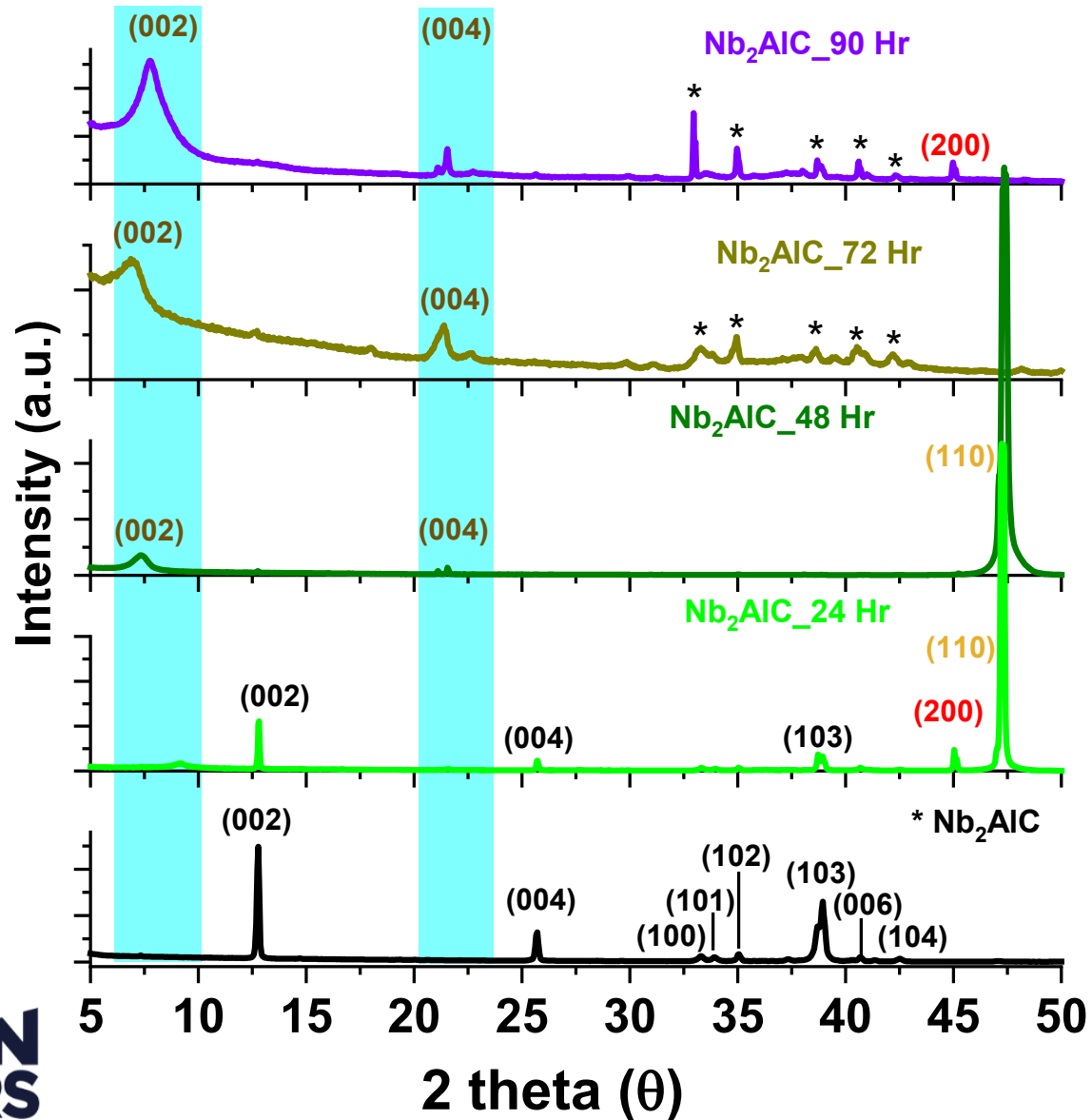


Nb₂AlC (commercially purchased)

