Electronic Supplementary Material (ESI) for Nanoscale.

Probing the size dependence on the optical modes of anatase nanoplatelets using STEM-EELS

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Supporting Information

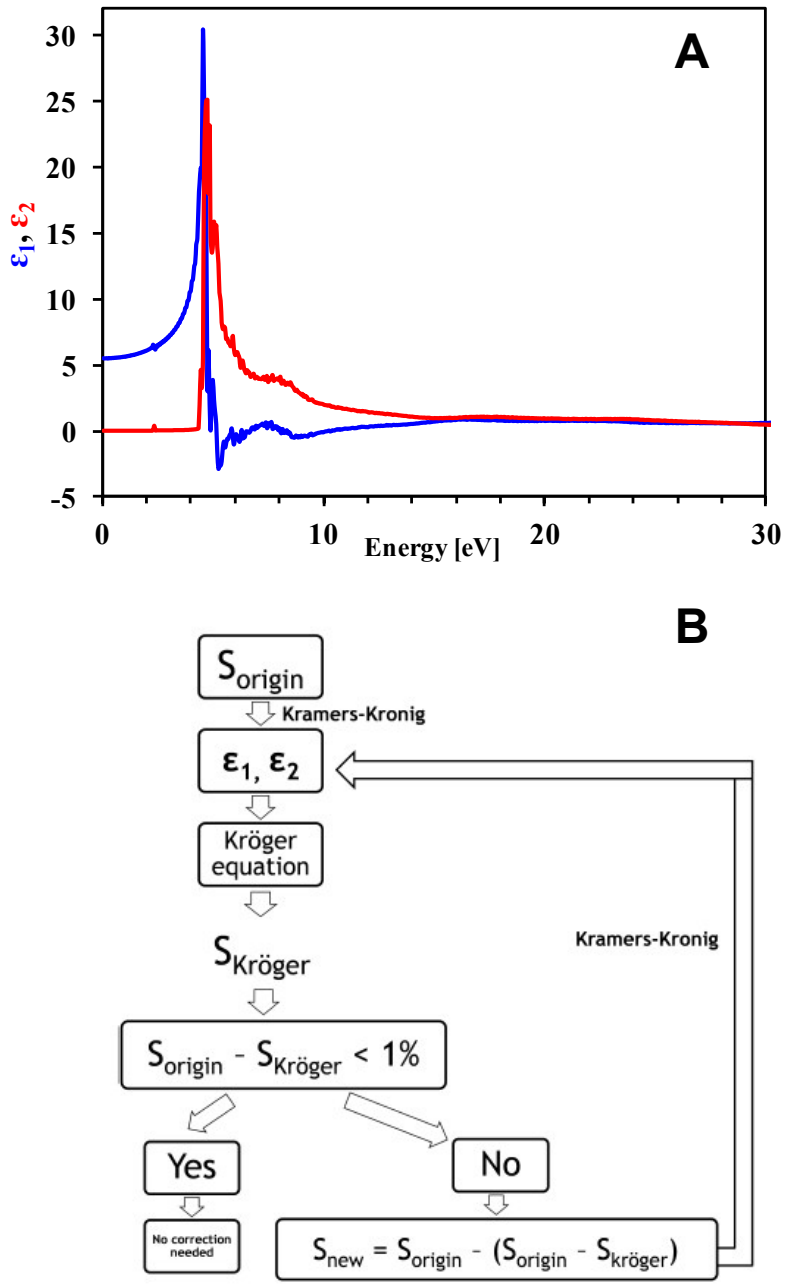

Figure S1. (A) Perpendicular component to the c-axis of the dielectric function of bulk anatase, obtained from a [001] substrate, separated into the real, ε_1, and imaginary part, ε_2, in the blue and red curves, respectively, obtained by applying the Kramers-Kroning transformations of the energy-loss function $S(E)_{[001]}$, shown in the inset in Figure 2 of the main text. Note that the intersection at 7 eV of ε_1 is an artifact of the Kramers-Kroning

transformations, as well as the absorption onset at 4.4 eV. However, they only affect simulations of the loss-function to a minor extent, as in the first case, only the actual shape of the volume plasmon is altered, while, the band gap onset is shifted towards higher energy-losses (see Figure S2a). Further details will be published elsewhere. (B) Flow diagram showing the off-line correction algorithm used for the removal of the Čerenkov losses.

