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## **Nanoscale Structural Peculiarities in Mono- to Few-Layer Crystals of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Revealed by TERS.**

We report first time ever Raman imaging of mono- and few-layer crystals of 2D  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene, ( $\text{T}_x$  stands for surface groups such as =O, -OH and -F) deposited on gold substrate enabled by tip-enhanced Raman scattering (TERS) with 785 nm and 830 nm excitation wavelengths, matching the transversal plasmon resonance of 2D  $\text{Ti}_3\text{C}_2\text{T}_x$ , which is located at 780-800 nm. TERS spectra collected on the monolayers are strongly dominated by the intense peak  $A_{1g}$  (Ti, C,  $\text{T}_x$ ) at  $203\text{ cm}^{-1}$ . As the number of layers increases, relative intensity of the resonant  $126\text{ cm}^{-1}$  and  $725\text{ cm}^{-1}$  peaks, as compared to the intensity of the  $203\text{ cm}^{-1}$  peak, also increases, though the absolute intensity of the peaks comes down. In addition to that, we observed peculiar TERS response from wrinkles in MXene sheets, which commonly appear in crystals of  $\text{Ti}_3\text{C}_2\text{T}_x$  (and other 2D materials) deposited from colloidal suspensions. TERS spectra of the wrinkles featured a strongly enhanced absolute intensity of the  $126\text{ cm}^{-1}$  and  $725\text{ cm}^{-1}$  peaks, even in wrinkles that were up to 20 nm high. Using TERS for nanoscale spectroscopic characterization of  $\text{Ti}_3\text{C}_2\text{T}_x$  allows collecting fast Raman maps with deep sub-diffractional resolution at the laser power density on the sample about an order of magnitude lower as compared to prior confocal Raman measurements. In addition to that, we show that the intensity of TERS response from the mono- to few-layer crystals of  $\text{Ti}_3\text{C}_2\text{T}_x$  can be used to track early stages of degradation in ambient conditions, well before noticeable morphological changes start to appear in these crystals.