Supporting Information

Nanoscale Topography of Anodic TiO_2 Nanostructures Is Crucial for Cell-Surface Interactions

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1. Long-range order of the nanostructures using a two-step anodization approach

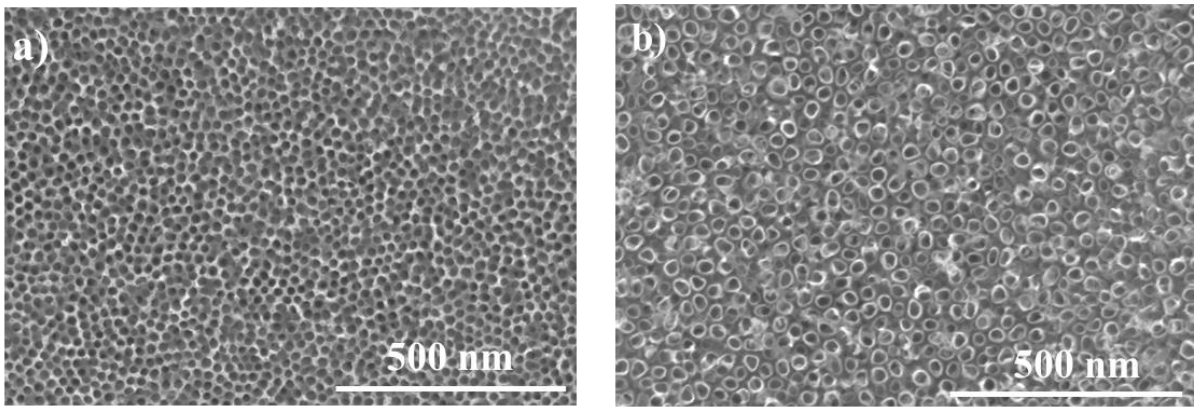

Figure S1. High-resolution SEM images of a) NPs and b) NTs showing very good long-range order.

