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# Near-field characterization of Nb<sub>2</sub>CT<sub>x</sub> MXene by non-destructive near-field microscopy

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## ABSTRACT

The Nb<sub>2</sub>CT<sub>x</sub> MXene was synthesized and optically characterized using Photo-induced Force Microscopy (PiFM), a nanoscale imaging technique combining AFM topography mapping and infrared spectroscopy. In bulk and single/few layered MXene flakes, distinct absorption peaks were observed, particularly in the 770-1860 cm<sup>-1</sup> range. The local IR spectra are then compared with FTIR and Raman spectroscopy to analyze the material composition. Our findings notably highlight the presence of a characteristic peak at 980 cm<sup>-1</sup> corresponding to the presence of niobium pentoxide.

**Keywords:** MXene, Nb<sub>2</sub>C, 2D materials, infrared spectroscopy

## 1. INTRODUCTION

MXenes are a very large family of 2D transition metal carbides and nitrides, produced by selective etching of MAX precursors. MXenes follow a general formula M<sub>n+1</sub>X<sub>n</sub>T<sub>x</sub>, where n can be 1, 2, or 3, representing three prevalent structures. M denotes an early transition metal (Zr, Ti, V, Hf, Sc, Nb, Cr, Ta, Mo), x represents carbon/nitrogen, and T<sub>x</sub> signifies diverse surface terminations, including fluorine (-F), hydroxyl (-OH), and/or oxygen (=O). Due to their unique morphology, they exhibit interesting properties such as high electrical conductivity, good chemical stability, and large surface area [1].

In this study, we aim to address the challenge of determining mid-IR resonance frequencies of MXene flakes, particularly Nb<sub>2</sub>CT<sub>x</sub>, by employing the recent technique of Photo-induced Force Microscopy (PiFM). PiFM is the combination of conventional AFM with a tunable IR source. It is a non-destructive nanoscale imaging technique, allowing for simultaneous topography mapping and infrared investigation of materials having an IR response. This capability makes PiFM an ideal tool for characterizing MXenes in the mid-infrared range.

In this work/paper, we report the spectroscopic characterization of Niobium Carbide (Nb<sub>2</sub>CT<sub>x</sub>) MXene 2D material (single flake and “bulk”) in the mid-infrared region.

## 2. MATERIALS & METHODS

### 2.1 Synthesis of MXenes

$\text{Nb}_2\text{CT}_x$  MXene was synthesized by selective etching of  $\text{Nb}_2\text{AlC}$  phase powder with an acidic mixture composed of hydrofluoric and hydrochloric acids. After etching, the solution was repeatedly washed with distilled (DI) water until reaching a pH superior to six.

The resulting sediment of  $\text{Nb}_2\text{C}$  MXenes was hence delaminated to obtain colloidal solutions of single- and few-layered  $\text{Nb}_2\text{C}$  with 5 mL of tetramethylammonium hydroxide. The mixture was repeatedly centrifuged and washed with DI water to obtain  $\text{Nb}_2\text{CT}_x$  flakes.

### 2.2 Fabrication of MXene samples

Single/few layered MXenes flakes were deposited on an activated undoped silicon wafer using the spin-coating method. The obtained sample was dried at  $120^\circ\text{C}$  for a few minutes. The stack/bulk MXene sample was fabricated by a drop-casting method on an undoped silicon wafer on a hot plate.

### 2.3 PiFM characterization

PiFM was performed to obtain the absorption-related near-field spectra of the prepared samples. The photo-induced mechanical force caused by a power-modulated IR laser source is detected through an additional mechanical oscillation of the AFM tip entailed by the periodic light excitation at the tip-sample junction. Contamination-free platinum-coated silicon cantilevers were used, and the system operates in non-contact mode. The infrared excitation was performed by a quantum cascade laser (QCL) ranging from  $770$  to  $1860\text{ cm}^{-1}$  and the beam was focused at the tip apex with a parabolic mirror. The PiFM system (VistaScope One, Molecular Vista) operates in the so-called “sideband” mode. This mode detects the photo-induced oscillation signal at the first mechanical tip frequency ( $f_1$ ) while the laser modulation is set at  $f_m = f_2 - f_1$  where  $f_2$  represents the second mechanical resonance frequencies of the cantilever.

