

Electronic Supplementary Information (ESI) for
**A superparamagnetic Fe₃O₄-TiO₂ composite coating on titanium
by micro-arc oxidation for percutaneous implants**

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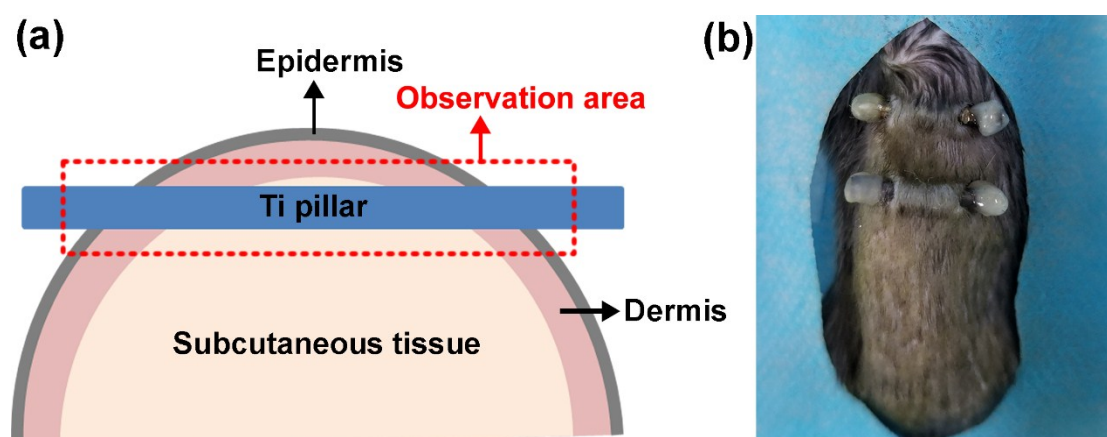


Figure S1 Schematic diagram showing the rectangle-marked region for histological analysis of
the coated Ti pillar percutaneously implanted in mice for 4 weeks.

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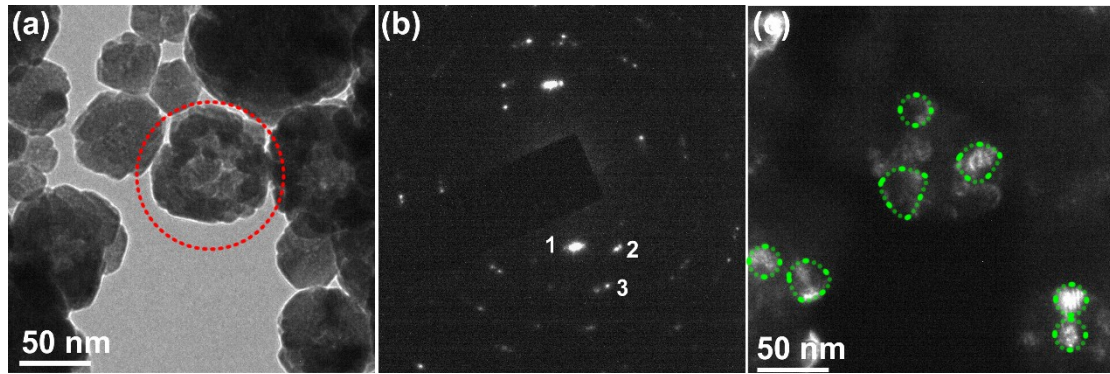


Figure S2 TEM micrographs of the as prepared $\text{Fe}_3\text{O}_4\text{-NH}_2$ particles: (a) bright field image; (b) SAED pattern of the particle marked with a ring in (a); (c) merged dark-field image corresponding to the spots marked with 1, 2 and 3 in (b).

Other Surface properties (adhesion strengths)

The adhesion strength between the coating and substrate plays a key role during the service lifetime of a bioactive layer coated metallic implant within the human body. A scratch test was used to identify the bond strengths of TiO_2 on CA and FT3. It consists of the generation of scratches using a spherical stylus (Rockwell C diamond) maintained at a constant speed over the surface under different loads. The critical load, L_c , was defined as the smallest load at which a recognizable failure occurred. It was determined from the loads versus SEM images. Three samples of each coating were used to obtain an average critical load. The critical load of CA is 32.2 ± 3.3 N (Figure S3(a)), and the incorporation of Fe_3O_4 NPs in TiO_2 coating does not obviously change their L_c values. The critical load is 30.2 ± 3.8 N for FT3 (Figure S3(b)). The amplified views of initial failures (insets in Figure S3) show that delaminations occurred in the interiors of TiO_2 layers, because Ca and P were always detected in the delaminations (EDX spectra in Figure S3). It indicates that all these TiO_2 coatings can strongly bind to Ti substrates.