In an EELS experiment, the energy-loss function in the anisotropic case can be written as[1]:

$$\mathrm{Im}\left(\frac{-2}{\varepsilon_{\parallel}\sin^2\gamma + \varepsilon_{\perp}\left(1+\cos^2\gamma\right)}\right)$$

where γ is the angle between the direction of the electron beam and the anisotropic axis. When the direction of incidence is parallel to the c-axis of anatase, γ is zero, and the energy loss function reduces to $\mathrm{Im}\left(\frac{-1}{\varepsilon_{\perp}}\right)$. Hence, $\varepsilon_{\perp}$ is measured by aligning the anatase crystal along a [001] zone axis (Figure S1). When the direction of incidence of the electron beam is perpendicular to the c-axis of anatase ([100] zone axis), γ is 90°, and the energy-loss function is $\mathrm{Im}\left(\frac{-2}{\varepsilon_{\parallel}+\varepsilon_{\perp}}\right)$. Hence, in Figure 2, both the parallel and perpendicular components of the loss function contribute to the dielectric function, a situation that cannot be avoided in a TEM. The differences found between the dielectric functions in Figure 2 in the main text, and Figure S1 are due to the anisotropic behavior of anatase.

To suppress the Cerenkov losses, the off-line correction algorithm proposed by Stöger-Pollach in ref [27] of the main text was applied to the single scattering distribution S(E) of bulk anatase. The algorithm was implemented in a MATLAB code according to the flow diagram in

Figure S1b. From the original EELS spectrum, $S(E) = S_{orig}$, $\varepsilon_1(E)$ and $\varepsilon_2(E)$ are determined by Kramers-Kronig transformations and input in the Kröger equation (eq. 6 in ref [27]). The resulting output is an EEL spectrum, $S_{Kröger}$, whose relativistic contribution is enhanced with respect to S_{orig}. The difference between $S_{Kröger}$ and S_{orig} gives the relativistic contribution that is subtracted to the original spectrum S_{orig}. The output gives a new S(E), S_{new}, which is used as an input to the next iteration. The algorithm iterates until $S_{Kröger}$ converges to S_{orig} with a predefined convergence criterion (1% in the flow diagram).