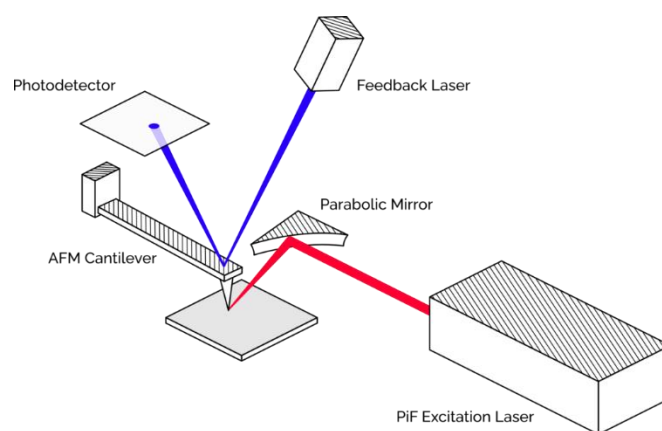


Figure 1 Simple PiFM scheme [2]

### 2.4 Conventional characterization

The morphology of the MXenes flakes was first observed through a scanning electron microscope (Hitachi FEG SU8030) and an atomic force microscope (Molecular Vista VistaScope One). Far-field absorption has been determined through  $\mu$ Raman spectroscopy (Horiba Scientific LabRAM HR Evolution) with laser excitation at  $532\text{ nm}$  ( $100\times$  and  $\text{NA} = 0.9$ ) and Fourier-transform infrared (FTIR Perkin-Elmer Frontier) was employed on MXene powder.

### 3. RESULTS & DISCUSSION

#### 3.1 Raman and infrared response on bulk Nb<sub>2</sub>CT<sub>x</sub>

A stack of Nb<sub>2</sub>CT<sub>x</sub> 2D flakes was first deposited on an intrinsic silicon wafer with an estimated thickness of 3 μm.

Figure 2 shows FTIR spectra of freeze-dried Nb<sub>2</sub>CT<sub>x</sub> powder in Attenuated Total Reflectance (ATR) and transmission mode. In both modes, the peak at 950 cm<sup>-1</sup> is distinguishable but more information can be extracted in ATR mode. Peaks at 1490 and 1640 cm<sup>-1</sup> are related to C-H bonding and C=C stretching respectively [3]. The peak detected by FTIR below 1000 cm<sup>-1</sup> has not been reported in the literature to our knowledge.

The Raman spectroscopy analysis provides additional insights into the bulk Nb<sub>2</sub>CT<sub>x</sub> (Figure 3). The bands observed at 258 cm<sup>-1</sup> (associated with the bending modes of Nb-O-Nb linkages) and 638 cm<sup>-1</sup> (attributed to the Nb-O stretching mode) are indicative of Nb<sub>2</sub>O<sub>5</sub>. Furthermore, the bands at 1350 and 1590 cm<sup>-1</sup> are denoted as the D and G bands respectively, in carbon bonding. The D band points to the presence of defects within the carbon-based structure, while the G band is linked to the in-plane vibration of sp<sup>2</sup> carbon atoms [4]. Moreover, a noticeable peak at 980 cm<sup>-1</sup> is observed in the Raman spectrum. According to the literature [4], it is observed that the intensity of this specific Raman peak increases with the degree of oxidation. This intensity can be considered as an indicator of the oxidation level of the MXene. Additionally, the correspondence of peaks associated with Nb and O bonds confirms the presence of oxide in our sample. Su et al. [5] demonstrated the occurrence of the 980 cm<sup>-1</sup> peak in Nb<sub>2</sub>CT<sub>x</sub> MXene mixed with Nb<sub>2</sub>O<sub>5</sub>. Collectively, these findings allow us to conclusively affirm the presence of oxidized niobium.

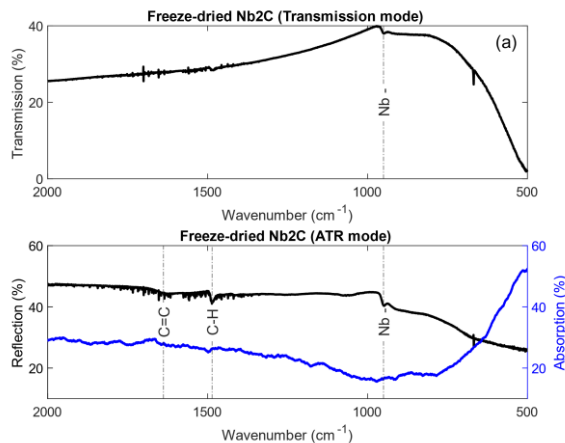


Figure 2 Nb<sub>2</sub>CT<sub>x</sub> powder FTIR spectra in (a) transmission mode and (b) attenuated total reflectance