Temperature dependent Nb₂AlC to Nb₂O₅

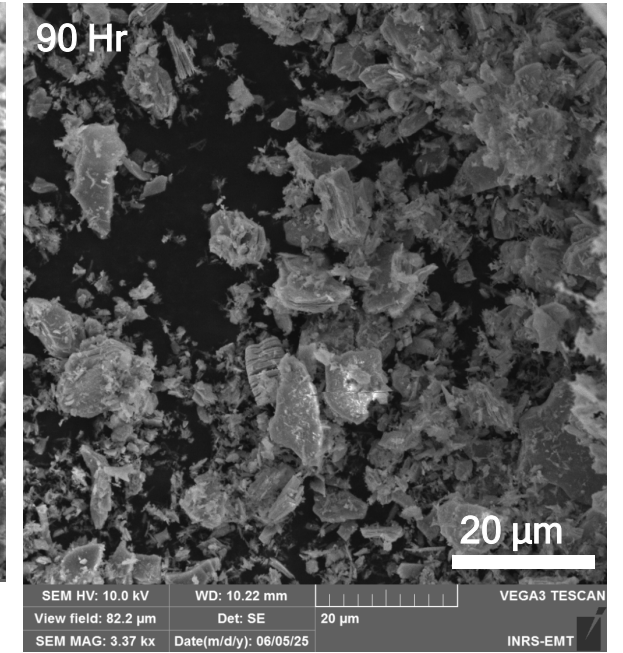
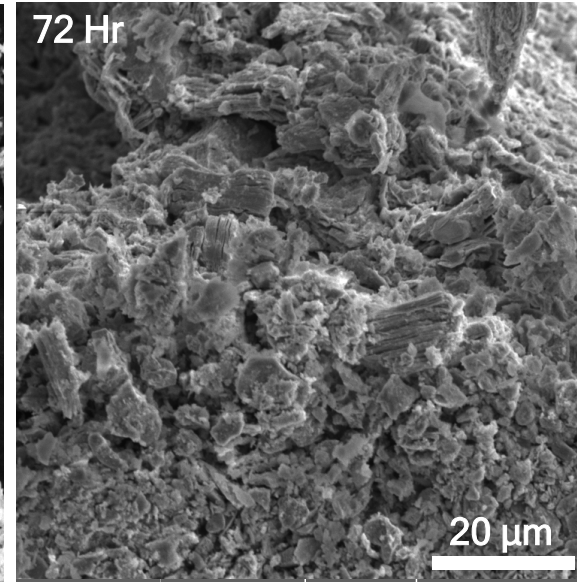
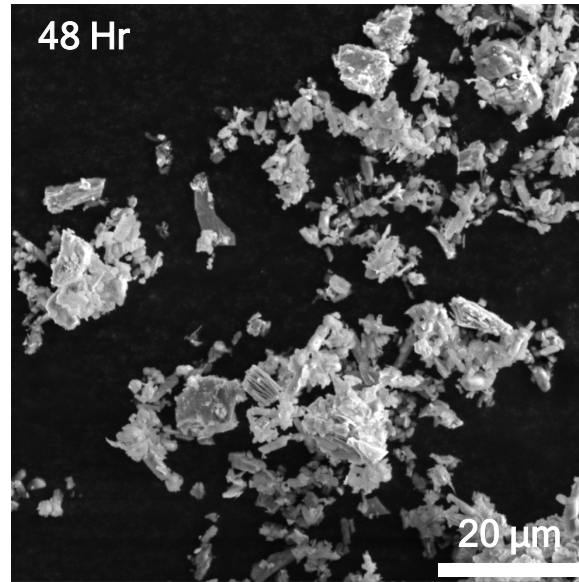
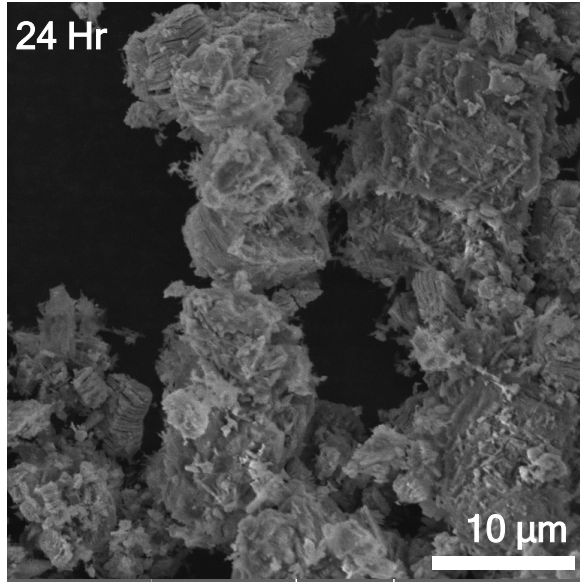
- XRD of MAX phase matching well with literature and SEM shows the layered structure of Nb₂AlC
