

Supplementary data

Chemically regulated bioactive ions delivery platform on titanium surface for sustained controlled-release

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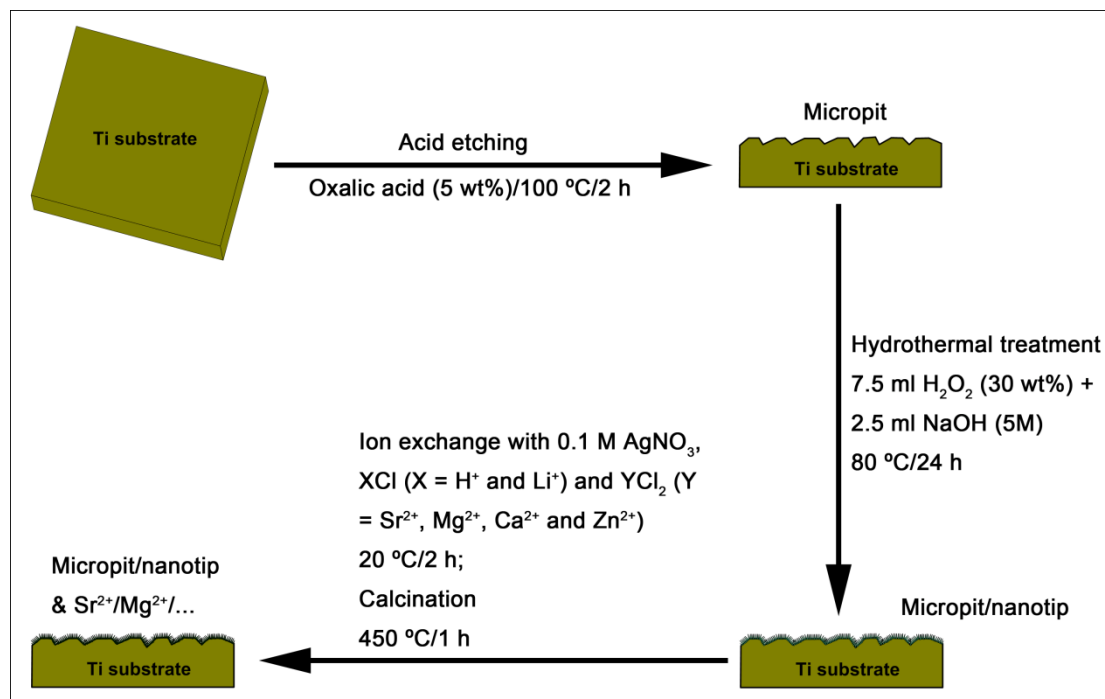
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Scheme S1. Schematic fabrication procedure of bioactive ions-loaded and hierarchical hybrid micro/nanotip film on Ti substrate by combining acid etching, hydrothermal treatment and ion exchange process together.

