Supplementary Information:
Interband, surface plasmon and Fano resonances in titanium carbide (MXene) nanoparticles in the visible to infrared range

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S1 Analytical approach

In order to use effectively the COMSOL Multiphysics® package, we first consider small nanoparticles and by applying quasistatic approximation, analytically identify the wavelengths range where the main peculiarities in optical spectra of MXene can appear. Wavelength dependent absorbed energy per unit time (absorbed power) is:

$$Q(\lambda) = \frac{2\pi c}{\lambda} \cdot \Im[\alpha(\lambda)]\,|E_0|^2, \tag{S1.1}$$

where E_0 is the incident electric field strength, $\alpha(\lambda)$ is polarizability and ω is the angular frequency of light For the following calculations we model the synthesized MXene sheets as ellipsoids in a way that the shortest semiaxes is equal to sheet thickness. In this case the polarizability has a form [1]

$$\alpha_L(\lambda) = \frac{\epsilon(\lambda) - \epsilon_m}{\epsilon_m + L_n[\epsilon(\lambda) - \epsilon_m]} \cdot \frac{V}{4\pi}, \tag{S1.2}$$

where V is the particle volume, $\epsilon(\lambda)$ is the dielectric function of the MXene [2] and ϵ_m is the dielectric permittivity of the surrounding medium, is the depolarization factor. When the electric field of the incident light is directed along one of the axes of ellipsoid the depolarization factor L_n becomes [1]

$$L_n = \frac{1}{2} a_1 a_2 a_3 \int_0^\infty \frac{\dot{\text{x}}}{(x + a_n^2)\sqrt{(x + a_1^2)(x + a_2^2)(x + a_3^2)}}, \tag{S1.3}$$

where a_n are semiaxes of ellipsoid. Performing integration in (S3) we obtain absorption spectra $Q(\lambda)$ for all three polarizations of incident light. In the limits of quasistatic approximation, independent from the ellipsoid sizes there always appear two absorption maxima which correspond to IBT and SP. For example, in case of a_1 = 5 nm, a_2 = 15

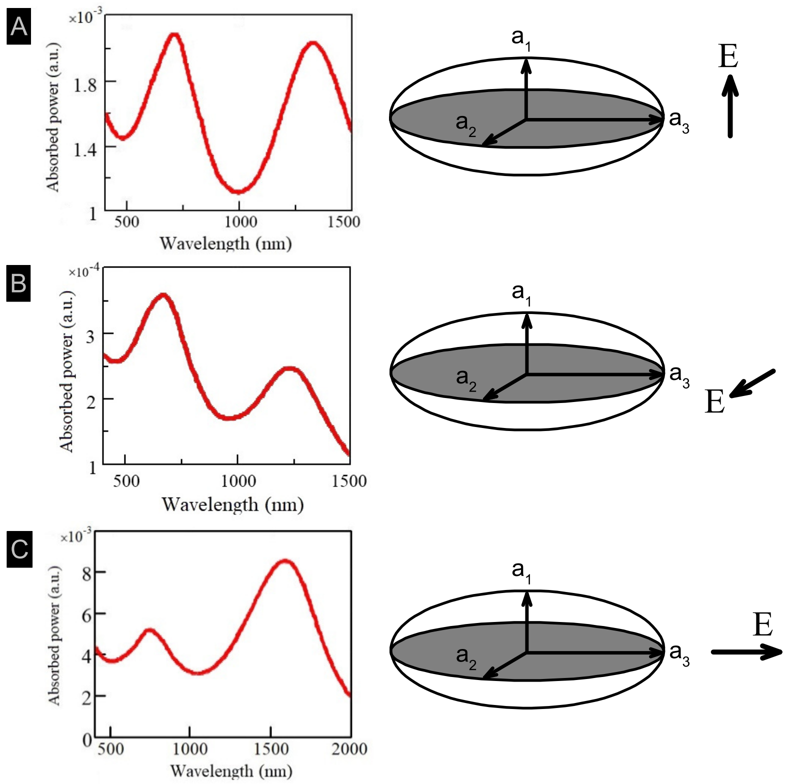

Figure S1: Absorbed power in a small ellipsoidal MXene particle for three polarizations. Electric field direction: A) along a_1, B) along a_2 and C) along a_3.

nm and $a_3 = 30$ nm, the calculated absorption spectra are presented in the Fig. S1 a), b) and c). The maxima at shortest wavelengths for all three polarizations correspond to IBT, whereas the maxima at longer wavelengths correspond to SPs and strongly differ from each other by position and height. The right peaks on Fig. S1 a) and b) correspond to TSPs while in Fig. S1 c) the right peak describes LSP.