- Disappearance of peak at 12.6° at 48-50°C .

Bulk material - Effect of time (0 to 90 Hours) at 48 °C

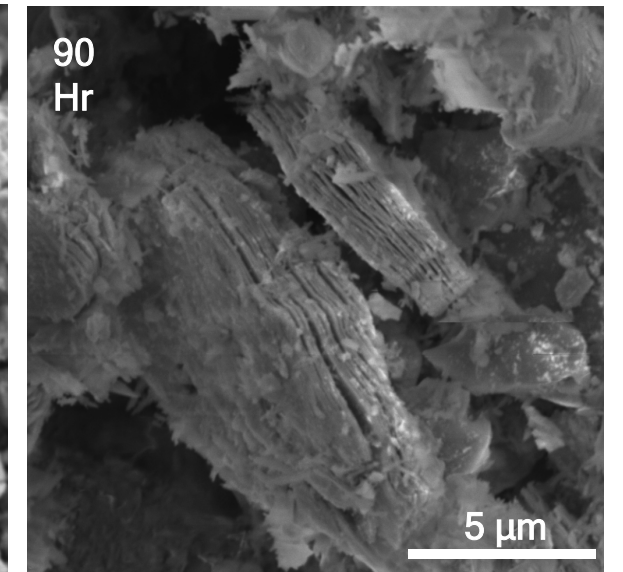
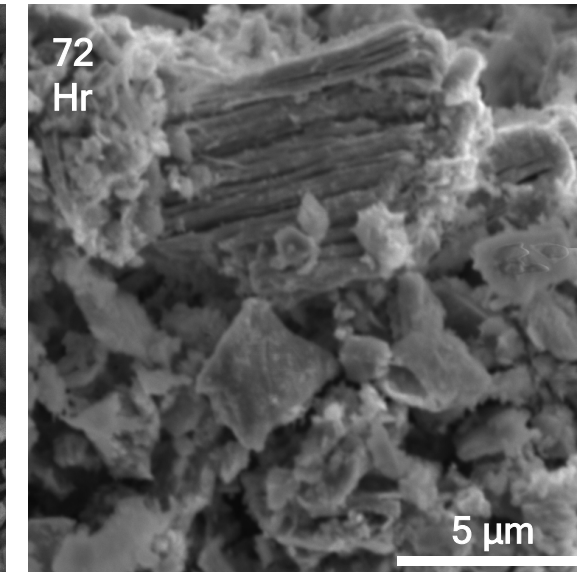
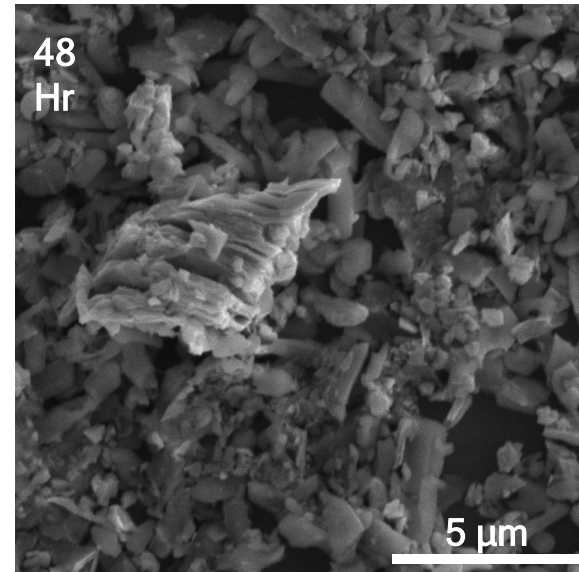
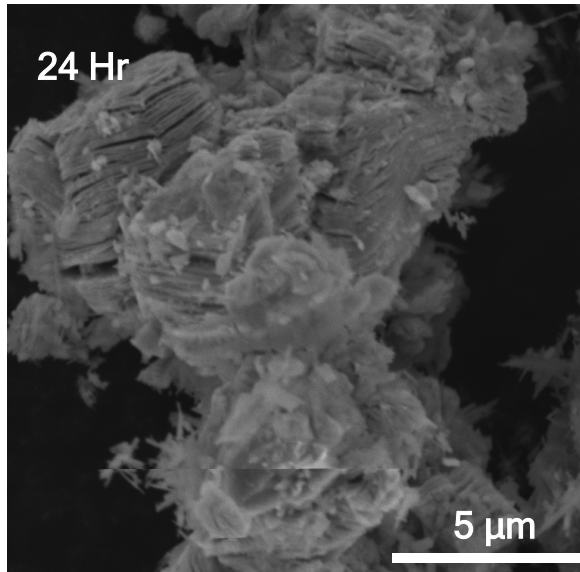