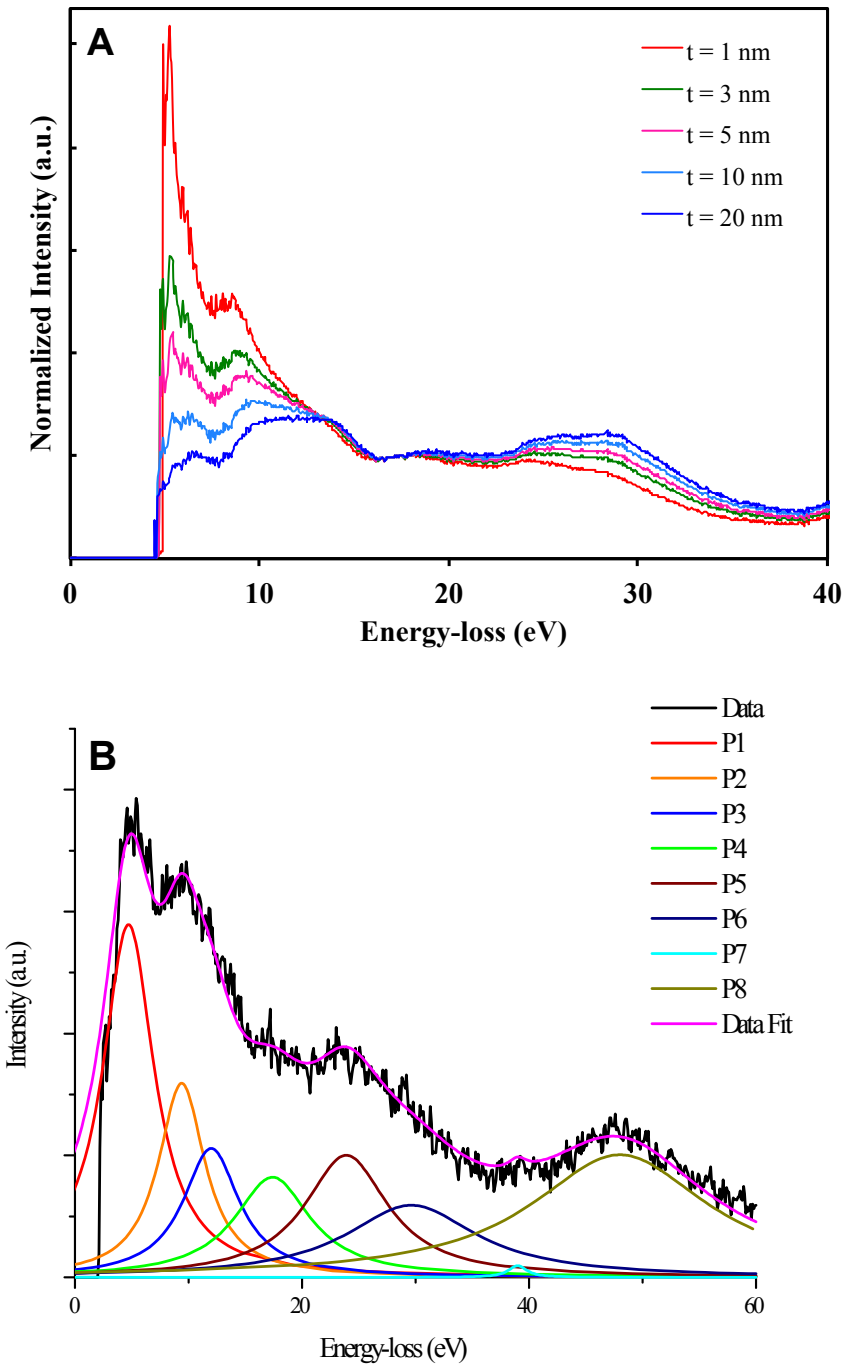

Figure S2. (A) Simulated relativistic inelastic scattering probability of 300 keV electrons penetrating at normal incidence a thin [001] film of anatase of different thicknesses (t). The EELS probability was calculated from the dielectric functions in Figure S1 and integrated over a collection semi-angle of 11 mrad. The spectra were normalized by their integrals. (B)

Data fitting of the experimental EELS spectrum of a flat anatase platelet of thickness t = 5 nm, extracted at x = -12 nm, as shown in Figure 1 of the main text. The peaks were fitted using Lorentzian functions.

