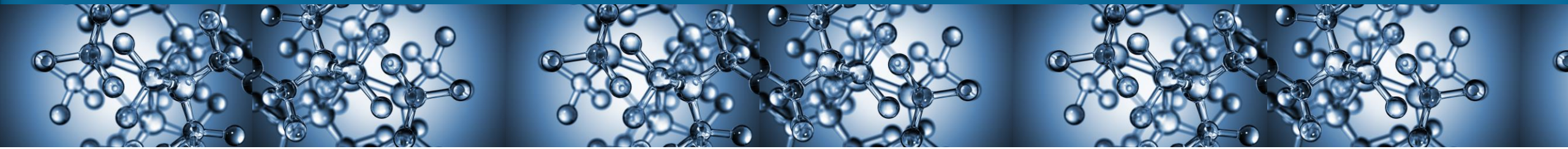
Tuning the electrode work function by the deposition of chemically functionalized MXenes-an SPM study



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EUROPEAN CONFERENCE ON CHEMISTRY OF TWO-DIMENSIONAL MATERIALS

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01/09/2021

MXenes – Overview

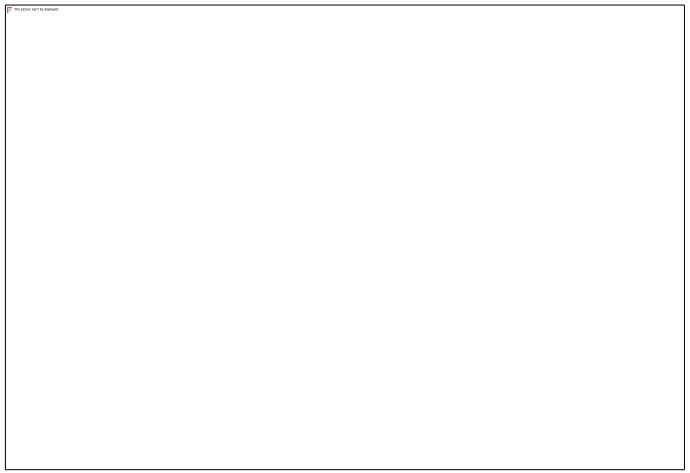
$M_{n+1}X_nT_x$

M: Early transition metal (Ti, Sc, Zr, etc.)

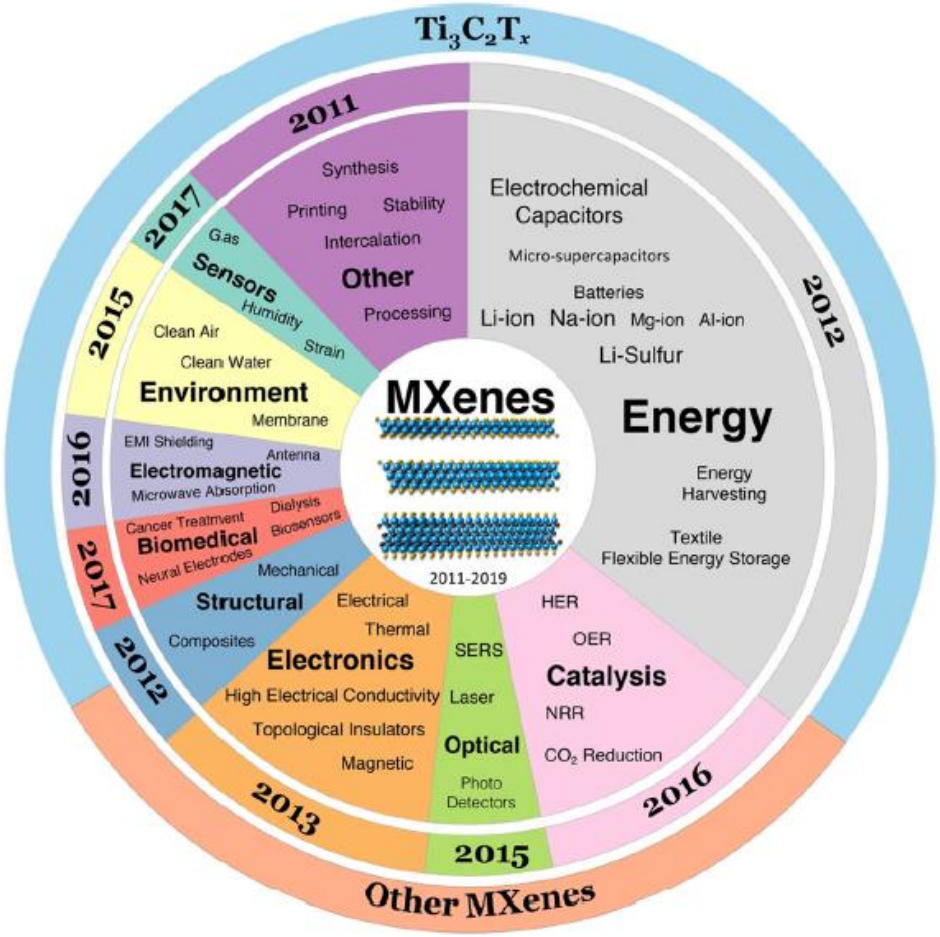
X: Carbon and/or Nitrogen

T_x: Surface terminations (OH, O, Cl, and/or F)

n: 1, 2, or 3

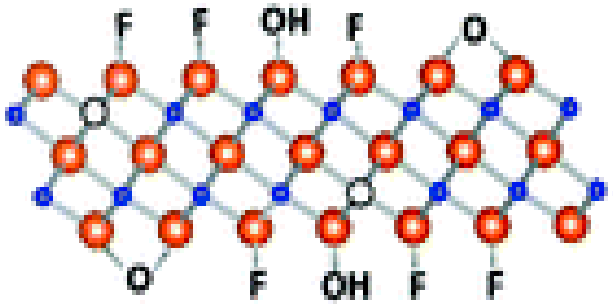


"**Green Mxenes turtle**" by Babak Anasori et. al, Department of Materials Science and Engineering, and A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, PA 19104, USA



Yury Gogotsi and Babak Anasori, The Rise of MXenes, *ACS Nano* **2019** *13* (8), 8491-8494

$Ti_3C_2T_x$ MXenes – Tuning of the materials properties



Surface chemistry of MXenes

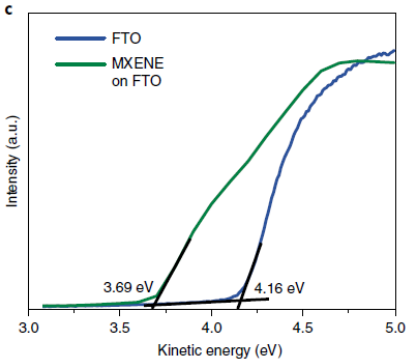
Surface functional groups:
- -F
- -Cl
- -OH
- -O-