- Samples taken for XRD are from bulk material after washing and purification.
- Reduction in the intensity of peaks at 12.8° and 25.3 ° 2 θ indicates conversion of MAX to MXene
- Disappearance of peak at 38.5 indicates etching of Al layer
- But conversion from MAX to MXene is not completed even after 90 Hrs of reaction.
- LiF peaks at 44.996 (200), PDF No. 00-004-0857
- Silicon substrate 46.75 (110) PDF no. 00-005-0565

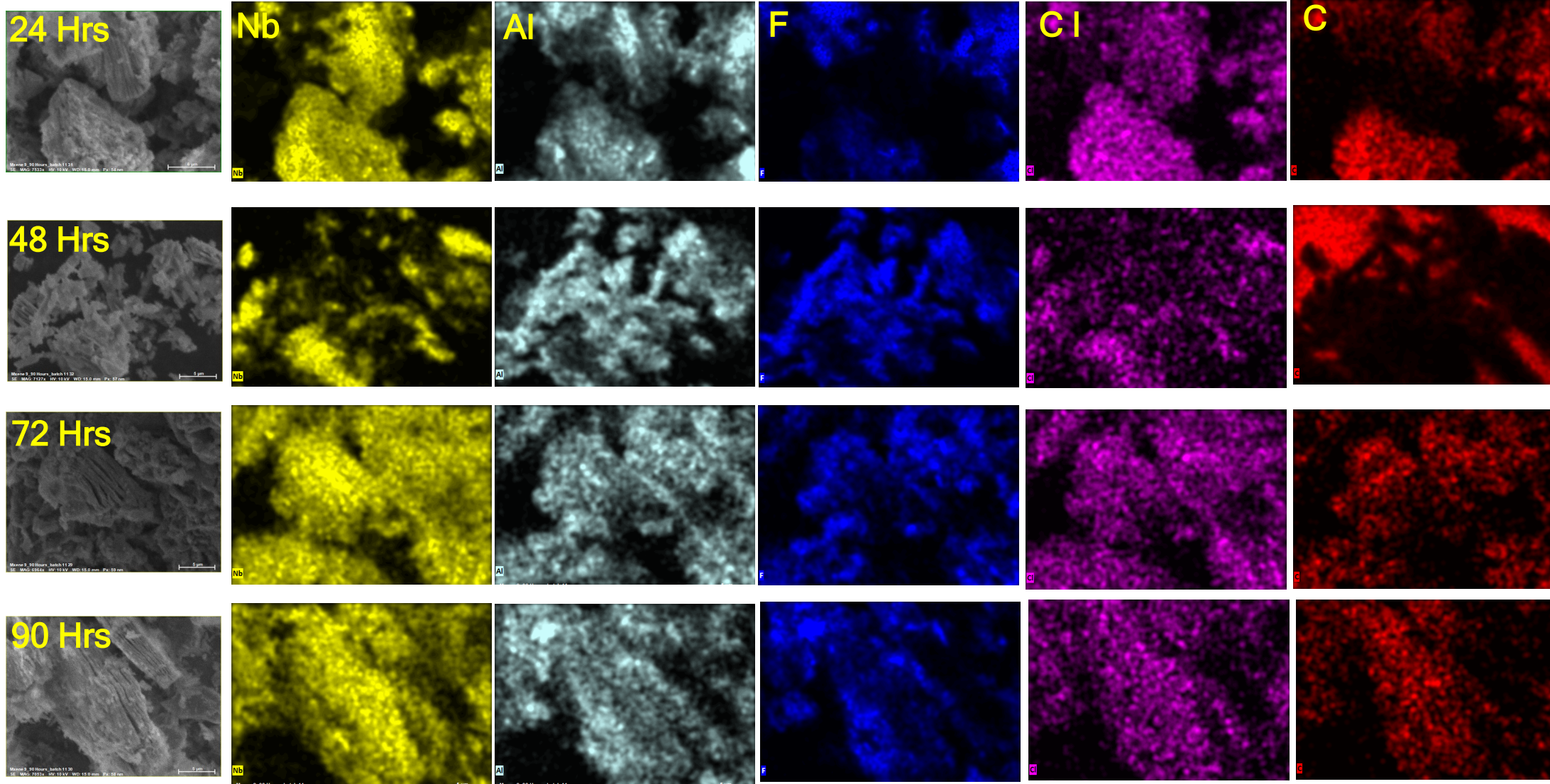
Bulk material Time dependent SEM of Nb₂AlC to Nb₂CT_x transformation