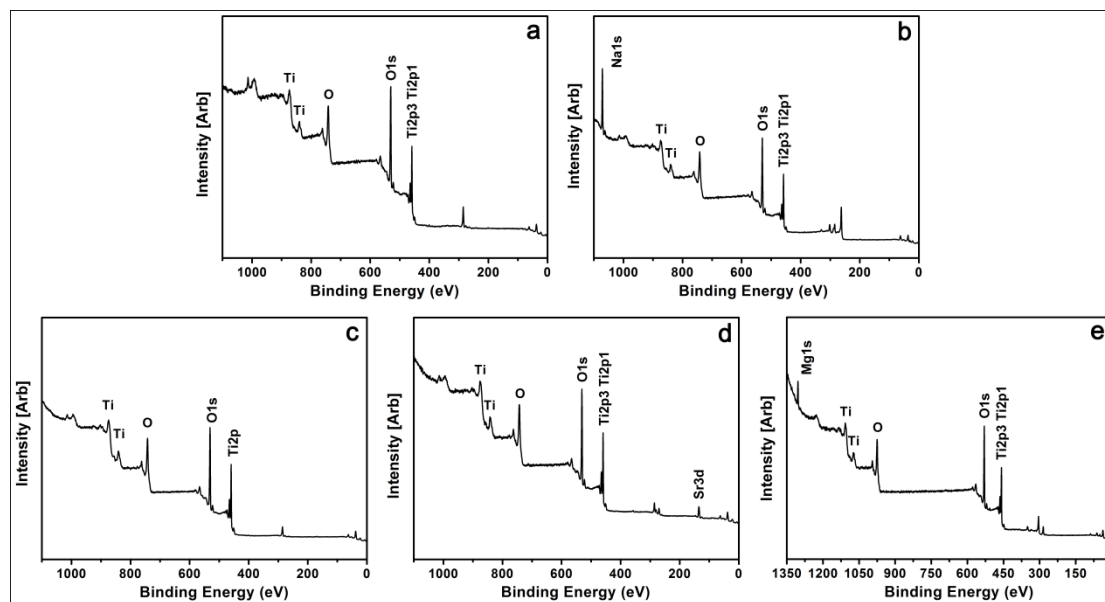


Fig. S1. XPS full spectra of Cp Ti (a), Na-NT (b), H-NT (c), Sr-NT (d) and Mg-NT (e) samples.

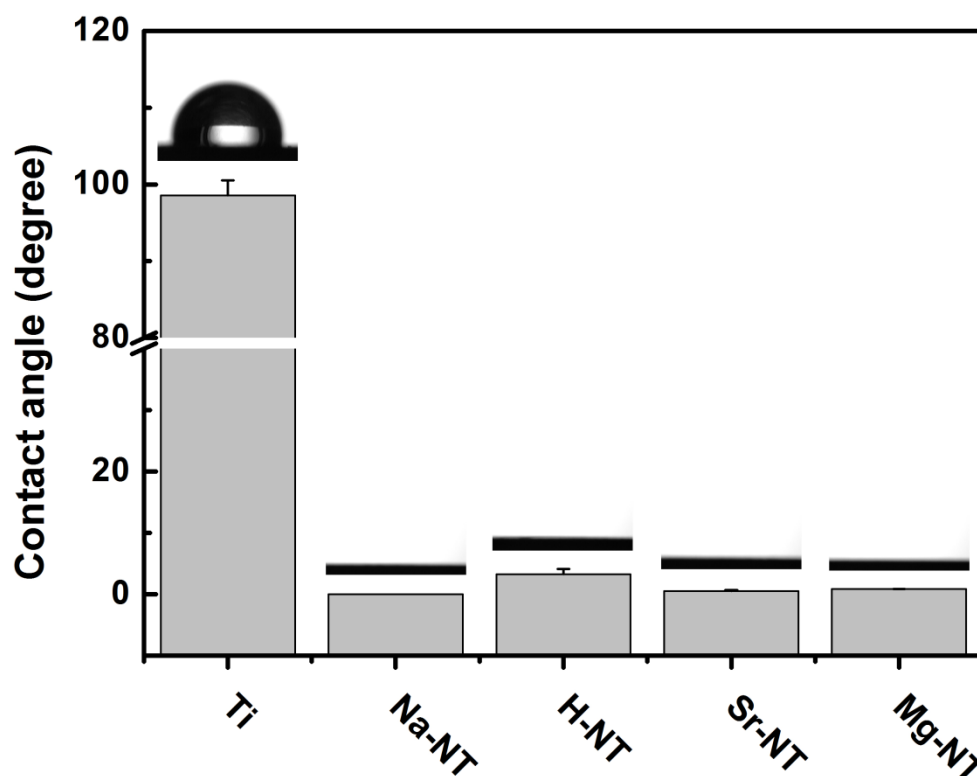


Fig. S2. Water contact angle measurements. The contact angles of Cp Ti, Na-NT, H-NT, Sr-NT and Mg-NT samples are displayed. The micro/nanostructured Na-NT, H-NT, Sr-NT and Mg-NT exhibited superhydrophilicity compared to Cp Ti. All the data are expressed as means \pm SD (standard deviation) and $n = 5$.