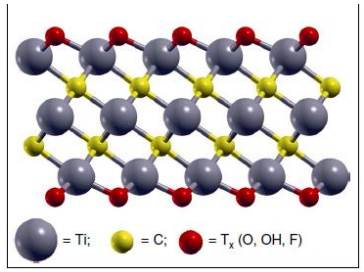
ARTICLES
https://doi.org/10.1038/s41563-019-0478-1
nature materials

Titanium-carbide MXenes for work function and interface engineering in perovskite solar cells

A. Agresti[1,2,7], A. Pazniak[3,7], S. Pescetelli[1,7], A. Di Vito[1], D. Rossi[1], A. Pecchia[4], M. Auf der Maur[1], A. Liedl[5], R. Larciprete[5,6], Denis V. Kuznetsov[3], D. Saranin[2] and A. Di Carlo[1,2*]

various termination groups (T*x*) to tune the work function (WF)





Surface functional groups or/and functionalization
→big influence on the **work function**

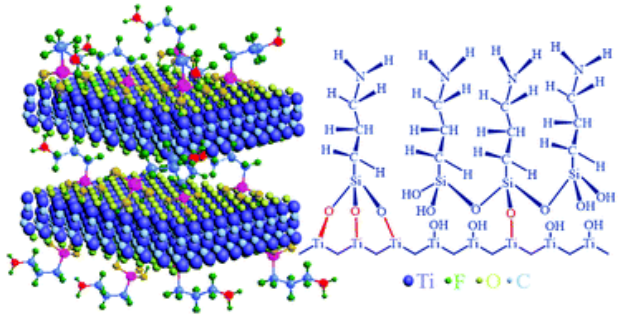
$Ti_3C_2T_x$ MXenes – Synthesis and processing

- **$Ti_3C_2T_x$ MXenes** – Preparation

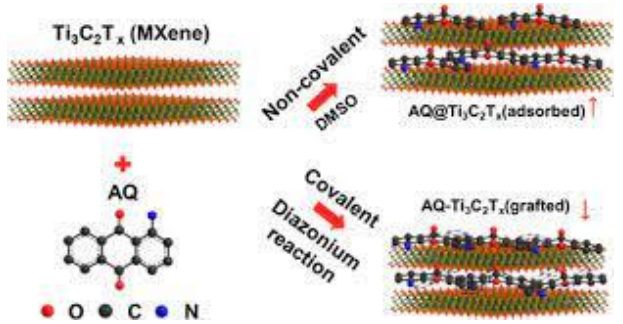
Babak Anasori, Maria L. Lukatskaya and Yury Gogotsi, 2D metal carbides and nitrides (Mxenes) for energy storage, *Nature Reviews,* **2017** (2), 16098

- **$Ti_3C_2T_x$ MXenes** – Covalent and Non-covalent functionalization of MXenes

Covalent functionalization

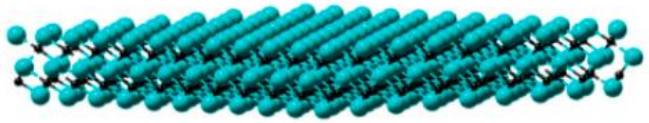


Non- Covalent functionalization



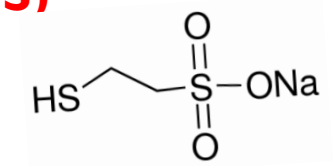
Pure MXenes (Ti_3C_2Tx) and different types of **functionalization**

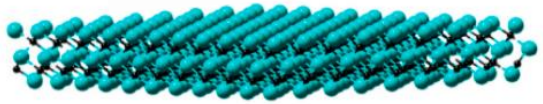
1. Pure MXenes ($Ti_3C_2T_x$)



Expected interaction: **Covalent functionalization** → The thiol group react with Fluorine group on MXene; HF was removed, and the -S bond to the surface MXene

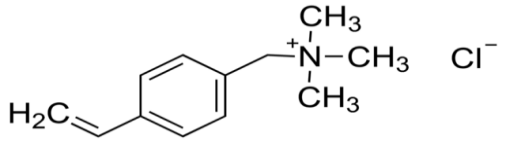
2. MXenes (Ti_3C_2) functionalized with **Sodium 2-mercaptoethanesulfonate (MPS)**

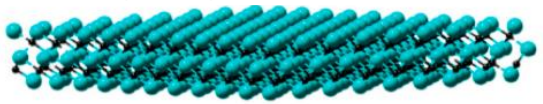




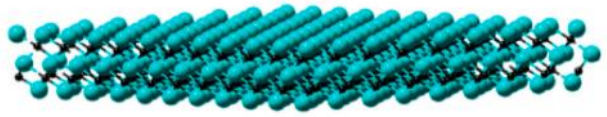
Expected interaction: **Non-covalent functionalization** → MXenes negatively charged

3. MXenes (Ti_3C_2) functionalized with **((vinylbenzyl)trimethylammonium chloride) (VTA)**





Pure MXenes – AFM Imaging and Analysis



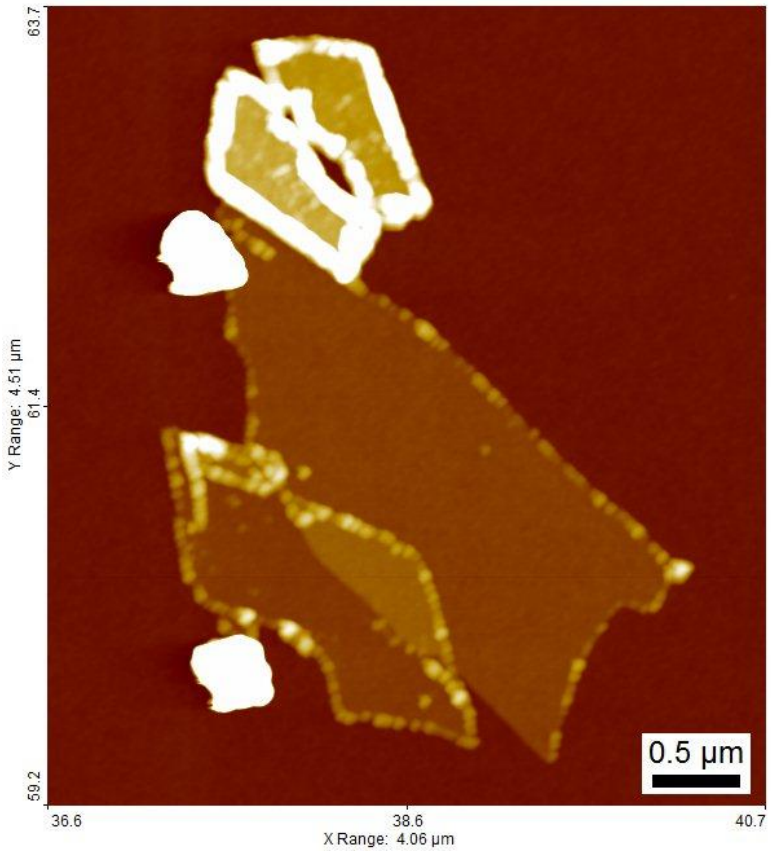


Figure 1. AFM image of Pure MXenes on Si substrate.