2. Typical initiation layer-covered TiO_2 nanotubes

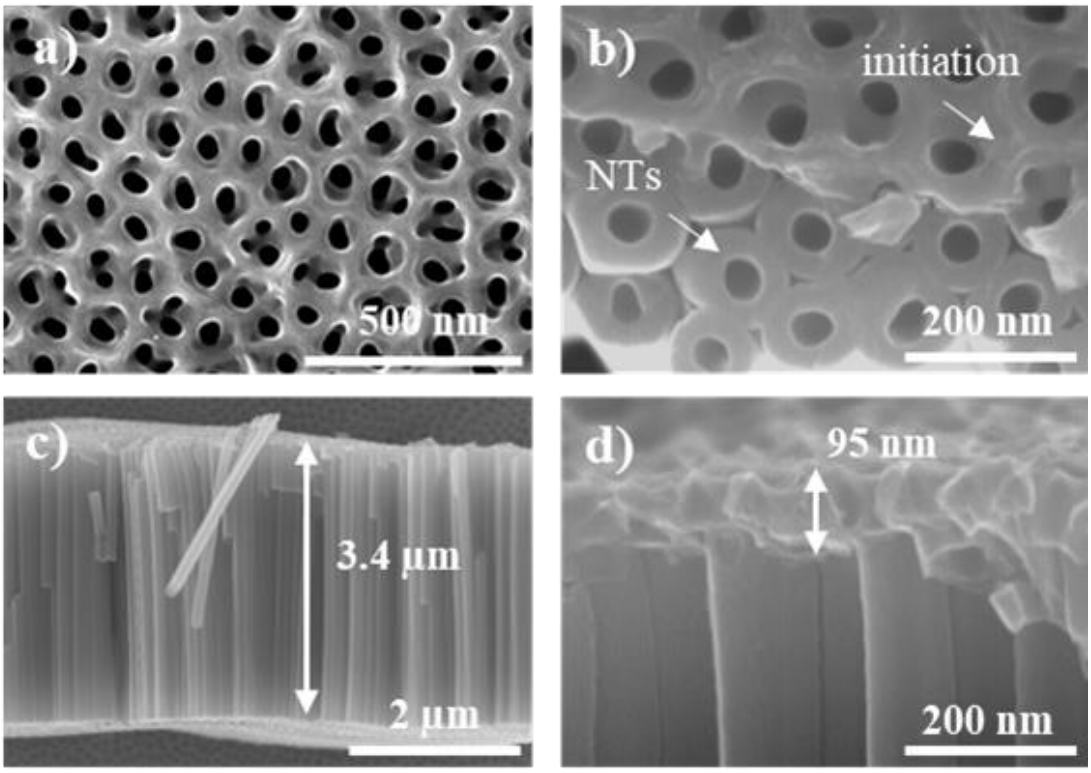

Figure S2. Typical NTs covered with a thin initiation layer obtained in ethylene glycol-based electrolytes with NH_4F (in a double anodization approach, in EG + 0.3 % w/v NH_4F + 1 % v/v H_2O, final anodization at 60 V for 10 min): (a, b) top-view SEM images, (c) cross-sectional SEM image, and (d) cross-sectional view showing the thickness of the initiation layer.

3. XRD patterns of the obtained nanostructures and of the Ti substrate

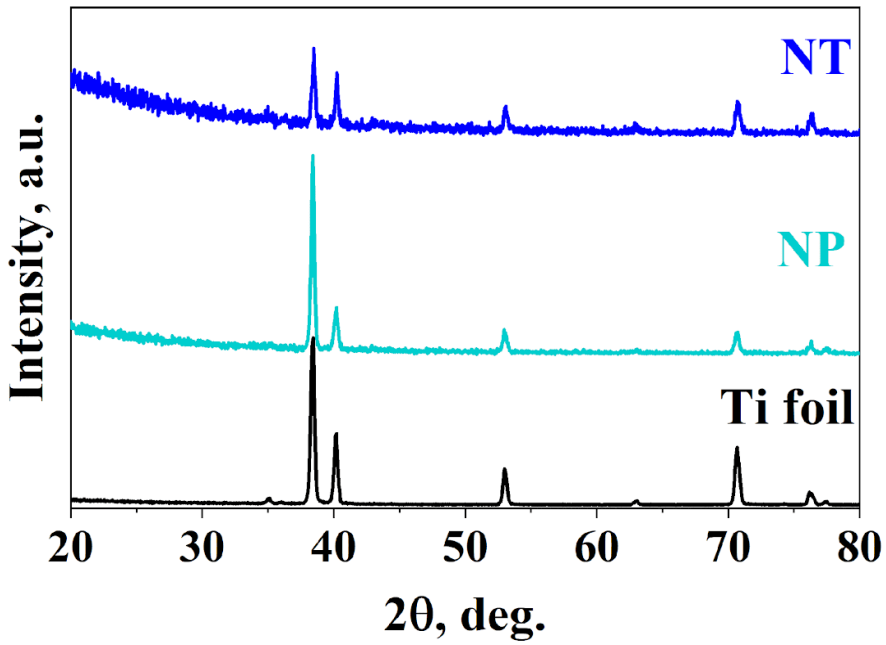

Figure S3. XRD patterns of the Ti foil, NP, and NT nanostructures show that the anodic layers are amorphous, as only the peaks of titanium (Ti foil) are observed.