The surface wettability of Cp Ti, Na-NT, H-NT, Sr-NT and Mg-NT samples was measured by contact angle measurement (Automatic Contact Angle Meter Model SL200B, Solon information technology Co., Ltd, China). After 2 μ l sessile distilled water droplet was dropped onto sample surface, the cover of contact angle meter was shut down to ensure a dark space. Once the water droplet calmed down, the equipped camera system would capture the photograph immediately. The room temperature was 20 $^{\circ}$ C with atmospheric relative humidity of 30 %. Contact angles of five droplets were analyzed on each sample and the experiment was repeated twice. Results are expressed as means \pm SD.

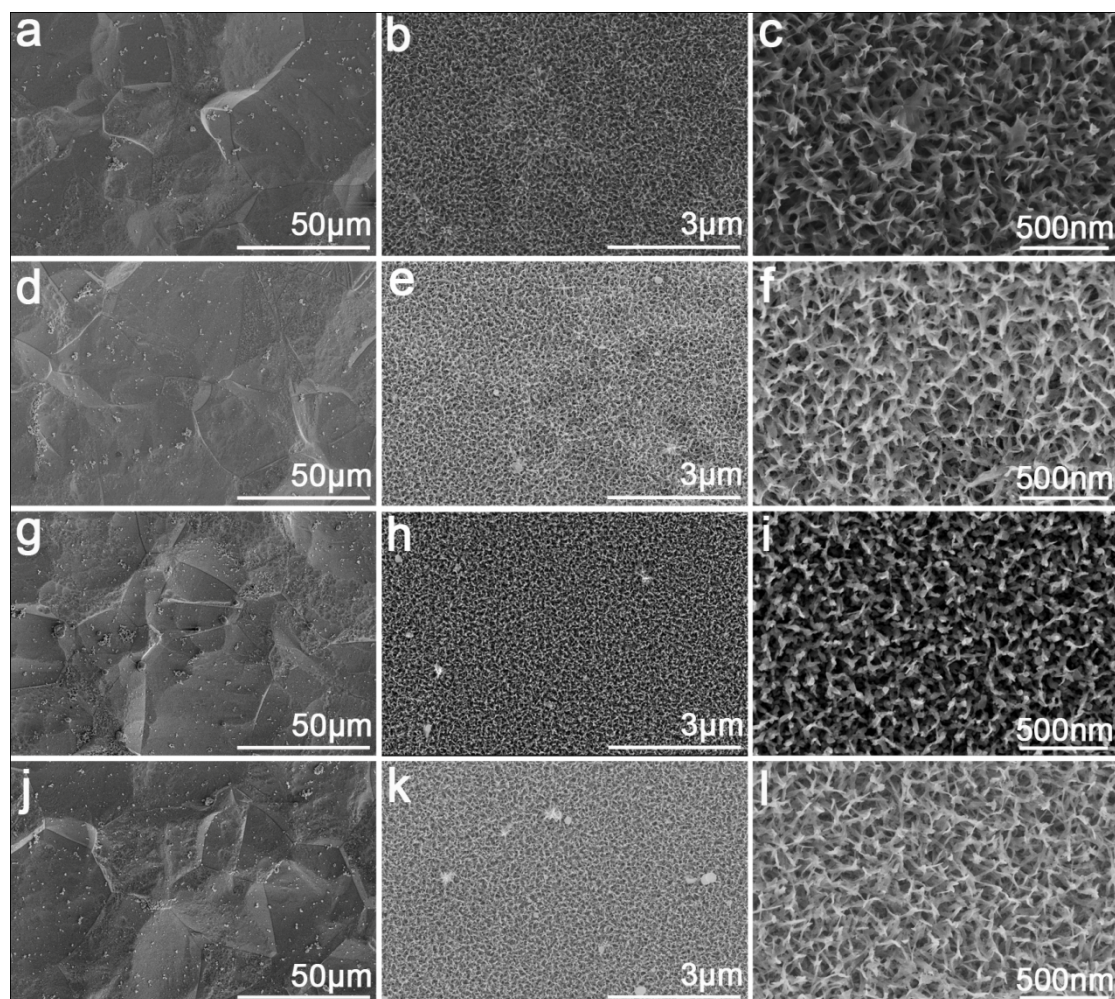


Fig. S3. SEM views of the as-prepared Ca-NT (a, b, c), Zn-NT (d, e, f), Ag-NT (g, h, i) and Li-NT (j, k, l) samples.