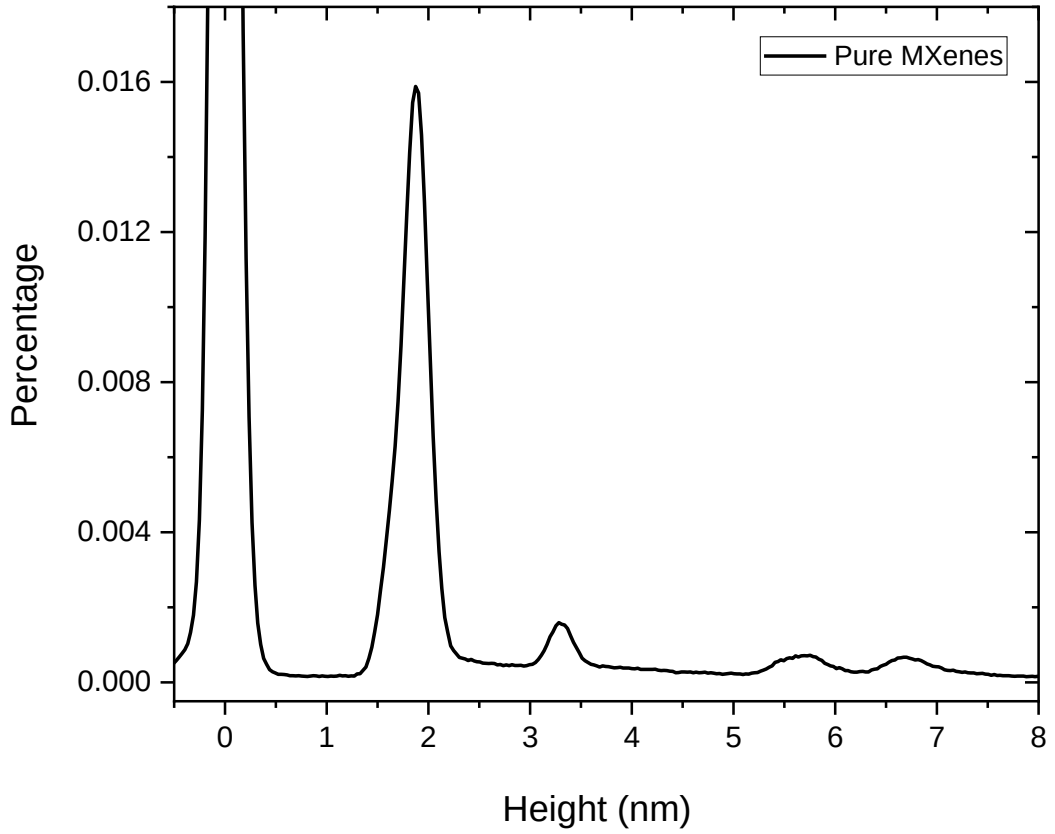
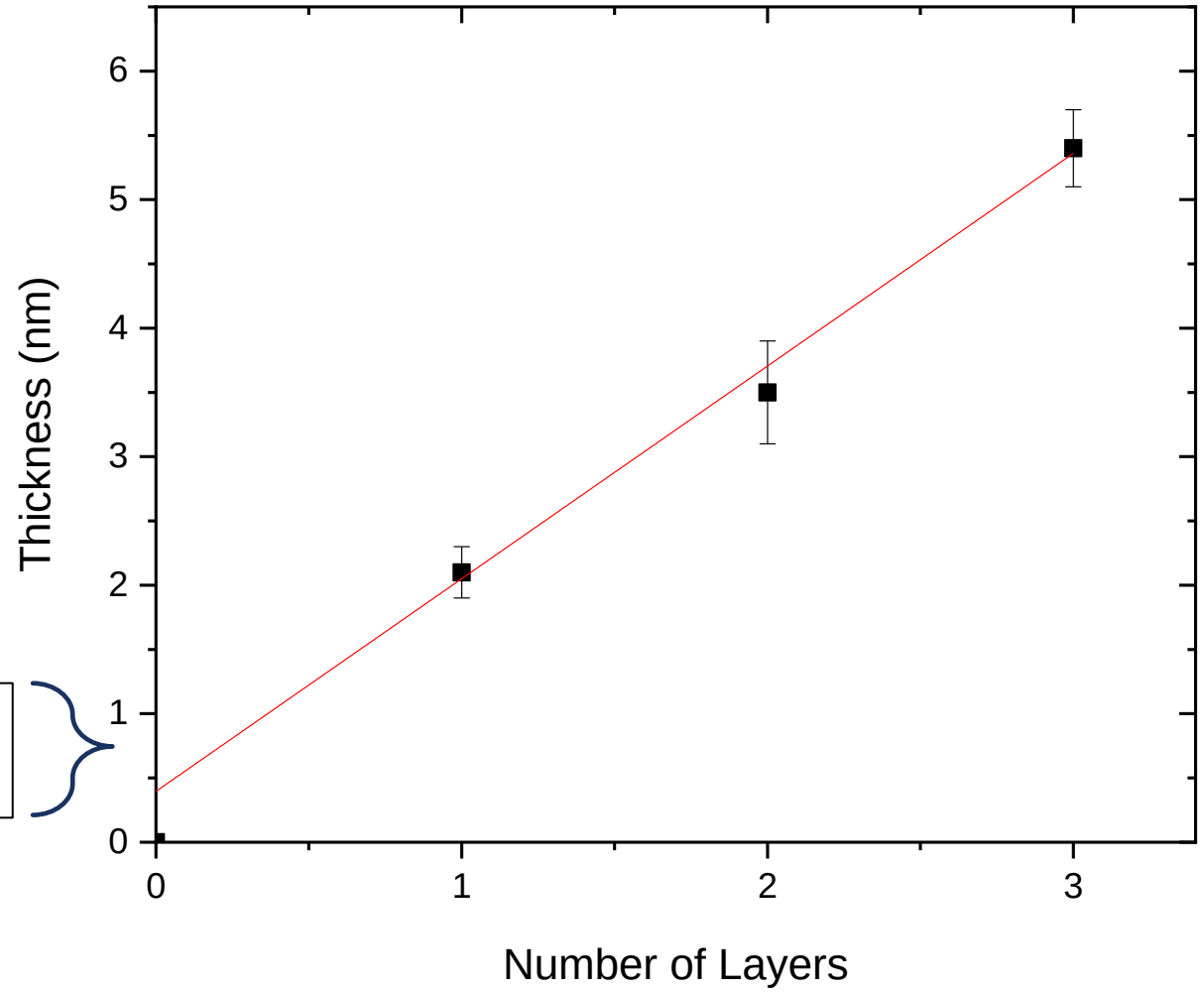


Diagram 1. Corresponding histogram of the flakes shown on the left AFM image.