4. EDX and XPS data of the NP and NT nanostructures

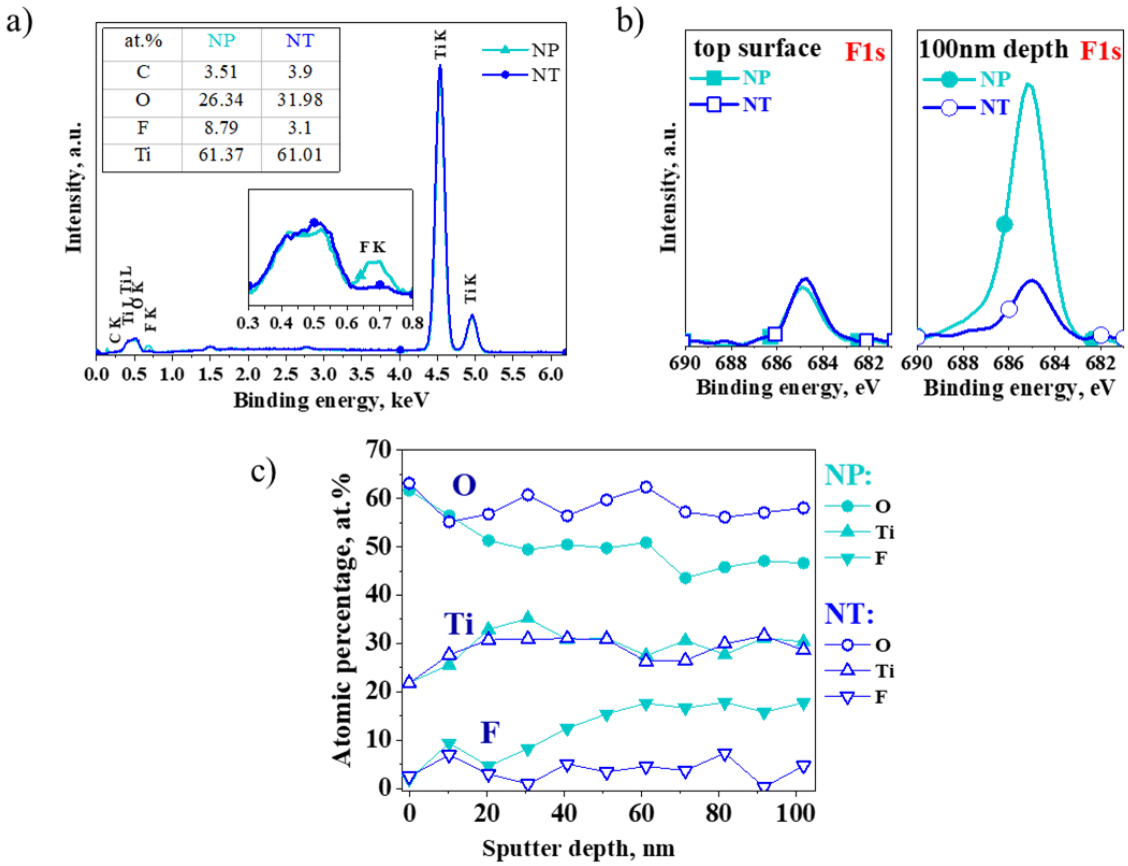

Figure S4. a) EDX spectra and at. % of the nanostructures; b) XPS high-resolution spectra of the F1s peak before and after sputtering 100nm; and c) corresponding XPS depth profiles of the first 100 nm, showing the atomic percentages of Ti, O, and F.

5. ToF-SIMS data of the NP and NT nanostructures

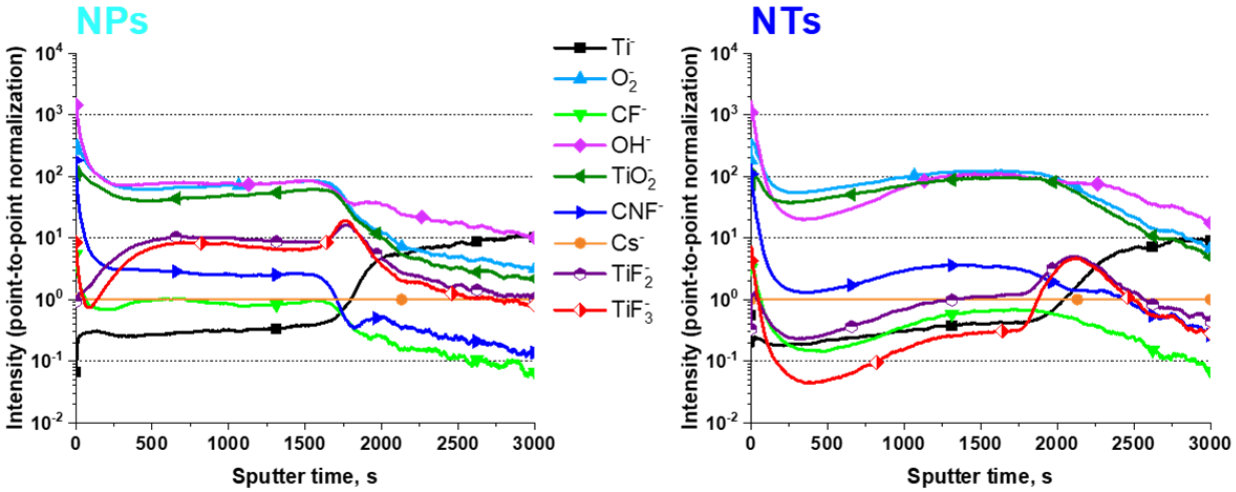

Figure S5. ToF-SIMS depth sputter profiles in the negative polarity of the NPs (left panel) and NTs (right panel) showing selected mass fragments of Ti^- (*m/z* 47.948), O_2^- (*m/z* 31.990), CF^- (*m/z* 30.999), OH^- (*m/z* 17.003), TiO_2^- (*m/z* 79.938), CNF^-(*m/z* 45.002), Cs^- (*m/z* 132.906), TiF_2^- (*m/z* 85.945), and TiF_3^- (*m/z* 104.943).

