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Multipolar Surface Plasmons in 2D $Ti_3C_2T_x$ Flakes: an Ultra-High Resolution EELS with Conventional TEM and In-Situ Heating Study

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MXenes are a rapidly emerging class of two-dimensional (2D) materials that have attracted significant attention due to a variety of unique optical and optoelectronic properties rooted in various quantum confinement effects [1]. In case of photonic applications, it is important to understand the fundamental mechanisms behind light interaction with MXenes at the nanometer scale. Generally, such light-matter interaction at the nanoscale is characterized by collective oscillation of free charge carriers, i.e. surface plasmons (SPs), resonating with incident electromagnetic field. The ability to manipulate light at nanometer scales through coupling with resonating SPs, is known to enhance the performance of numerous applications ranging from biological, chemical and optical sensors to photovoltaic devices, and surface-enhanced Raman spectroscopy. $Ti_3C_2T_x$ (T_x stands for surface-terminated moieties such as -O or -F), the most studied MXene by far, has demonstrated an outstanding performance in a plethora of applications including energy storage, sensing, and electronics. Lately, 2D $Ti_3C_2T_x$ flakes were shown to exhibit intense SP resonances when excited by electron beams [2]. However, to date, the energy and spatial distribution of such SPs over $Ti_3C_2T_x$ flakes have not been investigated

Herein, we use scanning transmission electron microscope (STEM) in combination with ultra-high resolution electron energy-loss spectroscopy (EELS) to conduct a comprehensive characterization of SPs sustained by mono- and multi-layered $Ti_3C_2T_x$ flakes. To resolve reliably the individual spectral features in low-loss energy range, we used a new alignment scheme for ThermoFisher (former FEI Co) Titan Themis Z (40-300kV) TEM equipped with a monochromator and a high energy resolution Gatan imaging filter (GIF 966). In the STEM-EELS regime it allows to maintain the energy resolution of about 40meV (full width at half maximum of the zero energy loss peak) on a regular basis with up to 40pA current of the electron probe at 80kVof the microscope acceleration voltage. With such resolution surface plasmons resonant maxima at energies down to ~110 meV with separation of just 40 meV were accessible.

As a result we have been able to detect and visualize transvers and multipolar longitudinal SP modes in addition to the inherent inter-band transition (IBT) supported by $Ti_3C_2T_x$ flakes (Fig.1a). The energy and spatial distribution of both the transverse SP mode and the IBT was shown to be invariant across the flakes, as expected. On the other hand, unprecedented edge and central longitudinal modes (see Fig.1 b-d) with distinctive multipolar characters demonstrated a substantial energy and spatial variation over mono- and multi-layered $Ti_3C_2T_x$ flakes, showing correlation to the morphological aspects e.g., shape, size and thickness of the flake, thus allowing for a selectivity of SP energies. Moreover, the independent polarizability of $Ti_3C_2T_x$ monolayers, in virtue of their weak interlayer coupling, was clearly evinced in multi-layered flakes, thus underlining the fundamental difference of $Ti_3C_2T_x$ material from “classical” (metallic) plasmonic nanostructures (gold, silver, etc.).

Additionally we used in-situ heating (starting from room temperature and up to 900 °C) combined with STEM-EELS, to trace the evolution of the longitudinal (Fig.1e) and transverse modes sustained by the $Ti_3C_2T_x$ flakes. Our results show that SPs energies can be also tuned by controlling the population of T_x via material annealing. At temperatures above 500 °C, fluorine desorption resulted in an increase in the metal-like free electron density of $Ti_3C_2T_x$. The simultaneous induced damping effect is also discussed. The results presented here underline the great potential of $Ti_3C_2T_x$ for photonic devices such as broadband photodetectors and plasmonic waveguides. Detecting of SPs and IBT within the same 2D structure may allow for coupling of photonic and electronic modes with implications for nonlinear optics and light harvesting. In general, our findings may also support the development of novel MXene-based devices relying on excitation and detection of single SPs.

References:

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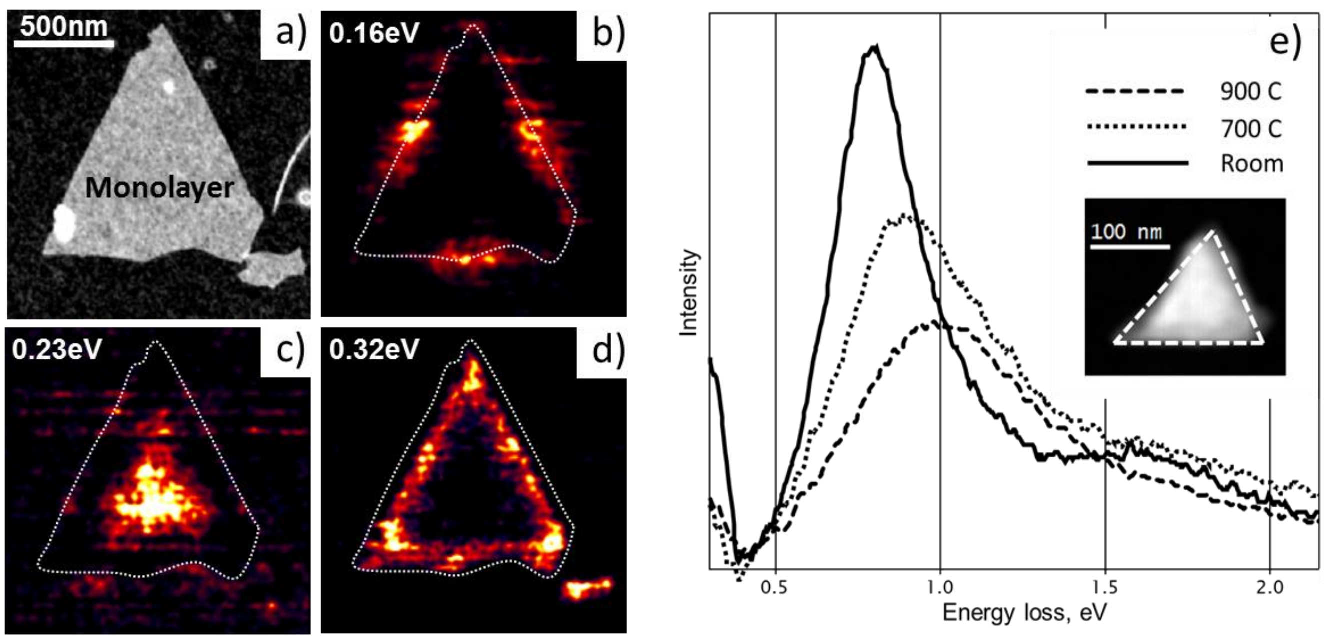

Figure 1. (a) STEM micrograph of a monolayer (1.52 nm ± 0.05 thick) $Ti_3C_2T_x$ flake. EELS fitted intensity maps of (b) quadrupole, (c) breathing and (d) "ring" modes sustained by the flake in (a). Note a smaller flake, attached to the big triangle, showing an independent plasmonic behavior. (e) ZLP-subtracted temperature-dependent EEL signals of the dipole SP mode sustained by small triangular flake (55.4 nm ± 0.04 thick) in inset.

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