Pure MXenes – AFM Imaging and Analysis

Presence of absorbed water

Intercept:
0.4±0.2 nm

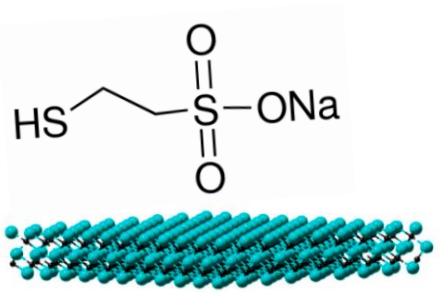


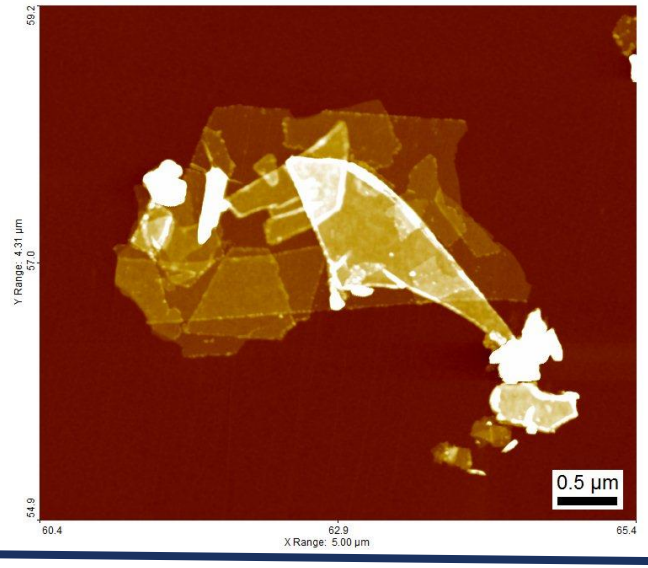
Interlayer distance:
1.6±0.1 nm

Diagram 2. Pure MXenes thickness/number of layers dependence diagram.

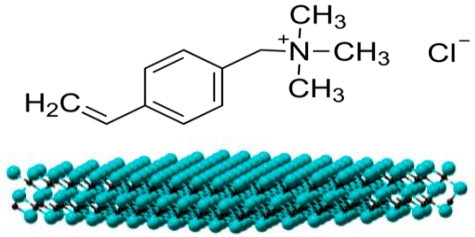
$Ti_3C_2T_x$ MXenes – AFM Imaging and Analysis

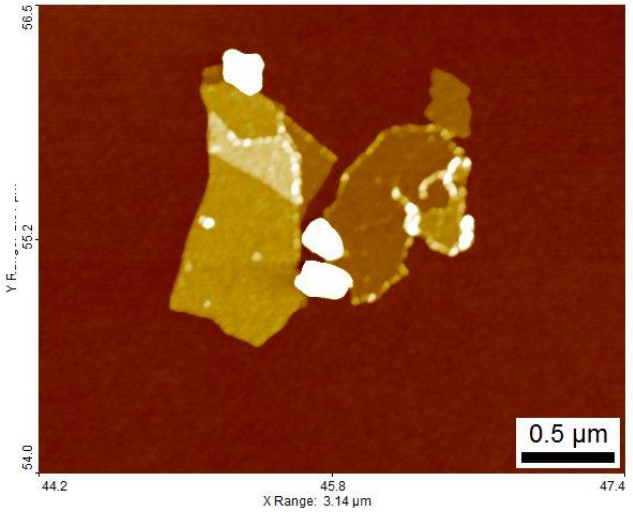
FMXenes (MPS)





FMXenes (VTA)





Materials	Interlayer distance(nm)	Absorbed molecules "sublayer"
Pure MXenes	**1.6±0.1**	**0.4±0.2**
FMxenes (MPS)	**1.6±0.1**	**0.4±0.1**
FMxenes (VTA)	**1.5±0.1**	**0.4±0.1**

Table 1. Summary table of different MXenes values of interlayer distance and steps from one layer to the other.

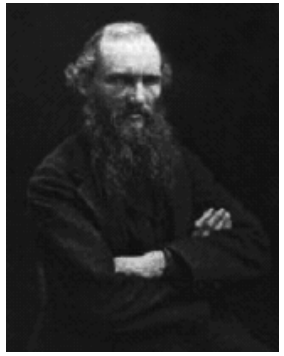
Theoretical values:
- 0.977nm[b] (Pure MXenes)

Experimental XRD value:
- 1.5nm

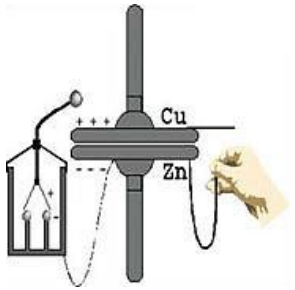
a. Hongyue Jing et. al, Modulation of the Electronic Properties of MXene (Ti3C2Tx) via Surface-Covalent Functionalization with Diazonium, *ACS Nano* 2021 *15* (1), 1388-1396

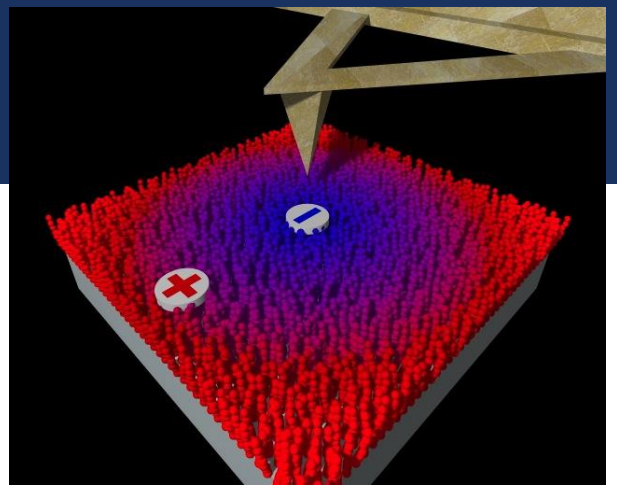
b. Two-Dimensional MXene with Controlled Interlayer Spacing for Electrochemical Energy Storage, P. Simon, *ACS Nano* 2017 *11* (3), 2393-2396