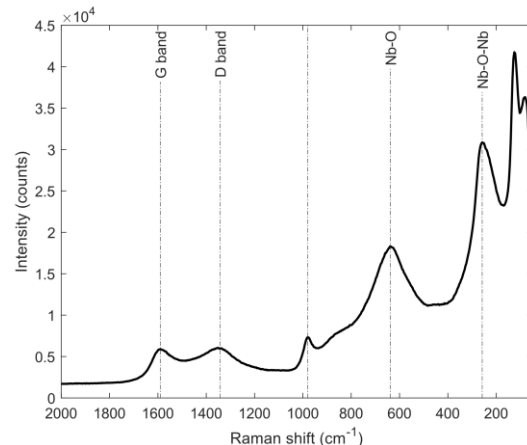


Figure 3 Nb<sub>2</sub>CT<sub>x</sub> Raman spectrum

#### 3.2 PiFM response on bulk Nb<sub>2</sub>CT<sub>x</sub>

Figure 3.a displays the normalized PiFM spectrum of bulk Nb<sub>2</sub>CT<sub>x</sub> compared to the substrate response (**Error! Reference source not found.**). Several peaks and bands of absorption are observed and can be associated with specific molecular vibrations according to the previously obtained FTIR and Raman spectra. The peak at 1640 cm<sup>-1</sup> is attributed to unsaturation, primarily arising from the C=C bond in the MXene structure [2,3], and can also be observed in the transmission FTIR spectrum (Figure 3). The sharp peak at 1490 cm<sup>-1</sup> can be associated with organic contamination (carbon contamination) or Nb<sub>2</sub>CT<sub>x</sub> flake degradation. Indeed, the formation of niobium oxide creates carbon monolayers. The broader, lower-intensity band at 1100 cm<sup>-1</sup> is attributed to the presence of SiO<sub>2</sub> from the AFM tip itself and/or the silicon substrate. We observed that this peak tends to intensify progressively during measurements. This is explained by the degradation of the platinum coating on the AFM tip, exposing the silicon core of the tip. Below 1000 cm<sup>-1</sup>, a substantial absorption band is noticeable. Based on our other characterization methods (FTIR and Raman spectroscopy), we hypothesize that it consists of a peak around 950-980 cm<sup>-1</sup> followed by a broad absorption band. This spectrum

demonstrates that PiFM detects the presence of niobium oxide, and this signal is predominant. Given that PiFM is a local probe technique, numerous perspectives are conceivable, including the possibility of mapping the distribution of this oxide on MXenes.

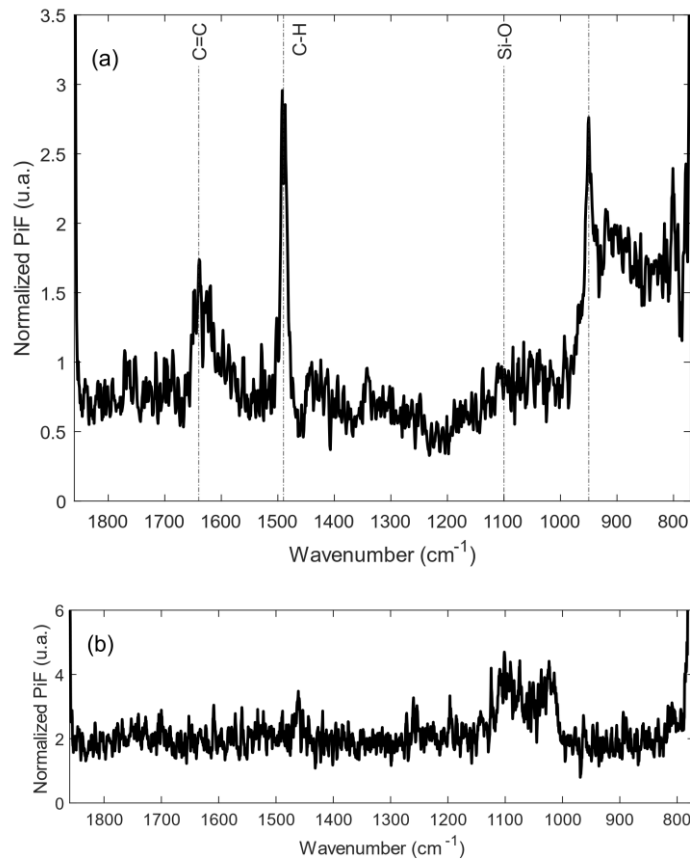


Figure 3 PiFM spectra of (a) bulk Nb<sub>2</sub>CT<sub>x</sub> and (b) undoped silicon wafer (substrate)

