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Supporting Information

Fe/Zn-modified tricalcium phosphate (TCP) biomaterials: preparation and biological properties

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1 characterization

1. Cell parameter

Table S1 Cell Parameters of Fe-TCP

Sample	a	b	c	Density (c)
β-TCP	10.429	10.429	37.38	3.12
Fe-TCP (2%)	10.429	10.429	37.38	3.12
Fe-TCP (5%)	10.3799	10.3799	37.234	3.159
Fe-TCP (10%)	10.3382	10.3382	37.125	3.1

Table 21 Cell Parameters of Zn-TCP

Sample	a	b	c	Density (c)
β-TCP	10.429	10.429	37.38	3.12
Zn-TCP (2%)	10.429	10.429	37.38	3.12
Zn-TCP (5%)	10.357	10.357	37.173	3.205
Zn-TCP (10%)	10.357	10.357	37.173	3.205

1. IR characterization

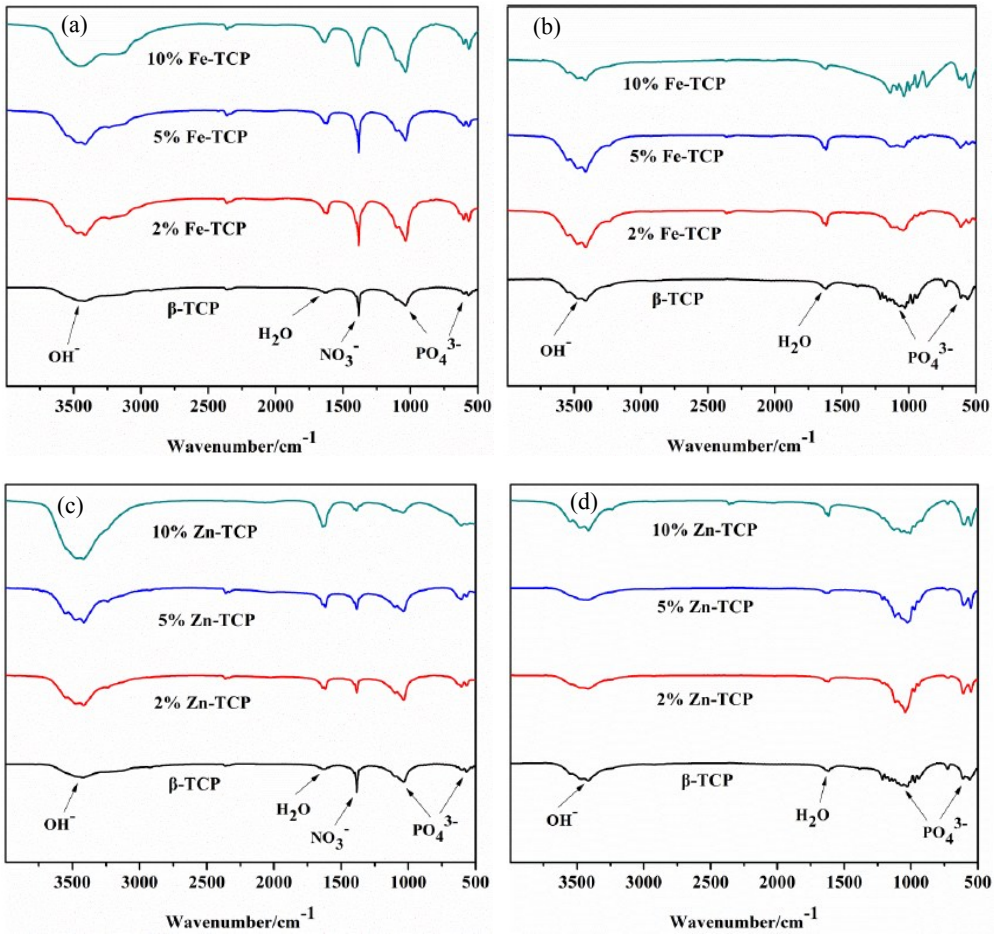

Figure S1. FT-IR spectrum of (a) Fe-TCP precursor; (b) Fe-TCP;
(c) Zn-TCP precursor; (d) Zn-TCP.

Characteristic peaks
PO_4^{3-}: 1030cm^{-1}, 600cm^{-1}
NO_3^-: 1380cm^{-1}
H_2O: 3400cm^{-1}, 1640cm^{-1}

The β-TCP and Fe-TCP have highly similar peak features since the IR characterization is sensitive to organic groups. The couple splitting of the P-O vibration peaks may be caused by the replacement of part Ca^{2+} by Fe^{3+} and the shrinking of the crystalline cell.

2. SEM

Interconnection micropores (400~600μm) can be clearly observed on all the three samples. When the Fe^{3+} content reached to 10%, the crystalline size increased and tended to accumulate together. When the Fe^{3+} content was 2% or 5%, there are micropores with 1μm dispersed in the structure. The crystalline size increased with the Fe^{3+} doping level increased, which may be caused by the deformation and shrinking of the crystalline cells due to the replacement of Ca^{2+} by Fe^{3+}. In this case, many crystals accumulated together forming larger crystals and the fuse point decreased after the agglomeration treatment.