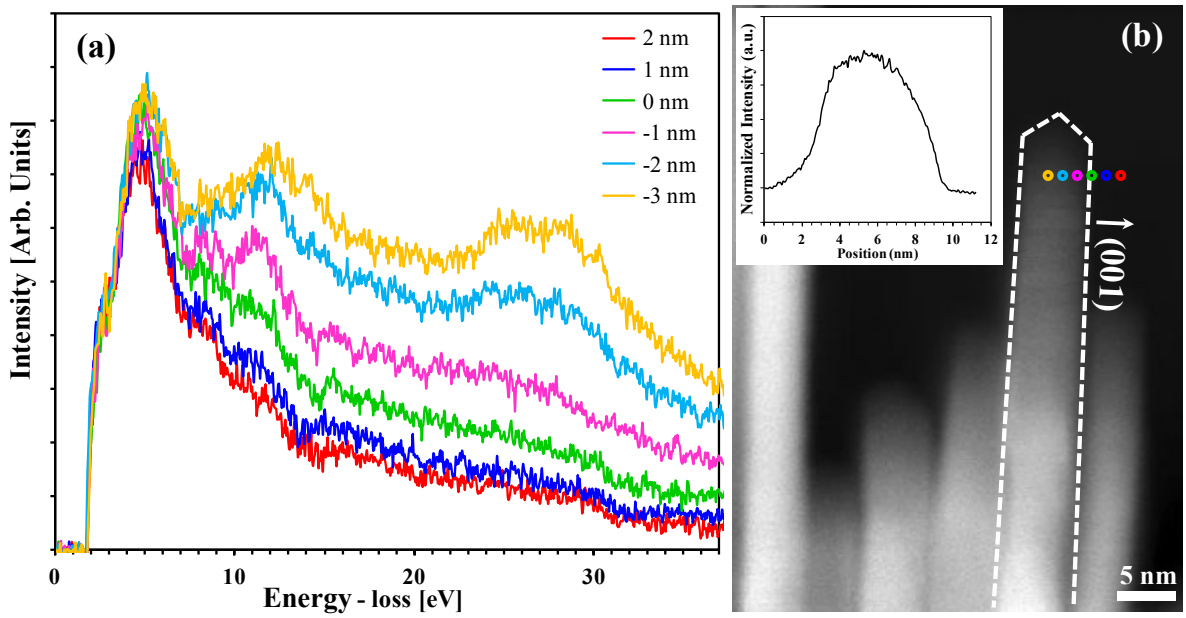

Figure S3. Valence electron energy-loss spectra (a) acquired from the edge-on platelet shown in the ADF image (b). The inset in (b) shows the intensity profile taken along the line of probe positions indicated by the open circles. The distance of the probe from the {001} edge of the platelet is positive in vacuum, or negative, in transmission. The spectra were acquired with an energy resolution of 0.7 eV, a collection semi-angle of 11 mrad, an energy dispersion of 0.05 eV/pixel, and a dwell time of 0.3 s/pixel.