The photo-induced force signal detected in PiFM can be attributed to various physical mechanisms. It has been demonstrated that the response is contingent upon the nature of the sample. For thin films of organic materials, the dominant force is identified as the result of thermal expansion, whereas for metallic samples exhibiting electronic resonances, the predominant force is often the gradient force [6]. Considering that Nb<sub>2</sub>CT<sub>x</sub> is predominantly composed of a transition metal, albeit with some organic contamination, it can be inferred that the primary physical mechanism at play is the gradient force.

### 3.3 PiFM response of single/few layered of Nb<sub>2</sub>CT<sub>x</sub> flakes

PiFM was then used to characterize single/few layered Nb<sub>2</sub>CT<sub>x</sub> flakes deposited on an undoped silicon substrate. The morphology of the flakes is observed by AFM and SEM characterization methods (Figure 4). It is visible that...

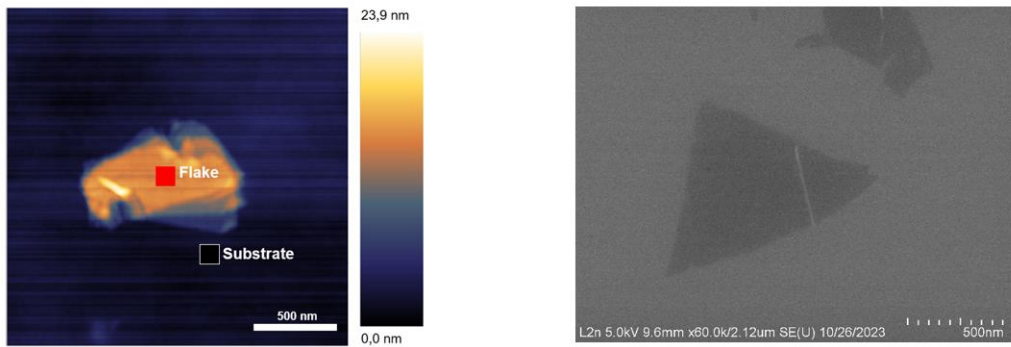


Figure 4 Nb<sub>2</sub>CT<sub>x</sub> flakes morphology obtained by (a) AFM and (b) SEM characterization methods

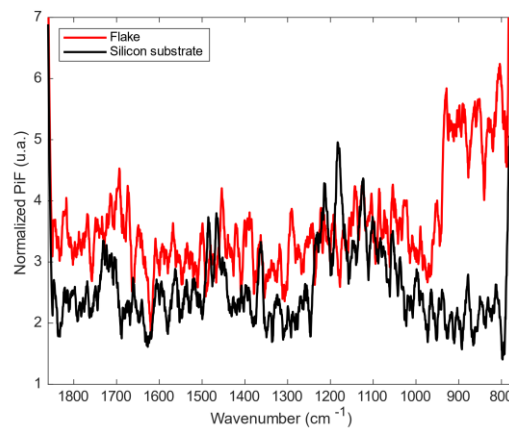


Figure 5 PiFM of a single Nb<sub>2</sub>CT<sub>x</sub> flake compared to the substrate (smoothed data)

Figure 5 displays the PiFM spectrum of an Nb<sub>2</sub>CT<sub>x</sub> flake (depicted by the red square in the figure) alongside the silicon substrate (highlighted by the black square). Despite the relatively low thickness of the flakes (approximately 15 nm), a signal discernible from the substrate is observed, highlighting the sensitivity of the PiFM method. Furthermore, the same peaks as those of the bulk sample are observed, confirming the chemical nature of the flakes.

#### 4. CONCLUSIONS

To conclude, this study has successfully demonstrated the synthesis and comprehensive optical characterization of Nb<sub>2</sub>CT<sub>x</sub> MXene using FTIR, Raman spectroscopy, and PiFM. The unique absorption features are observed in both bulk and single/few-layered MXene flakes within the 770 to 1860 cm<sup>-1</sup> range. The infrared characterization of this material using various techniques has revealed the presence of niobium pentoxide in our samples. PiFM has enabled local probing of this oxide and proves to be an intriguing tool for investigating this oxide on Nb<sub>2</sub>CT<sub>x</sub> at a nanoscale spatial resolution.

#### ACKNOWLEDGMENTS

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