The full ToF-SIMS negative depth profile spectra with additional mass fragments are shown in **Figure S5,** and SEM images of the sputter crater are in **Figure S6**. We observe a higher intensity count for the TiF_3^- and TiF_2^- mass fragments of NPs (TiF_3^- in **Figure 3c**, TiF_2^- in **Figure S5**), but both nanostructures show for these mass fragments a bump in intensity close to the interface, which can be attributed to the pore/tube bottom at the oxide layer/metal interface. There are also differences in the distribution of the CNF^- mass fragment over the length, *i.e.*, for NTs in the first part of the layer, the intensity is lower. This is consistent with the more pronounced V-shape of the NTs, with a thinner tube wall at the top. In addition, the interface for NPs is at ≈2150 s, while for NTs is ≈2700 s.

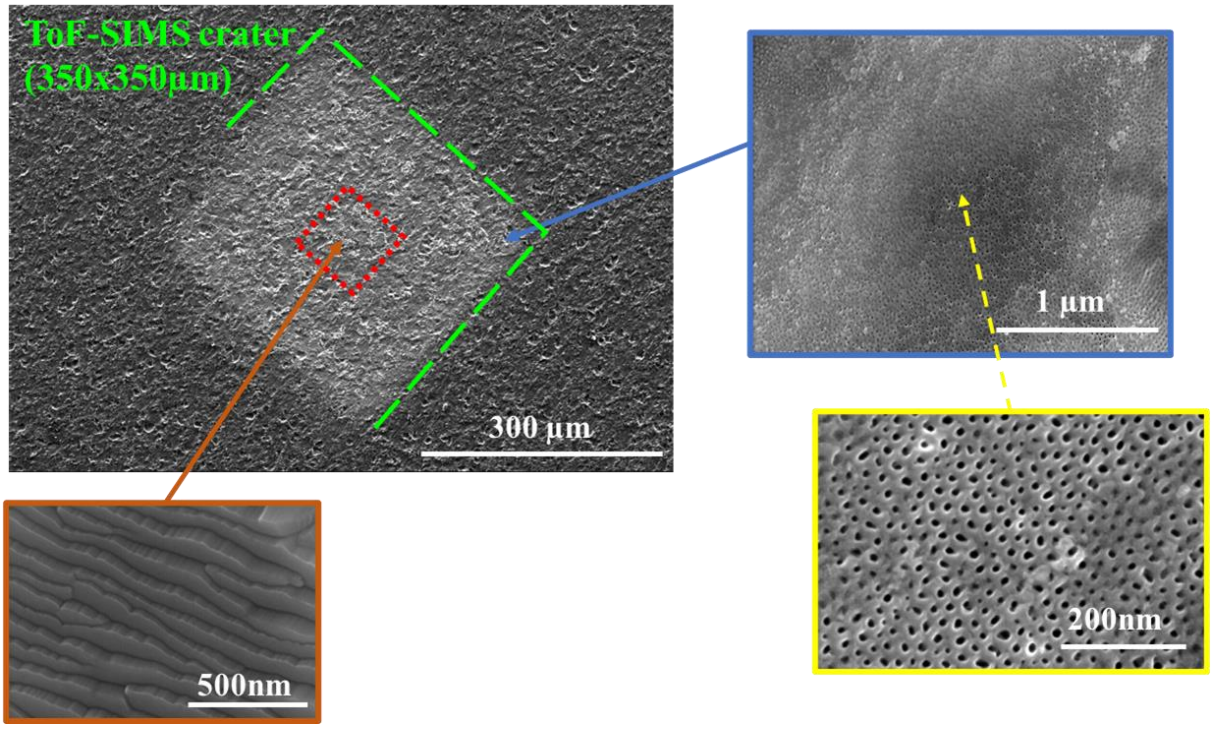

Figure S6. Example of the ToF-SIMS crater for the NPs, showing the 350 × 350 μm sputter crater (marked with dashed green line), the measurement area of 65.6 × 65.6 μm in the center of the sputter crater (marked with red dotted line), and high-resolution SEM images from the center of the crater, and from the edge of the sputter crater (showing the morphology of the NPs after sputtering).