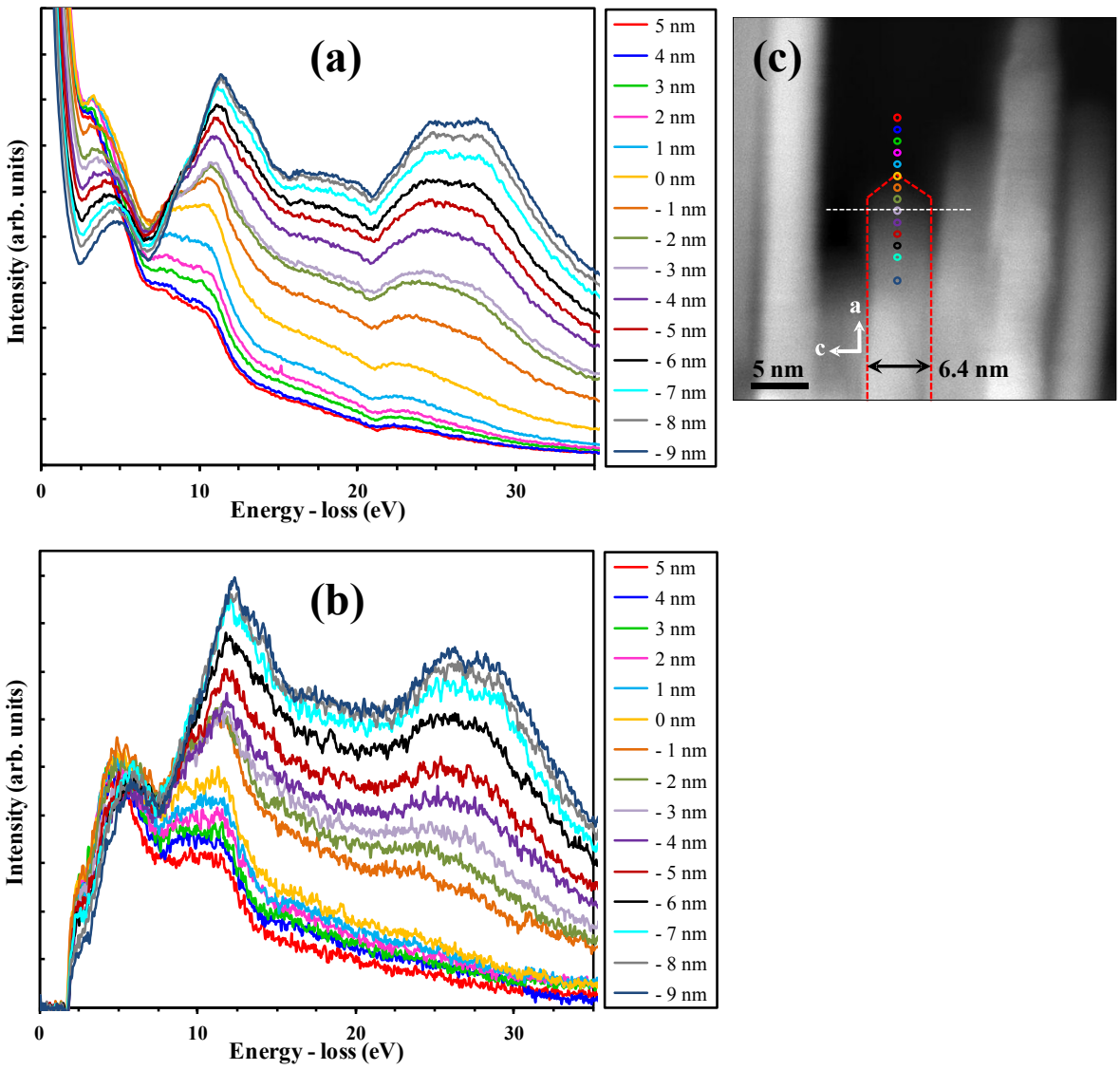

Figure S4. Valence electron energy-loss spectra (a) and corresponding deconvoluted spectra (b) acquired from the edge-on platelet shown in the ADF image (c). The probe positions are indicated with open circles. In transmission, the probe distance from the {100} edge is negative. The dashed line in (c) indicates a fictitious interface that separates the top and bottom region of the sampling area. In the bottom region, only bulk features are shown in the spectra. In the top region, the surface plasmon peak at 9.6 eV is faintly shown in transmission. In this case, the probe interacts with a specimen thickness of 6 nm, while in the previous case the probe interacts with a stack of four platelets. This stack acts as a

semi-infinite plane of anatase. The spectra were acquired with an energy resolution of 0.7 eV, a collection semi-angle of 11 mrad, an energy dispersion of 0.05 eV/pixel, and a dwell time of 1 s.