Figure S3 shows the surface topographies of Ti plates after undergoing acid etching, hydrothermal treatment and subsequent ion exchange with Ca^{2+} , Zn^{2+} , Ag^+ and Li^+ , followed by calcination, which can be seen that the nanotip topography was maintained and showed no significant difference from that on Na-NT surface at both low and high magnifications (Figs. 1g-i).

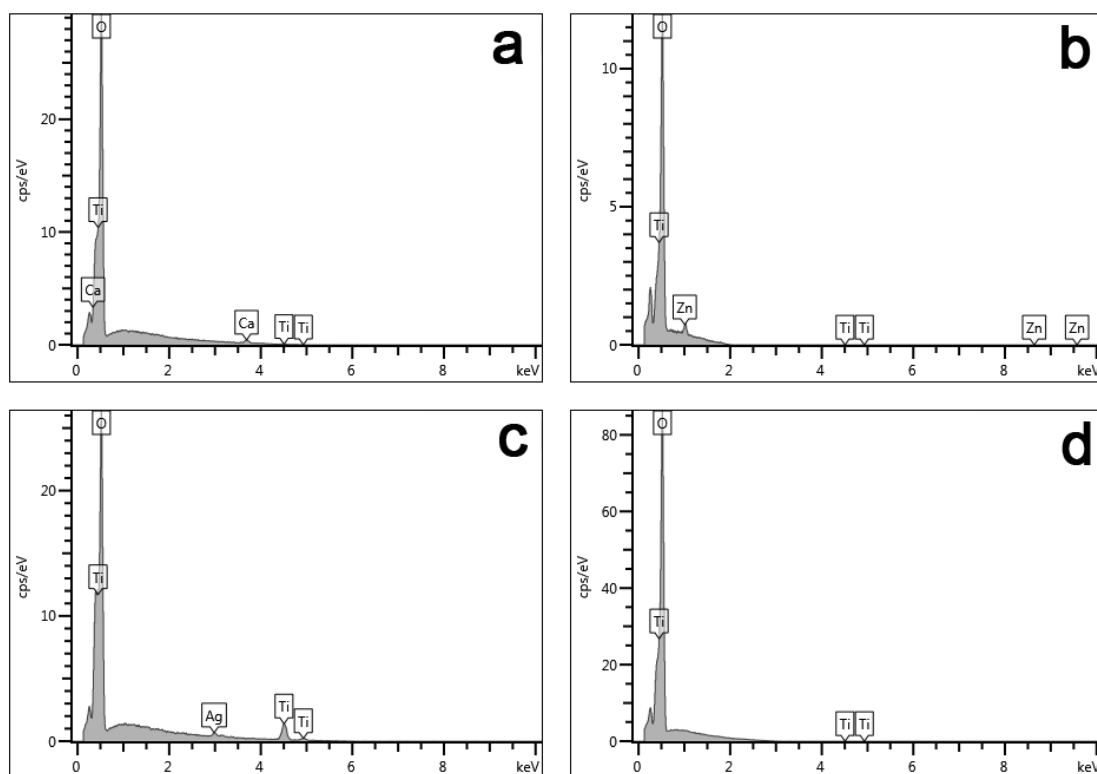


Fig. S4. EDS spectra obtained from Ca-NT (a), Zn-NT (b), Ag-NT (c) and Li-NT (d) samples. Note that the Li element cannot be detected by EDS.

As shown in Fig. S4, Na^+ ions in the titanate layer on Ti surface were completely replaced by Ca^{2+} , Zn^{2+} , Ag^+ , Li^+ respectively. In other words, Na^+ ions in the titanate layer can be thoroughly eliminated via this facile ion exchange strategy with desired ions, which simultaneously maintained the surface nanotip topography on titanium substrate. (Ionic radii: Ca^{2+} 0.1 nm; Zn^{2+} 0.074 nm; Ag^+ 0.115 nm; Li^+ 0.076 nm.¹)