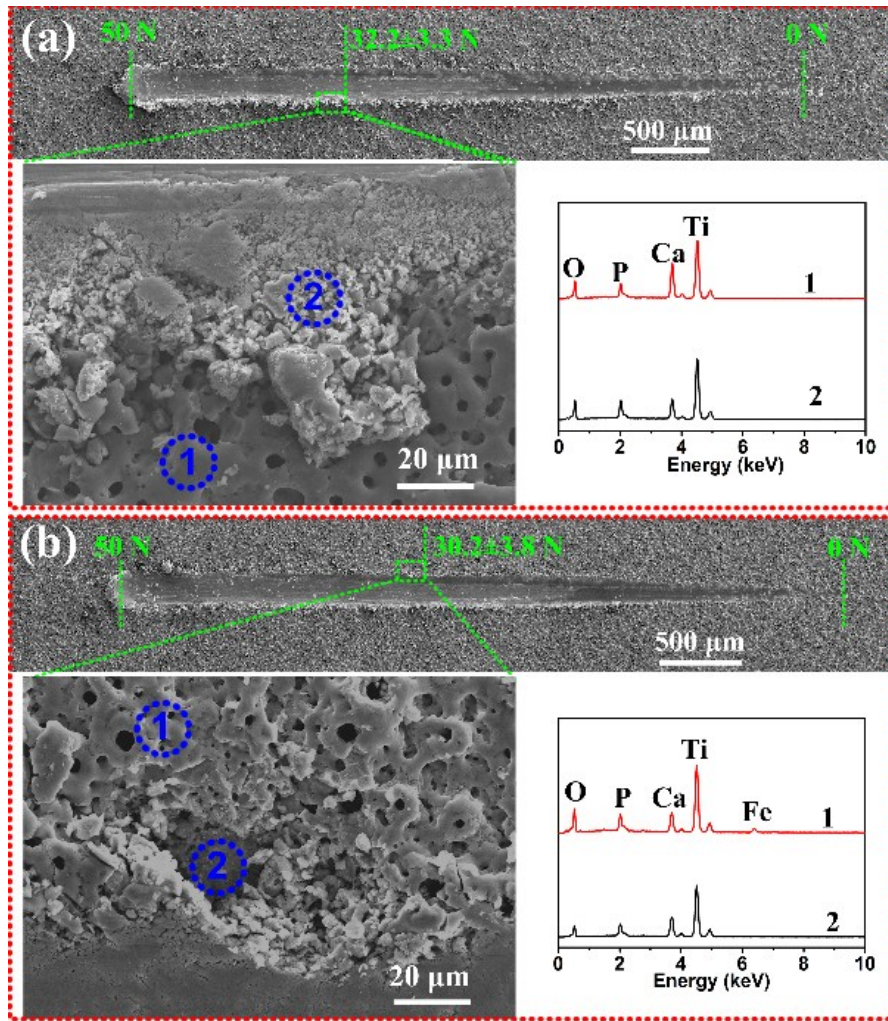


Figure S3 Scratch morphologies of different coatings, together with the amplified views of initial failure areas caused by *Lc*: (a) CA, (b) FT3; the EDX spectra in the inset in each of the amplified views were detected on the 1-marked surface and in the 2-marked delaminating region of the corresponding coating, respectively.

Other Surface properties (wettability and roughness)

The wettability of different surfaces was measured by a surface contact-angle measurement machine (DSA30, Kruss, Germany), then an image was captured and the contact angle between the droplet and the sample was measured by the analysis software (DSAI). Three samples from each group were measured and two measurements were performed on each surface to obtain an average.

The surface roughness measurements of the samples were performed laser scanning confocal microscope (LSCM; VK-9710, Keyence, Japan).

The wettability of implant surface plays an important role in cell adhesion. With the increased amount of Fe_3O_4 incorporated, the contact angle of water droplet slightly increases from 14.6° on CA to 21.0° on FT3 (Figure S4) and their roughness (Ra) are all about $2.5 \mu\text{m}$ (Laser scanning confocal images of CA and FT3 are examples in Figure S4), indicating that the incorporation of Fe_3O_4 did not change the wettability and topography of coatings obviously.

