

Enhancing Nanomechanical Properties of MXene through Tailored Surface Potential: PFQNM and Kelvin Force Microscopy Studies

Jing Li¹

¹Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

2D MXene (Ti₃C₂TX) possess distinct characteristics such as high electrical conductivity, adjustable surface chemical properties, and mechanical flexibility. These features make them valuable as building blocks for energy storage devices, serving purposes like electrodes, ion transfer regulation, electrocatalysts, and electrodeposition substrates. Enhancing the mechanical strength of MXenes has been achieved by combining them with 1D nanocelluloses from their stable colloidal dispersions. However, the practical application of MXene materials faces obstacles due to their tendency to swell unfavorably caused by weak interactions between nanosheet layers, convoluted pathways for ion transport channels, and susceptibility to oxidation in aquatic environments, consequently impacting the performance of EC devices. The current challenge in optimizing MXene properties is to maintain the EC properties during synthesis. Poly(ionic liquid) treated heterostructure Mexne membranes assembly with layered double hydroxide nanosheets via solution-phase showed high permeability and selectivity, the interaction with the oppositely charged surfaces accerate electrostatic crosslinking between MXene neighboring nanosheets driving the enhanced stability in colloidal phase.¹ Up to this point, there has been limited focus on nano-scaled mechanical studies using quantitative peakforce nanomechanical mapping (PFQNM) using a colloidal atomic force microscopy probe to measure the localized mechanical and nano-scaled force origins of HOLO cellulose nanofibers (HOLOCNFs) during interaction with Mxenes in a colloidal phase.

The PFQNM morphology results (Fig. 1.A) revealed a uniform distribution of the HOLOCNF network nanostructure, with HOLOCNFs tightly inserted into Mxene thin sheets. The height distribution of the composite indicated that the integration of HOLOCNFs reduced the roughness of the Mxene, enhancing the overall uniformity of the composite. Specifically, the roughness of the Mxene film (1×1 μm) was measured at 56.8 nm ± 71 pm, while that of the composite was 28.4 nm ± 69 pm. The fitted elasticity modulus (Derjaguin-Muller-Toporov model) for the composite was approximately 132.8 GPa ± 0.39 GPa, compared to approximately 27.6 GPa ± 13 MPa for pure Mxene (Fig. 1.B). The Young's modulus of the composite was approximately four times higher than that of pure Mxene films. Force spectroscopy was employed to quantify the adhesion force between HOLOCNF and the Mxene surface using a HOLOCNF-modified AFM probe (Fig. 1.C and D). Statistical Gaussian fitting of

the adhesion force measured during the coated probe's departure (retraction) from the Mxene surface revealed a force that was 10 times stronger ($17.2 \text{ nN} \pm 77 \text{ pN}$) than the adhesion force measured for the same Mxene film when a naked probe was used ($1.5 \text{ nN} \pm 1.2 \text{ pN}$). These results clearly indicate that the force interaction between nanocelluloses and Mxene originated from Van der Waals attraction, with adhesion being a long-range force at a separation distance of 150 nm. Remarkably, the negative force measured in the force-distance (FD) adhesion region during tip retraction showed a significantly larger dissipation of energy (energy loss) compared to the dissipation observed when a naked probe (solid black curve) was used. The difference in dissipation energy can be attributed to the deformation of the monolayer of HOLOCNF attached to the probe, whereas no layer existed when the Si₃N₃ surface of the naked probe was measured against Mxene. The force-distance curves unveiled a mechanism of force interaction between the surface of Mxene and the surface of HOLOCNF attached to the AFM probe. The revealed force origin elucidates the notable colloidal stability of the HOLOCNF-Mxene suspension during its synthesis procedure and provides quantitative information about the strength of attraction force when Mxene film interacts with nanocellulose during the functioning of Mxene films in real time. The strong adhesion force between HOLOCNFs originated from various chemical groups covering the entire nanocelluloses, which were retained during the mild synthesis of HOLOCNF, resulting in robust adhesion force against Mxene during tip retraction. In Fig 1 (E), the localized heterogeneous catalysis mechanisms occurring at the active sites of single layer Mxene and the residual chemical groups on the nanocellulose were in situ visualized by amplitude modulated Kelvin probe force microscopy (KPFM). The decreased surface contact potential (Φ) of the Mxene (1.7 eV) measured after its interaction with the HOLOCNFs in colloidal chemical phase, compare the surface potential of Mxene (4.7 eV). This result revealed the doping mechanism the formation of Ti–O···H– hydrogen bonding between MXene and the chemical groups on HOLOCNFs, which modulated the dipolarity of the MXene surface and thus decreased the work function. The results are agreed with previous report.² In short, the PFQNM and KPFM results revealed relationship between the structure, nanomechanical and surface chemical properties of Mxene-CNF at a single-fibril level and nanoscale. A future study aims to comprehend the mechanisms involved in electrochemical catalytic reactions in the presence of CO₂ using HOLOCNF-Mxenes as electrode in electrolytes.

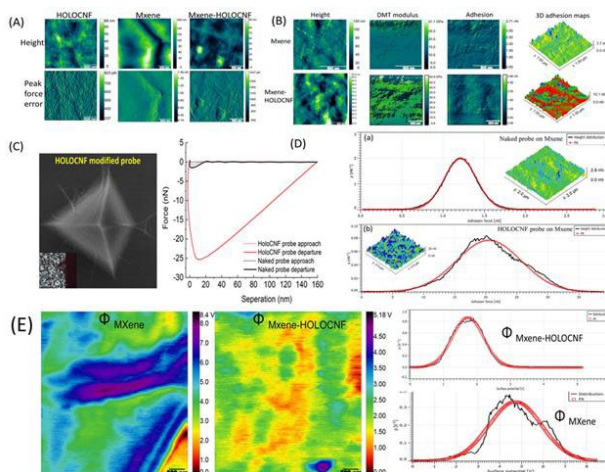
Figure 1. Representative results of (A) PFQNM morphology and Peakforce error of the materials; (B) PFQNM height, elastic modulus using Derjaguin-Muller-Toporov contact model, and adhesion force of the materials; (C) (left

)SEM of the HOLOCNF probe;(right) Force-distance curves (curves in red were measured using HOLOCNF colloidal probe); (D) Gaussian fitted adhesion force distribution of the HOLOCNF-Mxene and naked probe-Mxene. (E) KPFM surface potential (work function Φ) maps and fitted distribution of the maps for Mxene and Mxene-HOLOCNF obtained 50 nm lift height.

References

- (1) Lu, Y.; Zhang, M.; Chang, J.; Sikdar, A.; Wang, N.; An, Q.-F.; Yuan, J. Heterostructure Membranes of High Permeability and Stability Assembled from MXene and Modified Layered Double Hydroxide Nanosheets. *J. Memb. Sci.* 2023, 688, 122100. <https://doi.org/10.1016/j.memsci.2023.122100>.
- (2) Lyu, B.; Kim, M.; Jing, H.; Kang, J.; Qian, C.; Lee, S.; Cho, J. H. Large-Area MXene Electrode Array for Flexible Electronics. *ACS Nano* 2019, 13 (10), 11392–11400. <https://doi.org/10.1021/acs.nano.9b04731>.

Graphic:



Keywords:

SPM and AFM, Force spectroscopy