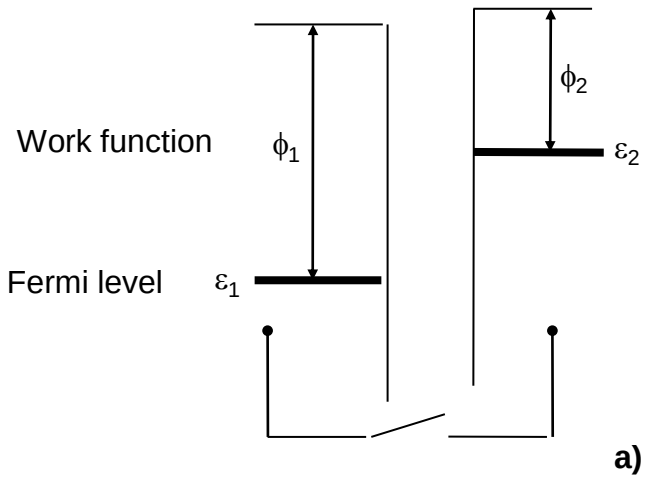
Kelvin Probe Technique - Overview

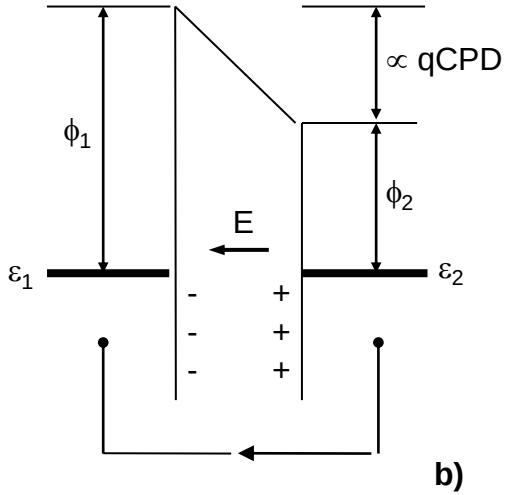


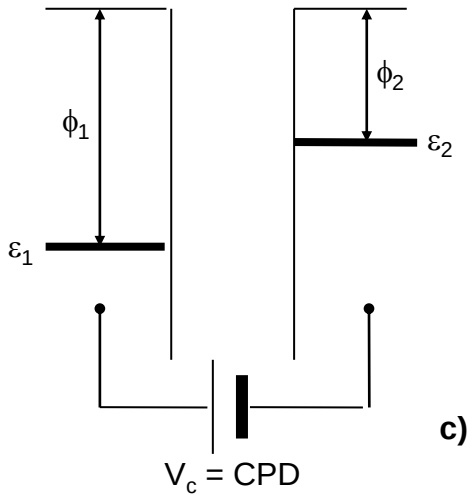
William Thomson, a.k.a. Lord Kelvin, 1898









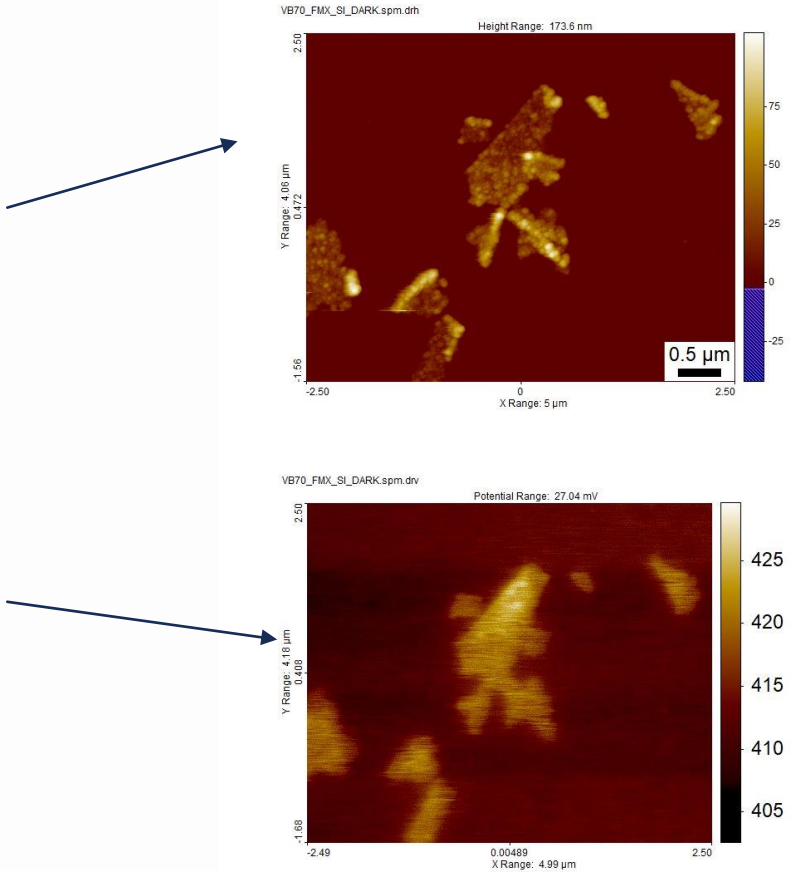


$$V_{CPD} = \frac{\Phi_1 - \Phi_2}{e}$$

Work function = energy needed to remove an elctron from a material

V. Palermo et al. *Adv. Mater.* **18**, 145 (*2006*)

Kelvin Probe Force Microscopy



How AFM Works 4-4 Scanning Kelvin Probe Microscopy (SKPM), youtube, Park systems, 2015

Significance of the substrate – Silicon Vs HOPG

Silicon substrate

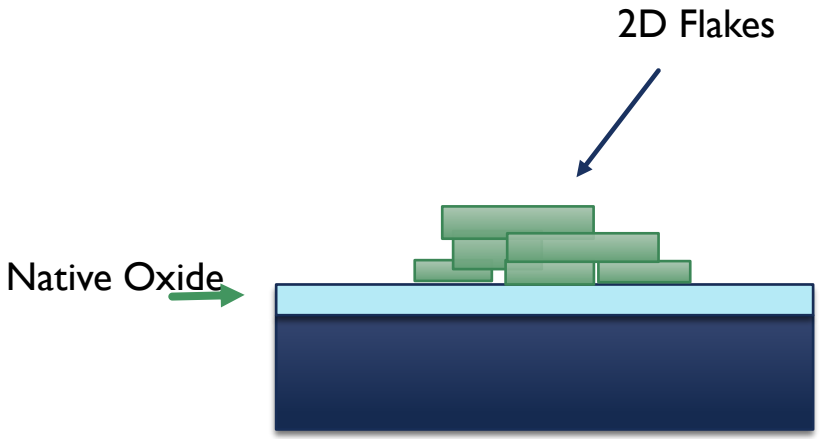


Figure 2. Commercially available Silicon wafer.