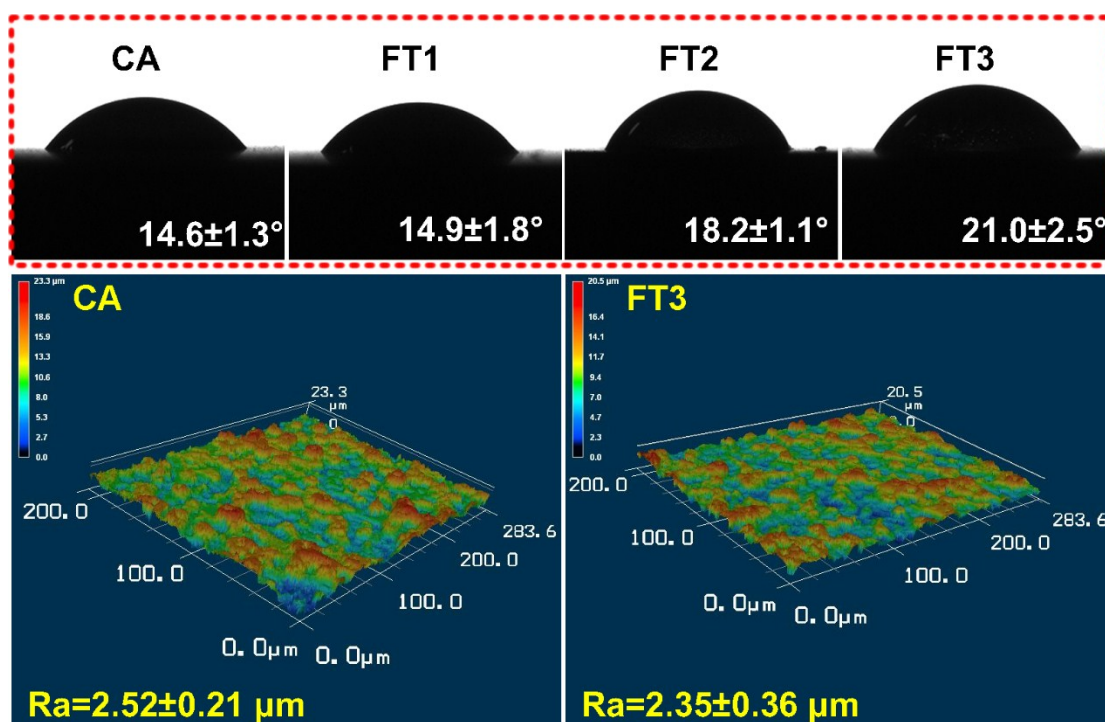


Figure S4 Contact angles and laser confocal images of different surfaces

Other Surface properties (ion release kinetics)

The specimens were immersed in 10 mL 0.9 wt% NaCl aqueous solution at 37°C for 0, 1, 3, 7, 14, and 28 days, successively. At the pre-determined time points, the leaching liquid was collected and the concentrations of Ca and Fe ions released were measured by inductively coupled plasma-

mass spectrometry (ICP-MS; Nu Instruments, Wrexham, UK). Meanwhile, the Ca and Fe ions concentrations in fresh NaCl aqueous solution were measured as the background. Three samples of each coating at each immersing time were measured to obtain an average value.

Ca and Fe released from the coatings after immersion for 1-28 days were evaluated. For each coating, Ca revealed a fast-releasing stage within the initial 7 d followed by a slow and steady release from 7 to 28 days (Figure S5). At each immersion time, there are no significantly statistic differences of accumulated concentrations of Ca released from coatings with and without Fe₃O₄. After immersion for 28 days, the accumulated concentrations of released Ca for different coatings are all about 12 ppm. The concentrations of Fe ions released from Fe₃O₄ incorporated coatings at each immersion time are below the detecting limit, indicating Fe ions were hardly released for the coatings during the immersion.

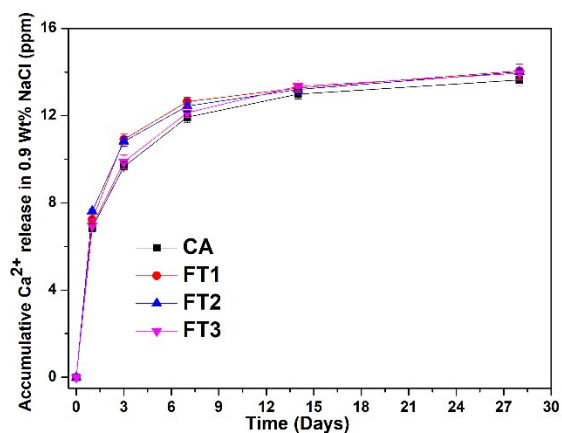


Figure S5 Ca²⁺ release kinetics of different coatings after immersion for different times.