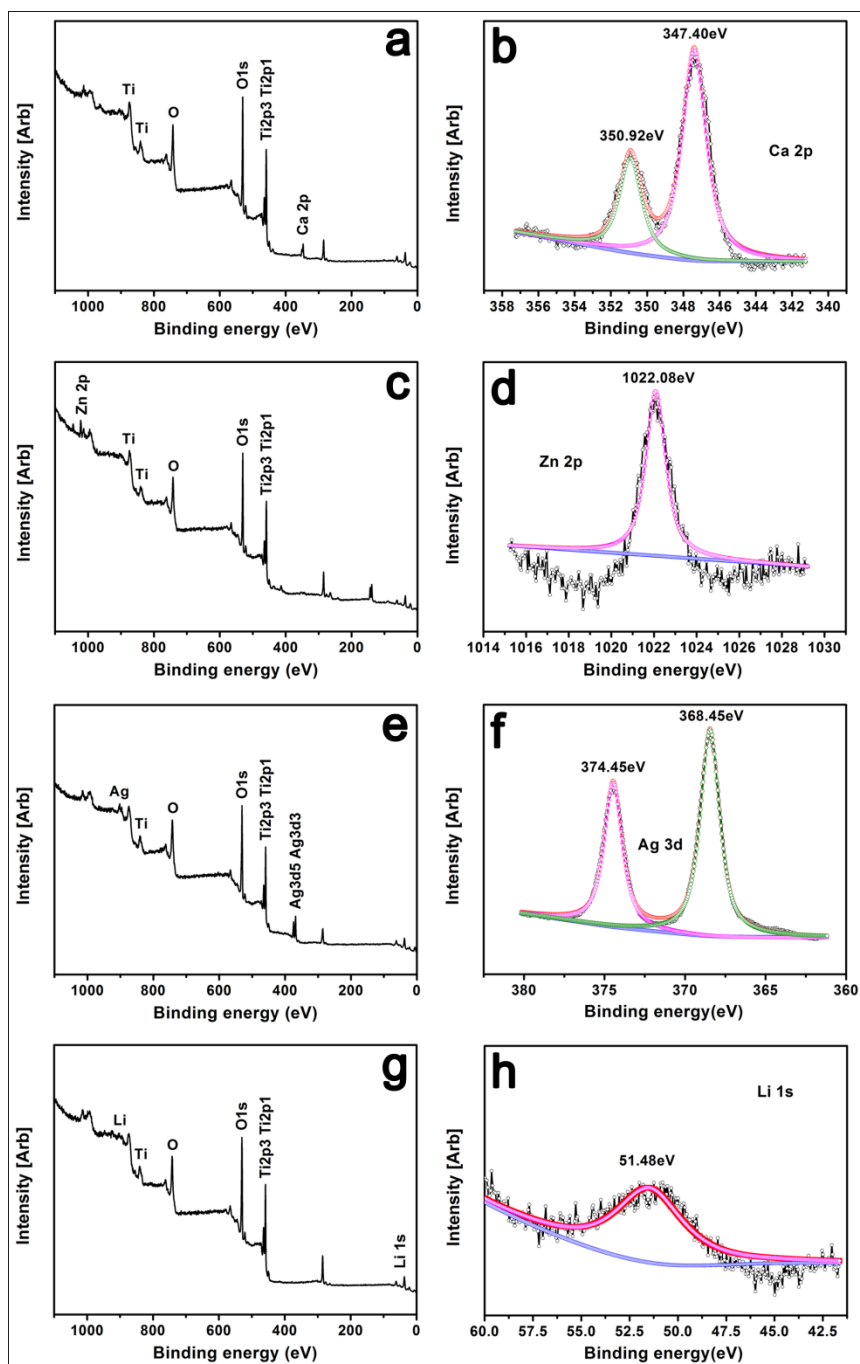


Fig. S5. XPS full spectra of Ca-NT (a), Zn-NT (c), Ag-NT (e) and Li-NT (g) samples, accompanied by the corresponding high-resolution XPS spectra of Ca 2p (b), Zn 2p (d), Ag 3d (f) and Li 1s (h).