Differences in heights in the Figs S1 a), b) and c) are conditioned by the values of corresponding polarizabilities, that vary with the length of the axis. Namely the longer the axis, the larger the polarizability and this peculiarity causes the differences in heights and magnitudes of redshifts in absorption spectra. Importantly, the peak positions of IBT in Figs S1 a), b) and c) change from 660 nm to 750 nm, which is a consequence of strong influence from higher SP peaks ("attraction" of peaks). The "attraction" of peaks is pure mathematical phenomenon, which is a result of simple overlapping of slopes of two neighboring peaks. Note that in Figs. S1 a) and c) the right hand side peaks are relatively strong. In these cases, in the vicinity of IBT peaks the slops of right hand side stronger SP peaks being increasing functions, overlap with IBT slops. That is why the addition of these two curves cause redshift. For the particular case when the MXene

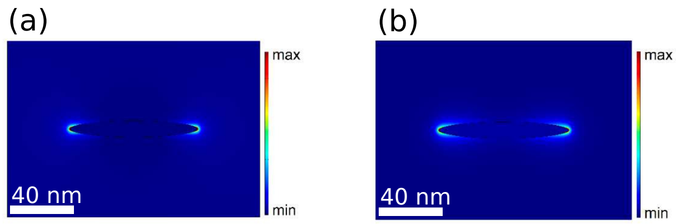

Figure S2: Electric field intensity map of a small spheroid at $\lambda = 780$ nm (a) and $\lambda = 2100$ nm (b). The presented above results in the part 1 of SI are exploited throughout the sections 2 and 3 of the main article for the identification of the ranges of resonance wavelengths corresponding to IBT and LSPs in single particles of various shapes.

sheet can be approximated as a small spheroid ($a_1 = a_2 = a$) the depolarization factor becomes

$$L_2 = \frac{1}{2\xi^2}\left[(1+\xi^2)\arctan\xi\right], \tag{S1.4}$$

where the spheroid eccentricity $\xi = a/\sqrt{a_3^2 - a}$. Next, inserting the measured values of $\epsilon(\omega)$ into equations (S1.1)-(S1.4), polarization dependent absorption spectra can be calculated. For example, for the spheroid of sizes $a_3 = 40$ nm and $a = 5$ nm, we obtain for IBT and LSP resonance wavelengths 780 nm and 2100 nm, respectively. The electric field intensity maps for identified two wavelengths are presented above.

S2 COMSOL Multiphysics® based simulations and method

COMSOL Multiphysics® is a computational software package which includes a module (called RF) for electromagnetics and optics calculations. Numerically, it is based on the finite element method. The computational domain is spherical. Scattering boundary conditions are applied to the boundary (outer spherical surface) of this domain. Inside the boundary, a perfectly-matched layer (PML) of 200 nm thickness is used to damp the scattered waves from the particles. The calculation of the absorption cross-section and near-fields of MXene spheroid and ellipsoids are performed on single, or multiple particles in homogeneous environment of refractive index n = 1. The surface of the particles is described by a triangular or quadratic mesh. The mesh size is adapted for each particle size in order to achieve convergent results and not to exceed the computer memory. The incident field is a plane wave. COMSOL solves the Maxwell's equations for the computational domain using the refractive indices of the materials inside, using the scattering field formulation. A sweep on frequency covering the defined region of the refractive index of the MXenes is done to obtain the near-field and the far-field distribution near the particles and the scattering cross-section.