At higher magnification

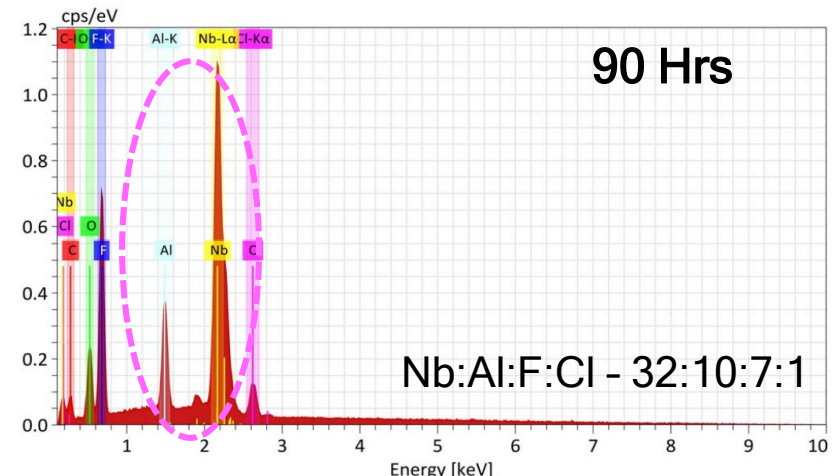
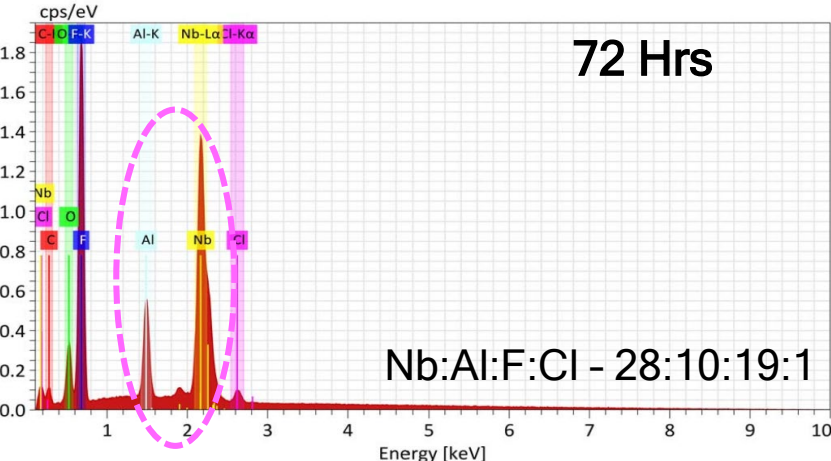
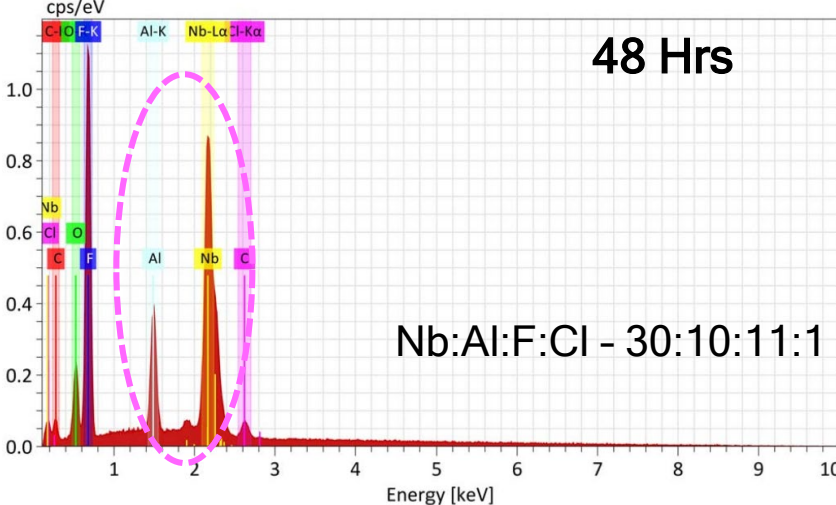
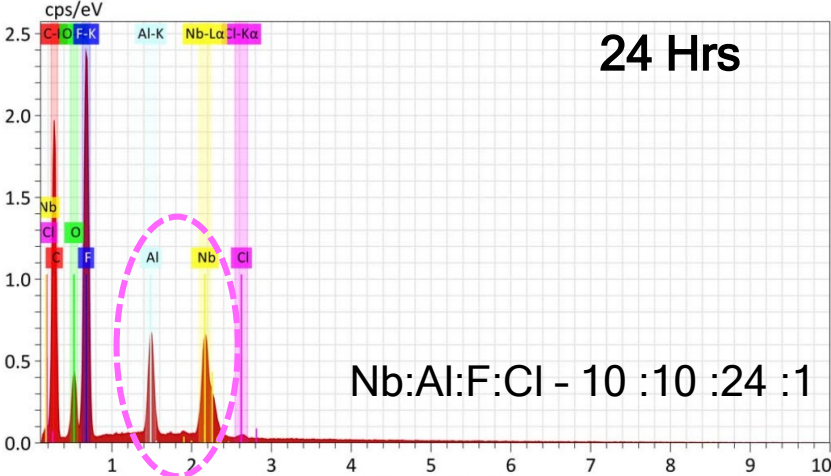