Compared with the XPS full spectrum of Na-NT sample in Fig. S1(b), after ion exchange with Ca^{2+} , Zn^{2+} , Ag^+ , Li^+ respectively, Na 1s peak disappeared and Ca 2p, Zn 2p, Ag 3d, Li 1s peaks were detected accordingly.

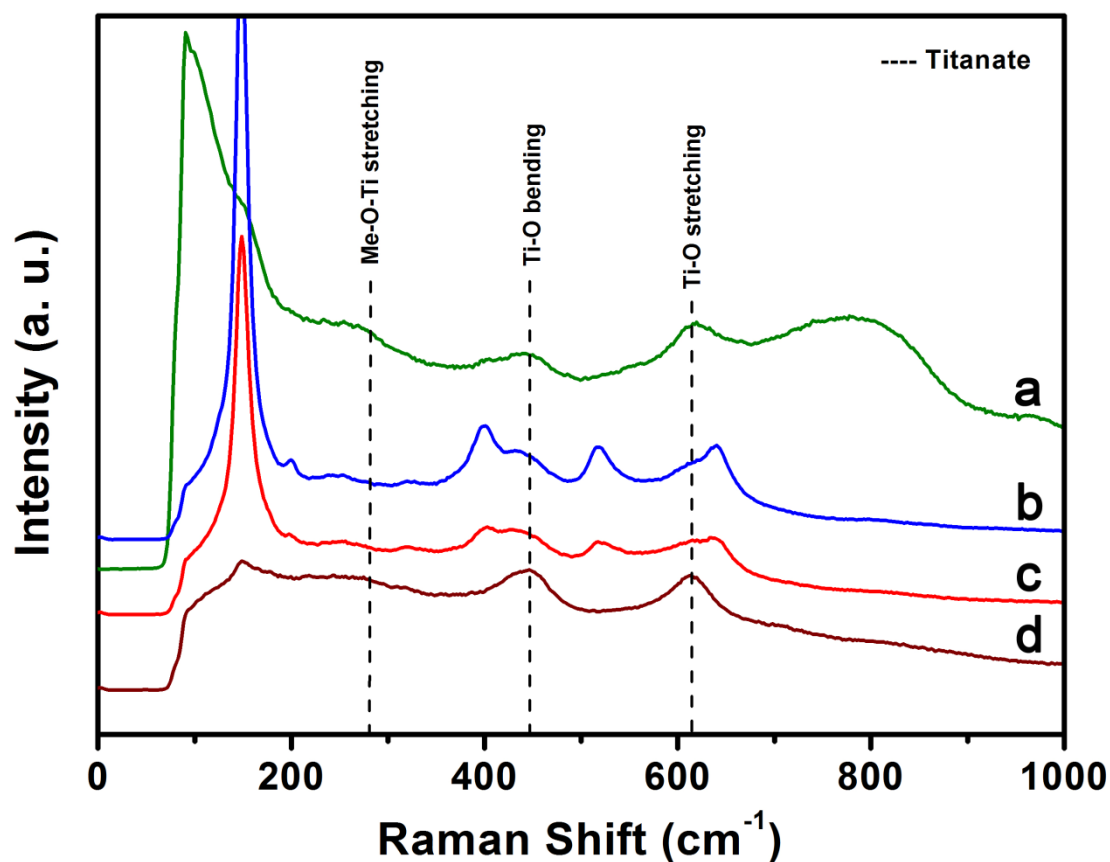


Fig. S6. Raman spectra acquired from Ag-NT (a), Li-NT (b), Zn-NT (c) and Ca-NT (d) samples respectively.

From Fig. S6, all of the bands were quite similar to the reported Raman data for titanates.^{2,3} The band at 280 cm⁻¹ was ascribed to the Ag/Li/Zn/Ca–O–Ti stretching vibration; the peaks at around 450 and 600 cm⁻¹ were assigned to the Ti–O bending and stretching vibrations involving sixfold-coordinated titanium and threefold-coordinated oxygen.

Notes and references

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3. Ma, R., et al., Structural Features of Titanate Nanotubes/Nanobelts Revealed by Raman, X-ray Absorption Fine Structure and Electron Diffraction Characterizations. *The Journal of Physical Chemistry B*, 2005. **109**(13): p. 6210-6214.