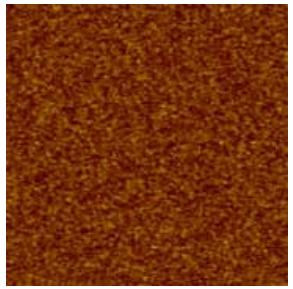
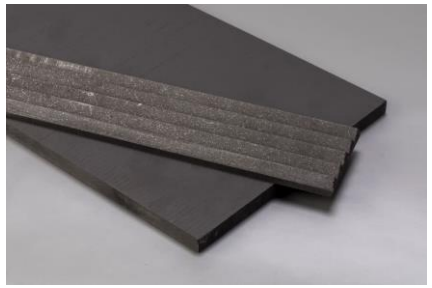


Figure 3. AFM image of the surface of a Silicon wafer.

HOPG substrate



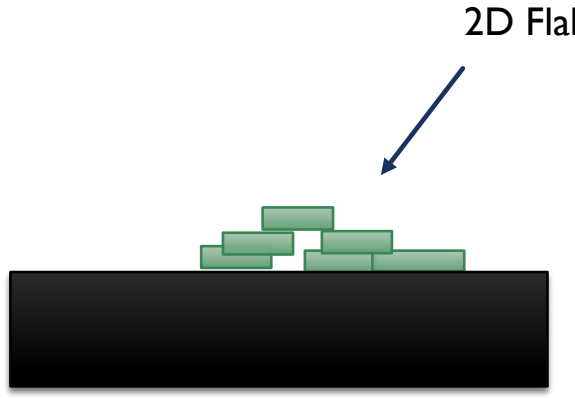


Figure 6. Commercially available graphite anodes.

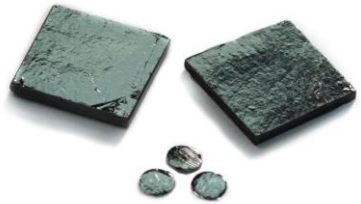


Figure 4. Commercially available HOPG.

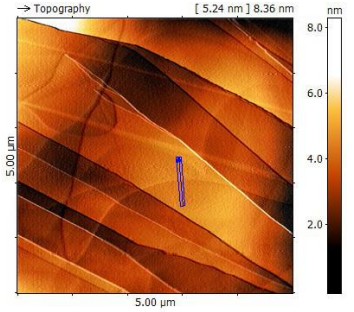
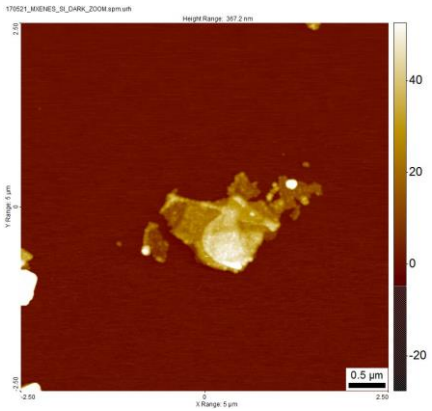


Figure 5. AFM image of the surface of HOPG.

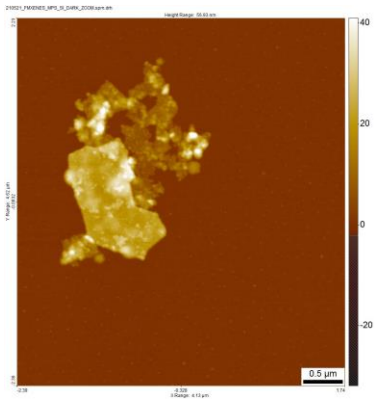
KPFM Measurements – Silicon substrate

Topography Figures

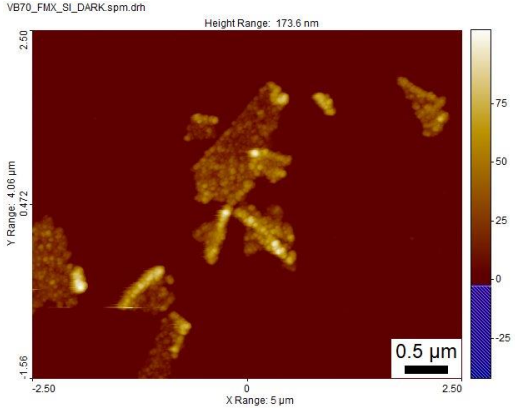
Pure MXenes



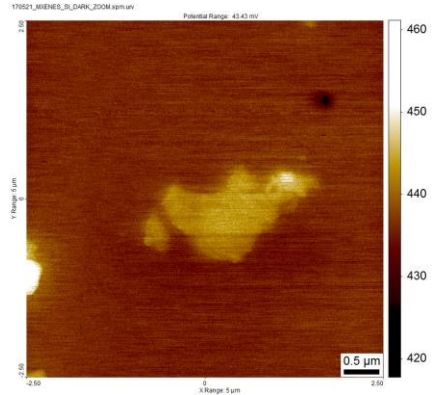
FMXenes (MPS)

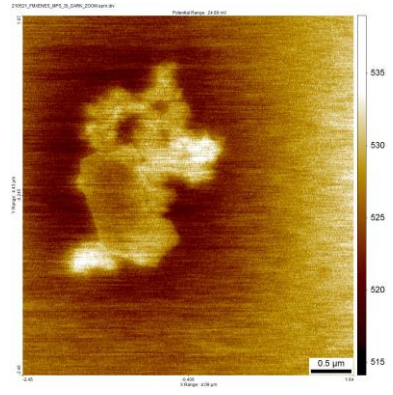


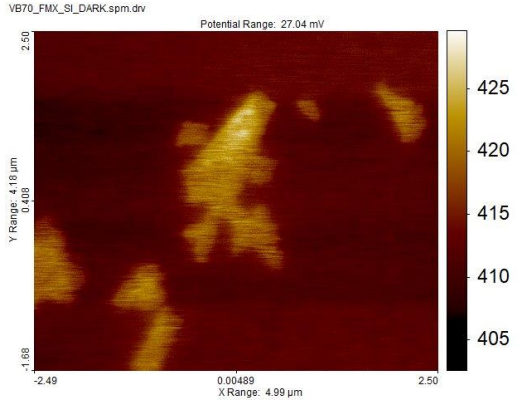
FMXenes (VTA)