Bulk material Mapping of all the samples



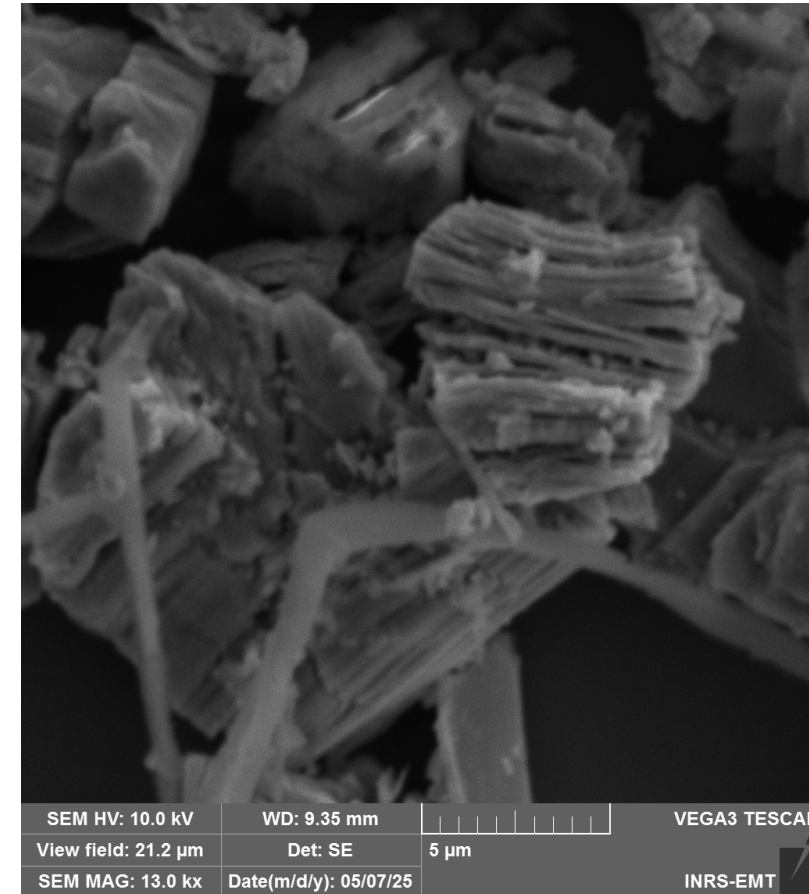
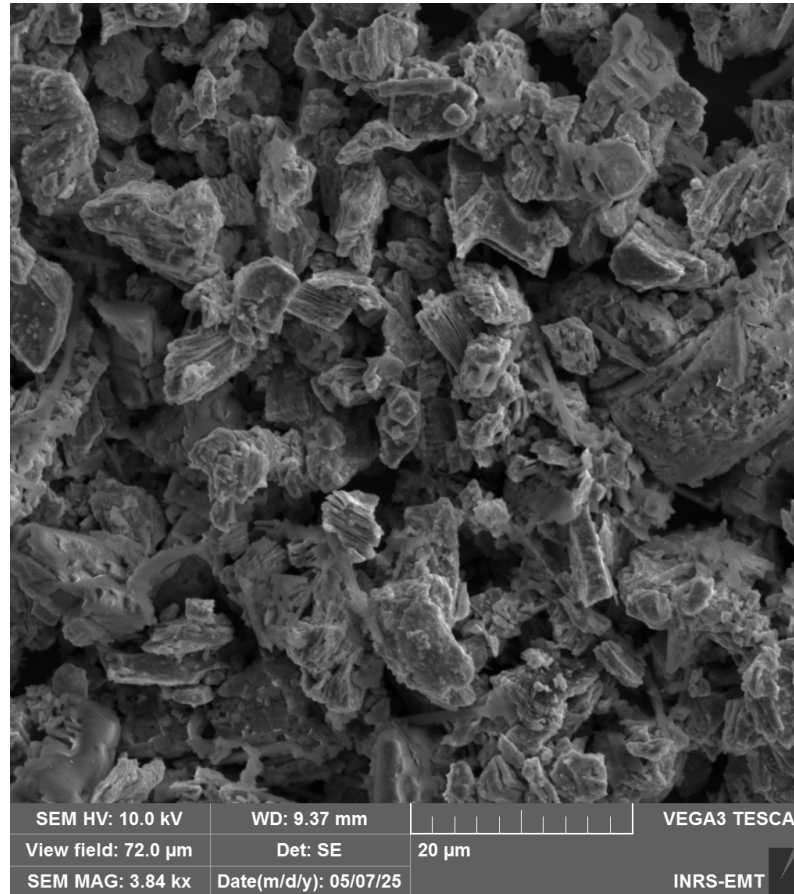
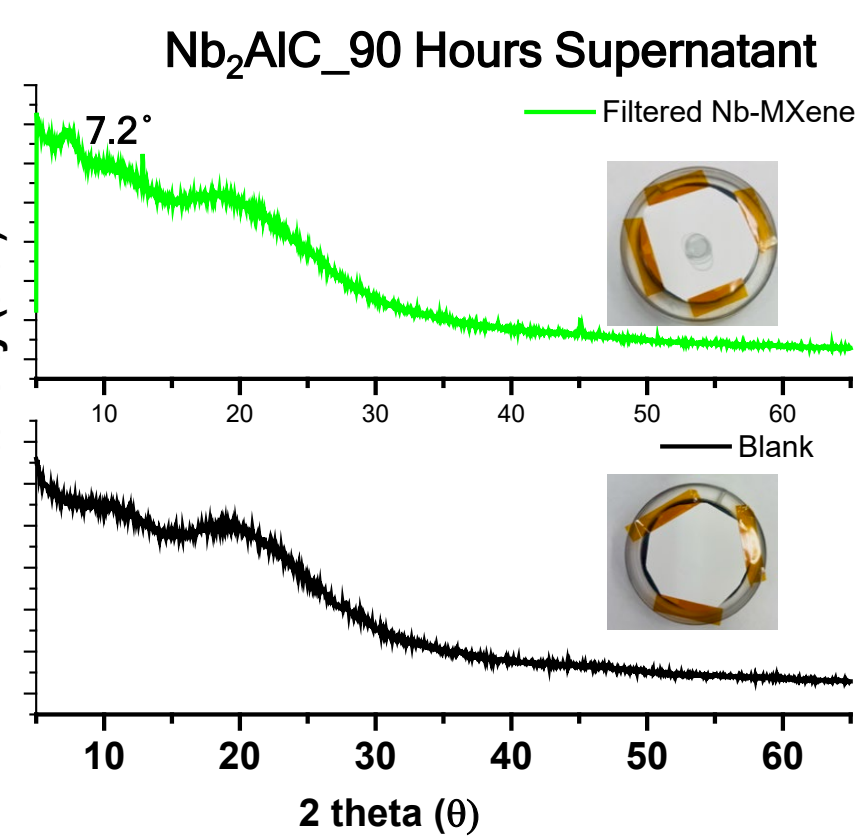
Presence of all the elements including Nb, C, Al and functional groups as F and Cl