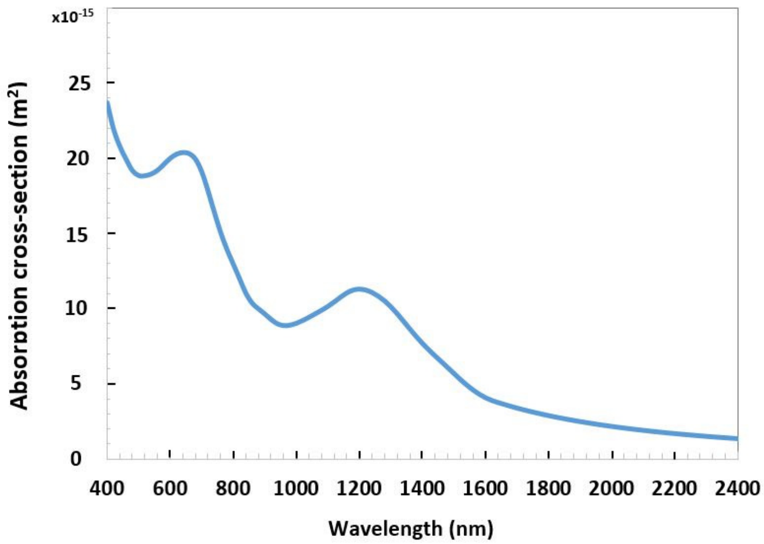

Figure S3: Simulated absorption cross-section (CS) of a $Ti_3C_2T_x$ disk of 1000 nm diameter with height 14 nm. The incident electric field is perpendicular to the base of the disk.

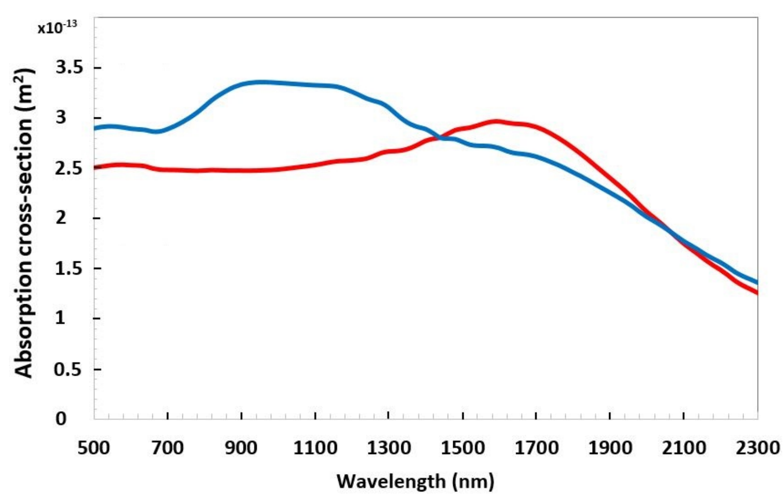

Figure S4: Simulated absorption CS of $Ti_3C_2T_x$ cylinder of diameter 500 nm with height 200 nm (red curve) and 300 nm (blue curve). The electric field is parallel to the base of cylinder.

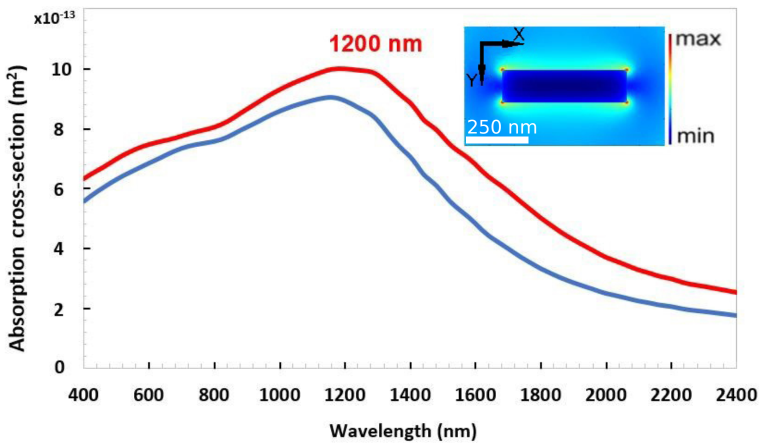

Figure S5: Simulated absorption CS of $Ti_3C_2T_x$ disk of diameter 500 nm with height of 300 nm. Electric field is perpendicular to the base of disk. Inset: electric field intensity map of cylinder of diameter 500 nm with height 300 nm at the wavelength of TSP resonance - 1200 nm.