Surface Potential Figures



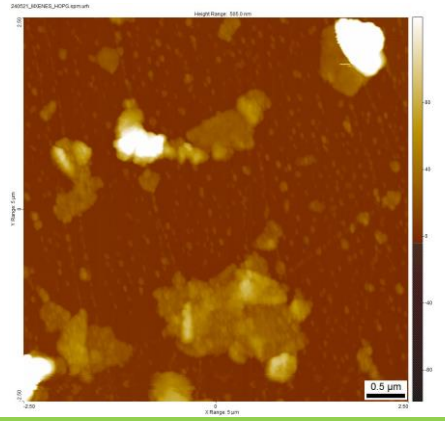




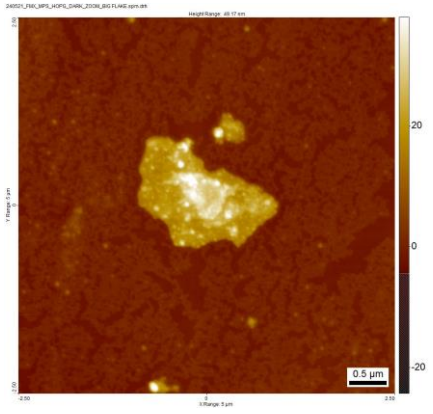
KPFM Measurements – HOPG substrate

Topography Figures

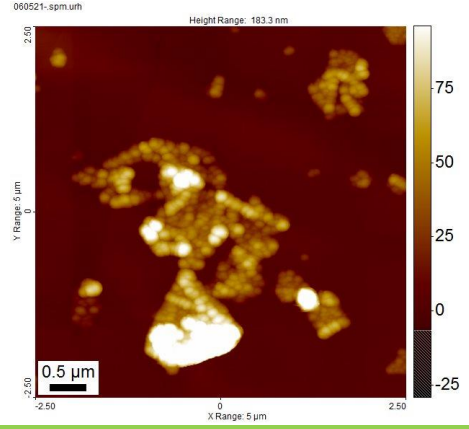
Pure MXenes



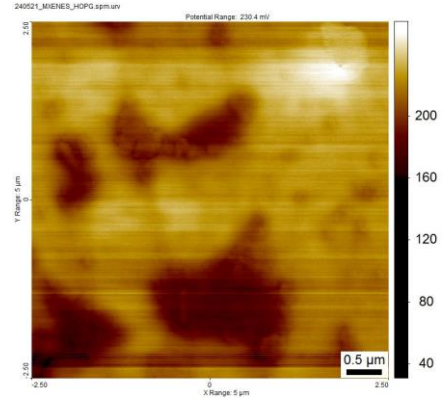
FMXenes (MPS)

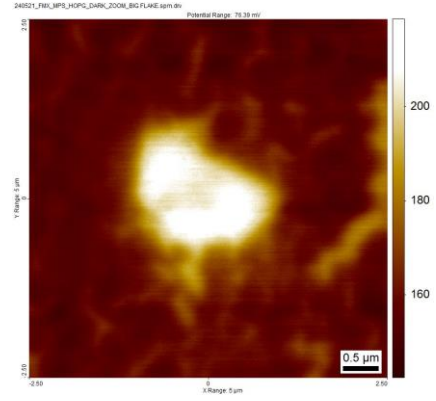


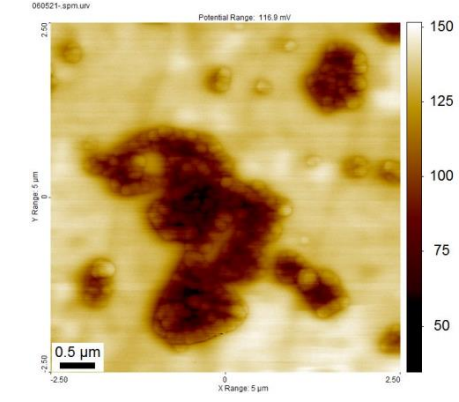
FMXenes (VTA)



Surface Potential Figures







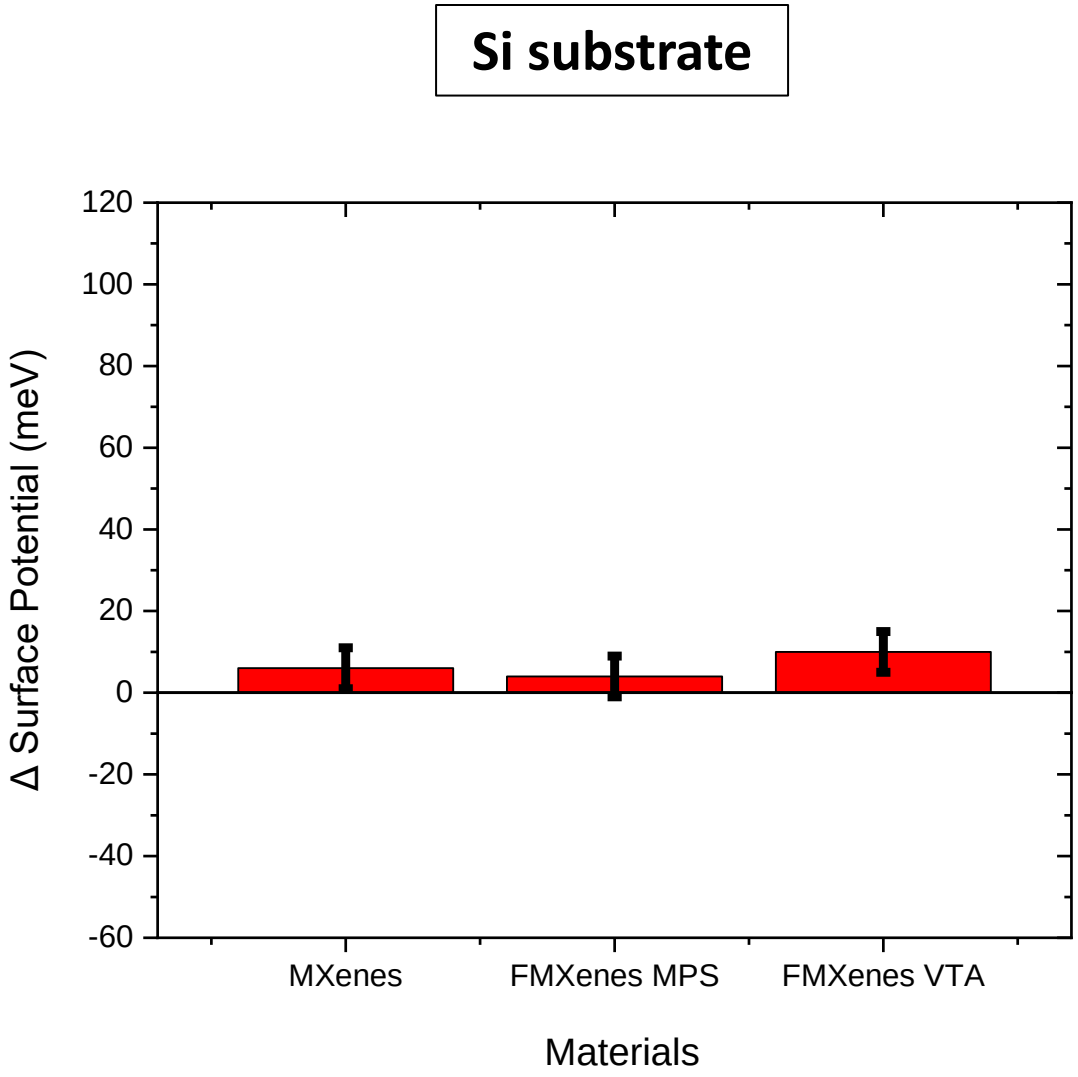


Diagram 3. Final diagram of all MXenes' surface potential values in respect to the substrate(Si)