Bulk material Elemental analysis of all the samples



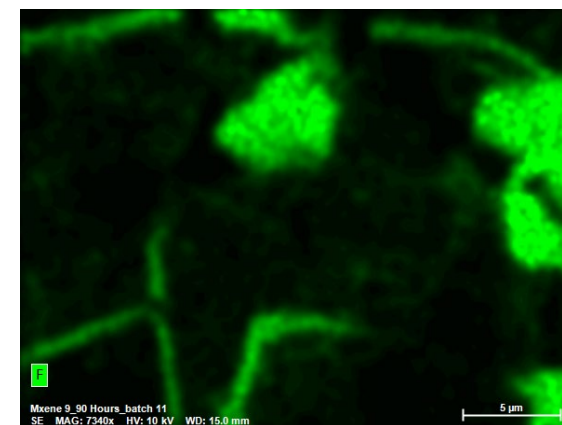
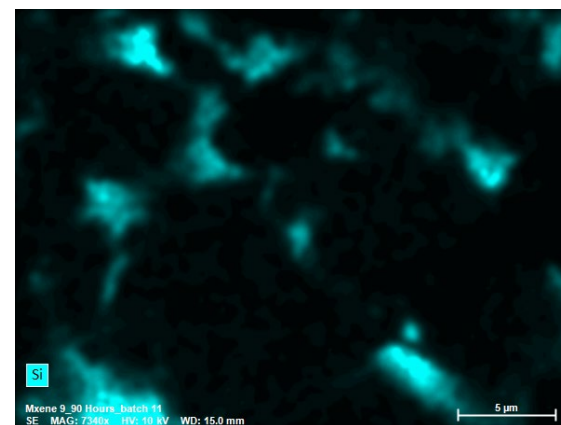
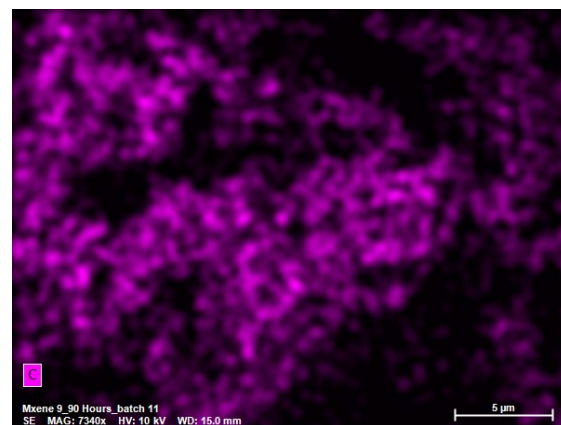
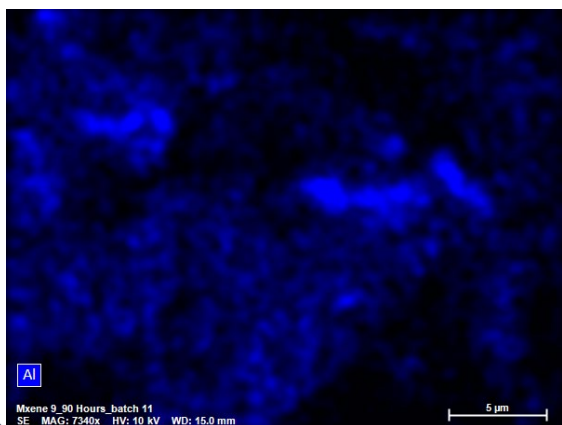
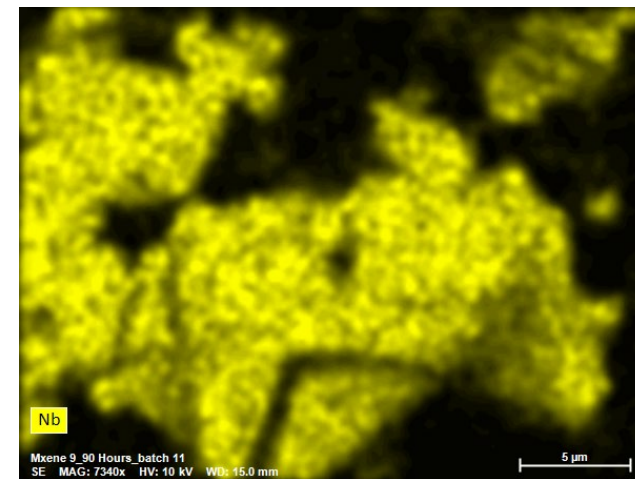
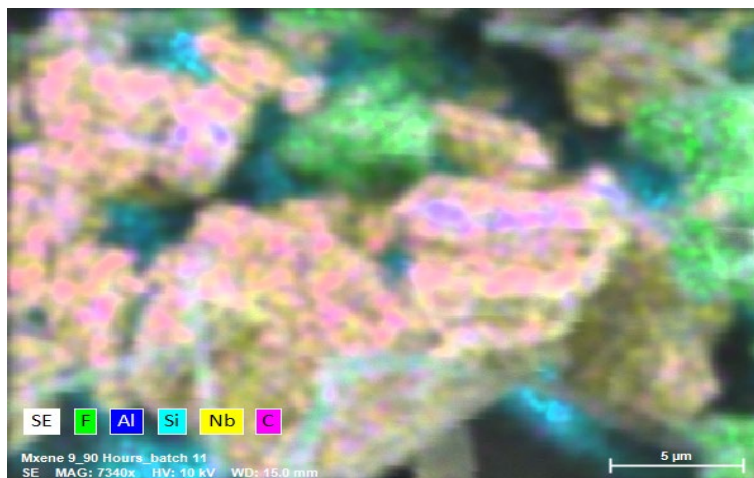
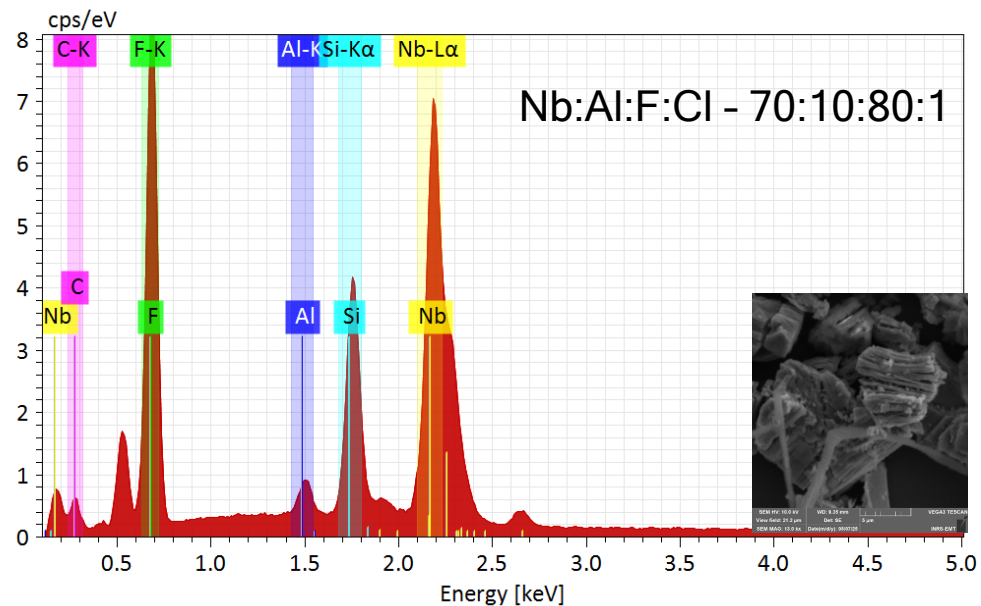
Intensity of Nb and Al at 24 hours is changing to more Nb content on increasing time period confirms the etching.

Supernatant's structure and morphology



- SEM performed on sample from supernatant solution after purification of 90 hours of reaction
- Uniformity of etched MXene can be observed on left image
- On magnification, increase in interspatial distance can be found, giving indication of etching of MAX phase

Elemental mapping of Nb_2CT_x (supernatant solution after 90 hr)



The signal of Al is very weak in supernatant solution indicating absence of aluminium salts (such as AlF_3)

