Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B. This journal is © The Royal Society of Chemistry 2018

Intrinsically ferromagnetic Fe-doped TiO₂ coatings on titanium

for accelerating osteoblast response in vitro

Kai Li, Ting Yan, Yang Xue, Lijun Guo, Lan Zhang*, Yong Han**

State-key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University,

Xi'an 710049, China

1. EDS spectra and EDS mapping for different surfaces.



Figure S1 (a) EDS spectra of different coating surfaces; (b) the distributions of detected elements

(P, O, Ti, Ca and Fe) on Fe1, Fe2 and Fe3.

2. Figure S2 shows an enlarged view of XRD pattern in the 25-28 $^\circ\,$ of 20 for different coatings.

Table S1 presents the grain sizes, relative percentages and lattice parameters (a and c) of anatase

^{*} Corresponding author, e-mail: lan.zhang@mail.xjtu.edu.cn; Tel.:+86 13488463311; fax: +86 02982663453

^{**} Corresponding author, e-mail: yonghan@mail.xjtu.edu.cn; Tel.:+86 02982665580; fax: +86 02982663453

and rutile in different coatings. The grain sizes and lattice parameters from XRD data were calculated subsequently by whole pattern fitting, cell refining, and Rietveld refining using the analytical software Jade 6.0. The external standard method was carried out in order to quantify the relative percentage of anatase and rutile by using NIST SRM 676a α -Al₂O₃ as the external standard.



Figure S2 An enlarged view of XRD pattern in the 25-28 $^{\circ}$ of 2 θ for different coatings.

Table S1 Grain sizes, relative percentages and lattice parameters (a and c) of natase and rutile in different samples.

Samples	Phases	Relative	Grain size (+2 nm)	Lattice parameters (±0.01 Å)	
		percentage	,	a	c
CA	anatase	33.8	27.5	3.785	9.524
	rutile	66.2	54.6	4.592	2.955
Fe1	anatase	32.5	25.6	3.792	9.521
	rutile	67.5	47.8	4.570	2.954
Fe2	anatase	30.8	22.0	3.795	9.528
	rutile	69.2	45.4	4.587	2.952
Fe3	anatase	28.5	20.2	3.798	9.512
	rutile	71.5	43.6	4.590	2.951

3. The details of curve fitting procedure of XPS spectra.

The software XPSPeak 4.1 was used to do the curve fitting procedure of XPS spectra. The constraints and procedure used to perform the spectra are as follows. (1) Select the binding energy

range for background subtraction. (2) Select the Shirley method for the background subtraction. (3) Select Gaussian-Lorentzian (GL) ratio (initial number is 0) to determine peak shape. They are 50:50, 60:40, 80:20, for Ti2p, Fe2p and O1s, respectively. (4) Select peak number (initial number is 0). (5) Select full width at half maximum (FWHM) for the specific peaks, and the peaks with same binding energy have the same FWHM. (6) Select the best fitted curves for experimentally obtained Ti2p, Fe2p and O1s until the best chi squared was given. The curve fitting parameters, i.e. full width at half maximum, asymmetry factor, relative area ratios of peaks were automatically calculated by the software (XPSPeak 4.1)

Table S2. Percentage areas of the peaks in Fe 2p and O 1s spectra

Film		Fe 2p fitting (eV)	O 1s fitting (eV)			
	Fe-O i	in TiO ₂	FePO ₄			
	710.4 and 723.9	718.5 and 731.7	714.7 and 729.3	530.1	531.3	532.8
CA				49.3	44.0	6.7
Fe1	60.6	6.0	33.4	58.9	36.5	4.6
Fe2	60.7	6.0	33.3	88.9	8.5	2.6
Fe3	61.0	5.5	33.5	94.6	4.4	1.0

4. Adhesion strengths of different coatings.



Figure S3 Scratch morphologies of different coatings, together with the amplified views of the

areas of marked initial failure caused by Lc: (a) CA, (b) Fe1, (c) Fe2 and (d) Fe3; 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.

5. Estimated ratios of Ca and P leached from different coatings after 28 days of immersion.

After immersion for 28 days, the surface morphologies of the coatings were all examined by FESEM. No obvious changes of morphologies were observed compared with those before immersion, indicating that all the coatings are stable during the immersion. The contents of Ca detected on the immersed surface are all less than those before immersion, indicating the releasing of Ca during the immersion process, whereas, the contents of Fe are almost unchanged compared with those before immersion, indicating that Fe is hardly released from TiO₂ during the immersion. The surface microstructures of CA and Fe3 are shown in Figure S4 as examples. The amounts of Ca and Fe on different surfaces after 28 d immersion and their leaching percentages relative to the initial amount are shown in Table S3.

 Table S3 The relative amounts and leaching percentage of Ca and Fe on different samples after 28 d immersion.

		Ca	Fe		
Samples	Relative amount	Leaching percentage	Relative amount	Leaching percentage	
	(Wt%)	(%)	(Wt%)	(%)	
CA	8.54	18.2	/	/	
Fe1	8.25	17.5	2.25	0.8	
Fe2	7.80	18.5	4.64	0.2	
Fe3	7.49	17.8	10.98	0.3	



Figure S4 SEM surface morphologies of CA and Fe3 after immersion for 28 d, the inset tables

showing the corresponding EDS results.