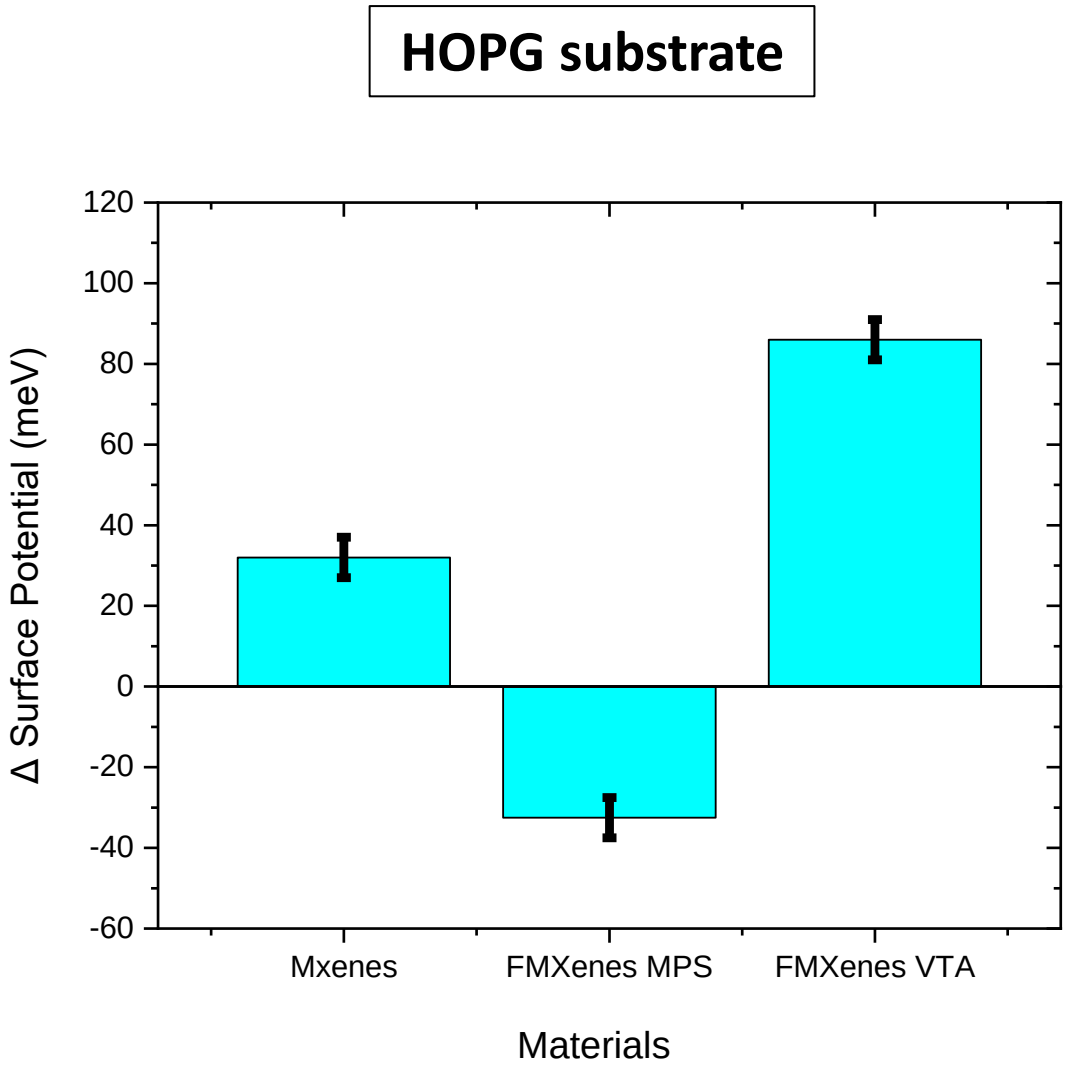
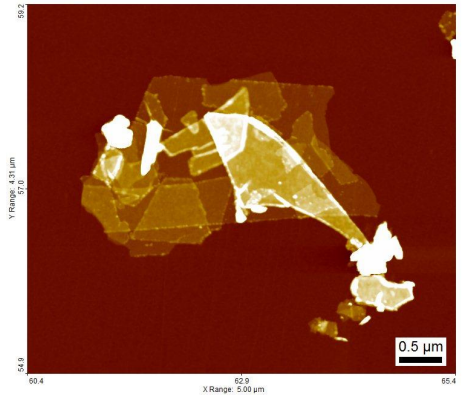
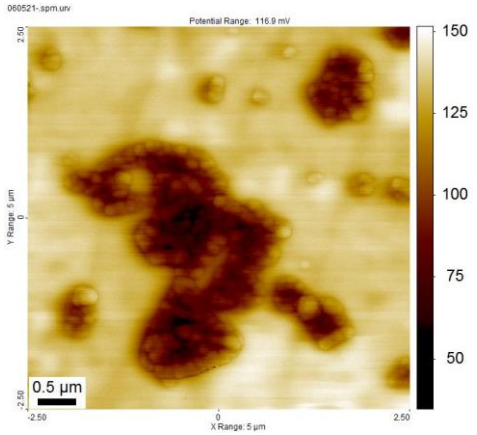


Diagram 4. Final diagram of all MXenes' surface potential values in respect to the substrate (HOPG)

Conclusions

- ✓ Morphological characterization of pure and functionalized MXenes (interlayer distance, presence of absorbed molecules detected)
- ✓ Work function tuning of the substrate depending on the specific functionalization (despite the similar morphological characteristics)
- ✓ More suitable as substrate → HOPG





Future Work

- ➢ Test other possible substrates
- ➢ Light illumination → observe possible changes
- ➢ Test other types of functionalization

ISTITUTO PER LA SINTESI ORGANICA E LA FOTOREATTIVITA'

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Thank you for your Attention!

chem2Dmat

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