Electrochemical studies of Nb₂CT_x_90 hours bulk vs supernatant

Electrode preparation

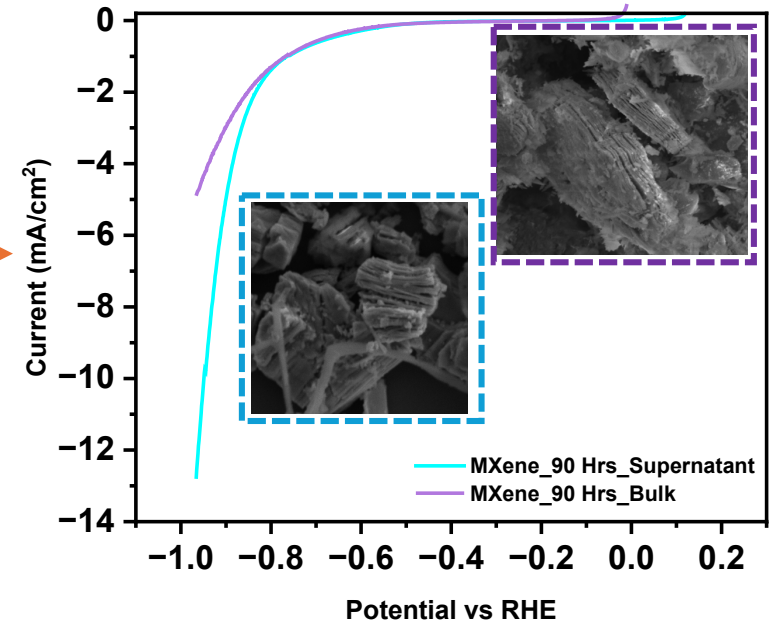
- Bulk or supernatant powders + dispersion in IPA, DI water and Nafion

15 min of sonication



All studies are performed in 0.5 M H₂SO₄ at 20 mV /s scan rate

Picture of electrochemical cell



Parameter	Bulk	Supernatant
Interlayer spacing / nm	1.14 nm	1.20 nm
Particles lateral size / µm	> 10 µm	< 10 µm
Average number of layers	14	15
Nb:Al at%	3.2:1	7:1

Conclusion

- Successful synthesis and characterization of time dependent transformation of Nb_2AlC to multilayer Nb_2CT_x type materials.
- With MAX/MXenes, the complete removal of Al not possible under these synthesis conditions.
- Electrochemical activity for hydrogen evolution reaction (HER) of supernatant is higher than the bulk like MXene after 90 hours of reaction.

Future Outcome

- Additional chemical analysis of the materials using X-ray photoelectron spectroscopy and EELS .
- Time dependent prepared samples will be studied for hydrogen evolution reaction.
- Long term stability tests will be performed using chronoamperometry.

Acknowledgements



**NSERC
CRSNG**

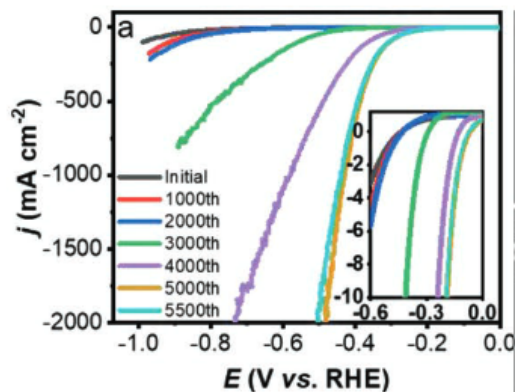
PRIMA
Les matériaux pour avancer



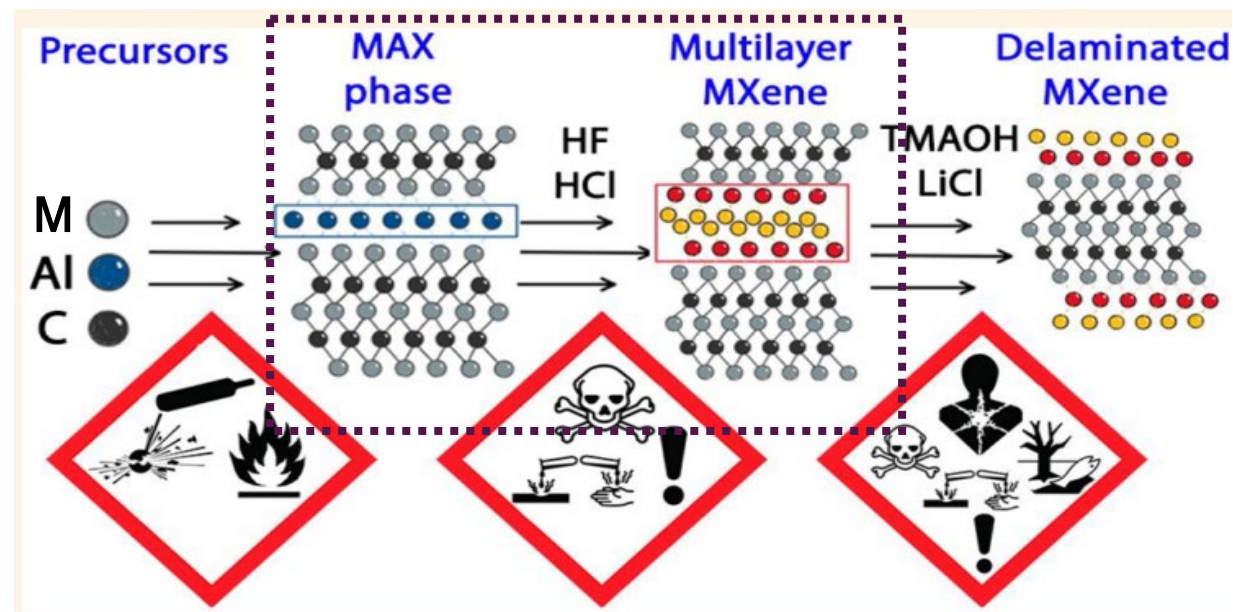
NioBay
METALS

I am removing the following slides; but keep this information while speaking.

major synthesis methods and safety issues



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Challenges in lab :

- Reproducibility
- Long purification steps
- Aggregation and storage
- Large scale production
- Thermal and oxidative stability

We are majorly following etchant method (Minimally Intensive Layer delamination; (MILD; LiF/HCl))

To avoid the hazard issues with HF, MILD method (LiF/HCl) is preferred