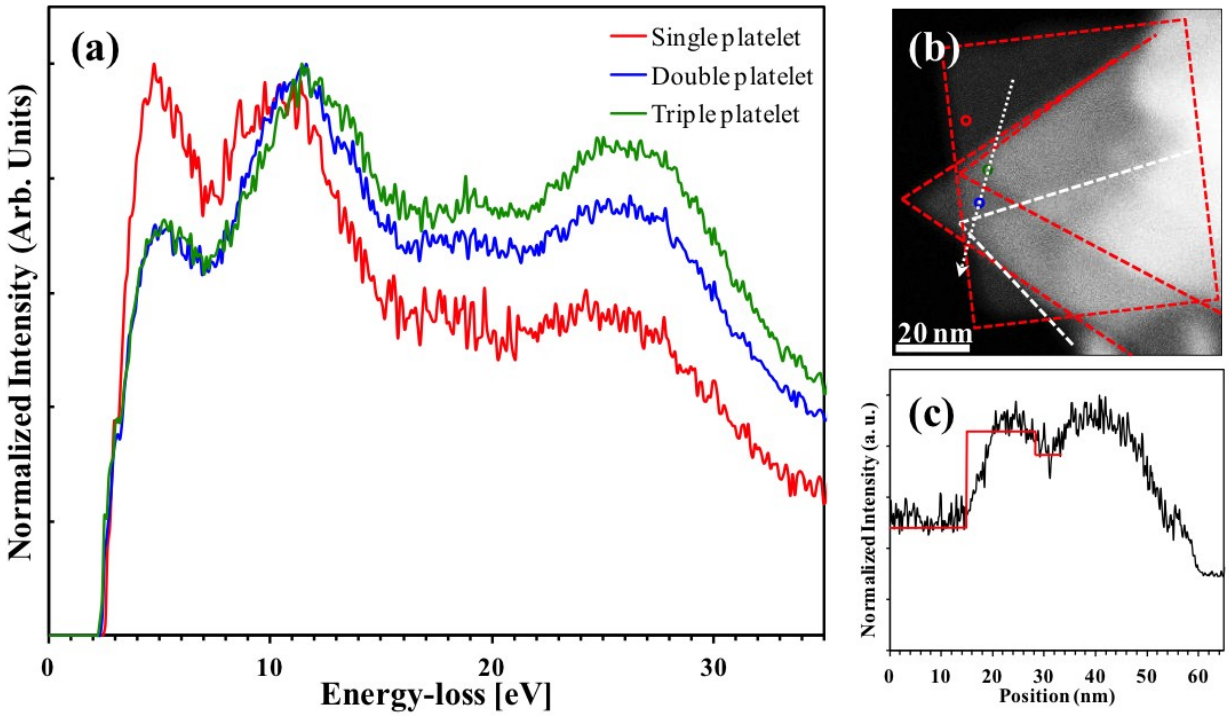

Figure S5. Valence electron energy-loss spectra (a) acquired from the stack of platelets shown in the ADF image in (b). The intensity profile in (c) was taken along the dotted line in (b), in the direction indicated by the arrow. The enhancement of the bulk feature with respect to the surface features occurs in agreement with the increment of thickness, given by the overlap between platelets. The spectra were acquired with a probe step of 4 nm, an energy resolution of 0.7 eV, a collection semi-angle of 4.5 mrad, an energy dispersion of 0.05 eV/pixel, and a dwell time of 1 s/pixel.

The analysis of the size distribution of the platelets was conducted by means of intensity profiles measuring the edge length and the thickness along the c-axis of 75 edge-on platelets. Figure S6 and S7 are histogram graphs showing the length and thickness distributions,

respectively. The edge lengths are distributed over a 20 – 110 nm range, with a mean value of 50.1 nm and standard deviation of 17.8 nm, while the mean thickness is 4.5 nm, with standard deviation 0.7 nm.

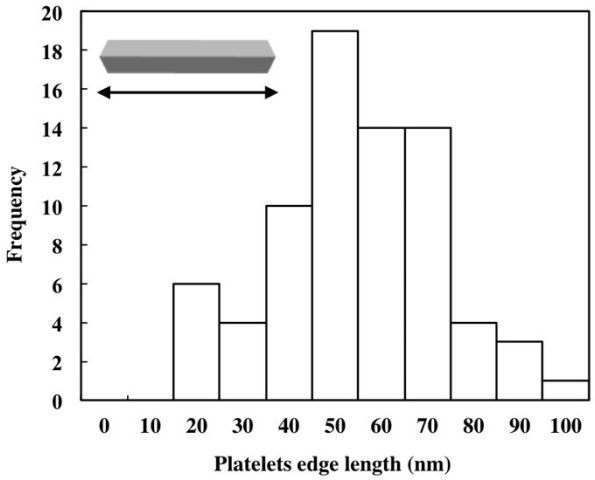

Figure S6. Histogram graph showing the length distribution of 75 anatase platelets.

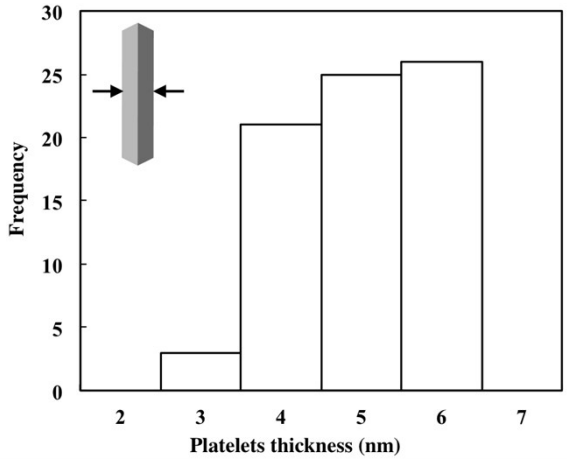

Figure S7. Histogram graph showing the average thickness of 75 edge-on platelets.

(1) D. Taverna, PhD Thesis, *Electronic excitations of individual nano-objects, analysed by Electron Energy Loss Spectroscopy with high spatial resolution*, Université Paris Sud, 2005.