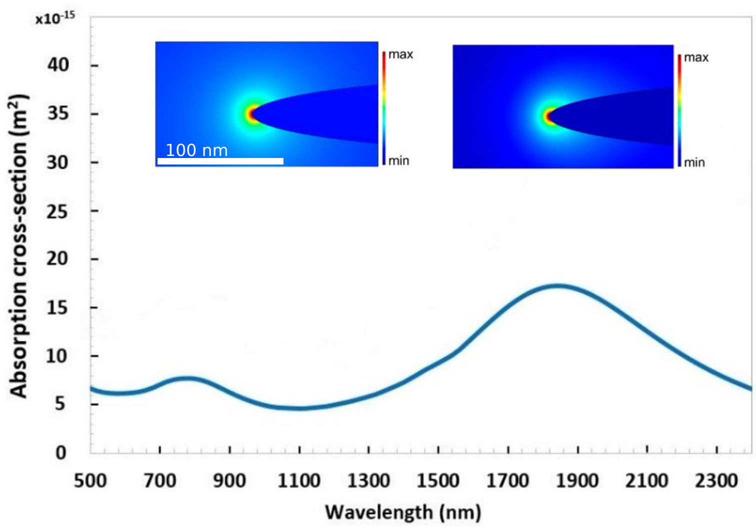

Figure S6: Simulated absorption CS of a single $Ti_3C_2T_x$ ellipsoid of semiaxes a_3 = 100 nm, a_2 = 40 nm and a_1 = 10 nm. Insets: electric field intensity maps at 780 nm and 1840 nm.

S3 Occurrence of Fano resonance

In the physical picture described below, each arrow shows the direction of displacement of positive charge at instantaneous time. Interestingly, dipole plasmons oscillate in-phase, whereas the quadrupole plasmons oscillating counter-phase generate in their turn transversal plasmons also oscillating counter-phase. In fact, strong hybridization caused by attraction of TSP modes in two particles leads to strong red shift of transversal oscillation wavelength of coupled system, which makes up to 500 nm (see Fig. 9).

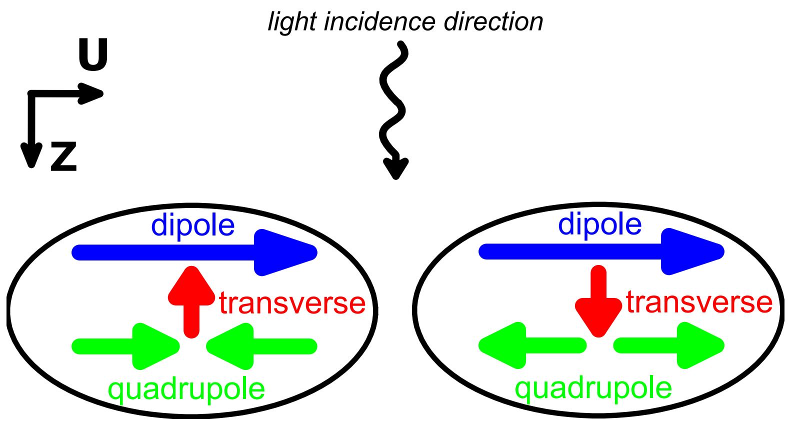

Figure S7: Schematic representation of three plasmon modes in each spheroid: dipole (blue), quadrupole (green) and transversal (red).

References

[1] Craig F. Bohren and Donald R. Huffman. *Absorption and Scattering of Light by Small Particles*. Wiley, Apr 1998.

[2] Andrew D. Dillon, Michael J. Ghidiu, Alex L. Krick, Justin Griggs, Steven J. May, Yury Gogotsi, Michel W. Barsoum, and Aaron T. Fafarman. Highly Conductive Optical Quality Solution-Processed Films of 2D Titanium Carbide. *Advanced Functional Materials*, 26(23):4162–4168, Apr 2016.