The EDS results of Fe/Zn-TCP with 2%, 5%, and 10% content are illustrated as (d), (e), and (f) parts in Figure S2 and S3. The result that the replacement of Ca^{2+} by Fe^{3+} was confirmed by the EDS analysis combined with the XPS results (Figure 4. The mole ratio of Fe/(Ca+Fe) is higher than the theoretical

calculation, which may be explained by the emergence of vacancy defect to balance the charge due to the metal ion replacement in the crystalline cell. Under the high-resolution SEM, there are micropores of 1μm with irregular shape dispersed in the structure. The crystalline particles got larger with the increased content of the doped Fe^{3+}/Zn^{2+} ions.

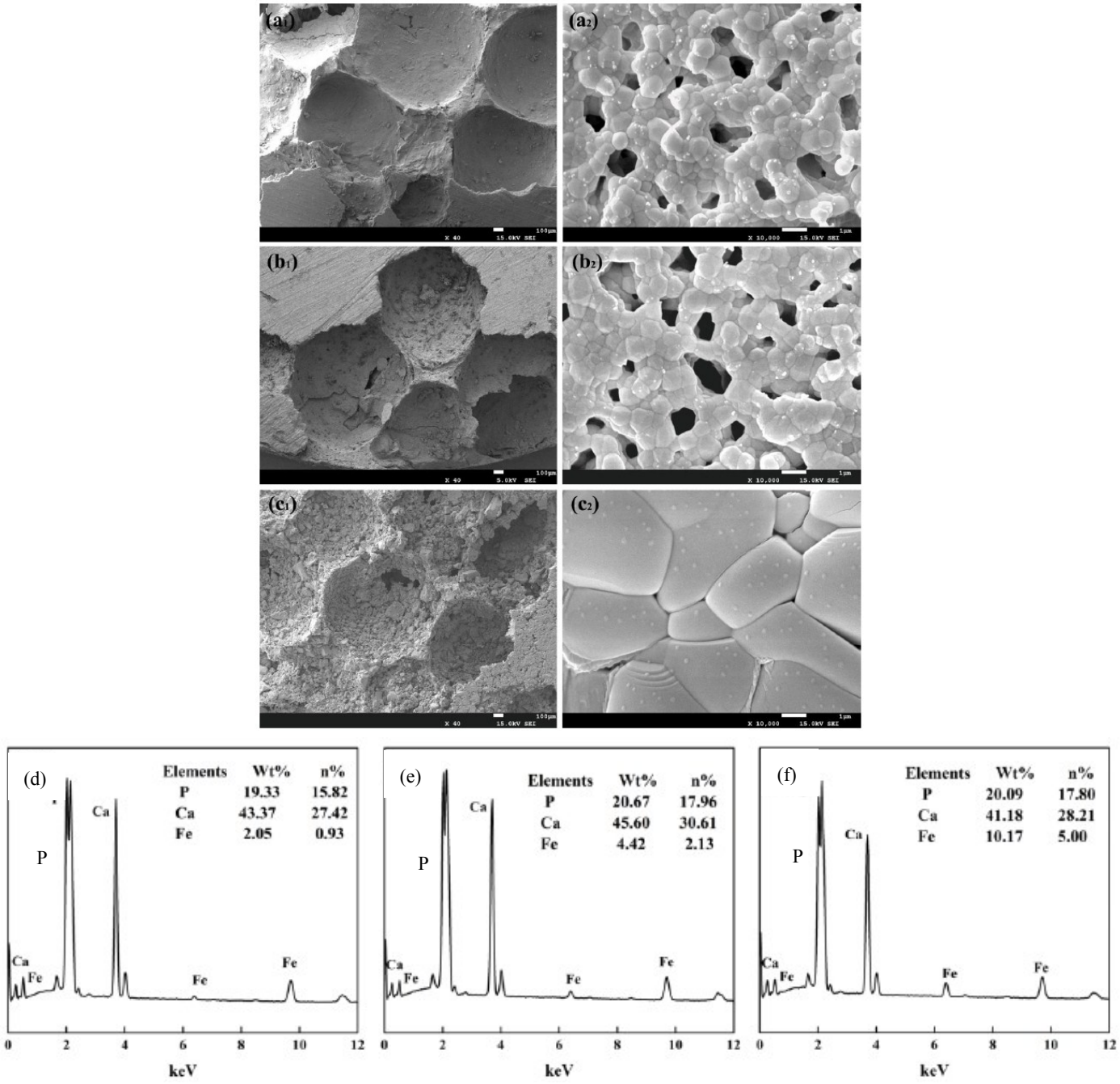

Figure S2. SEM images of Fe-TCP of (a1) (a2) 2%; (b1) (b2) 5%; (c1) (c2) 10%; EDS of Fe-TCP of (d) 2%; (e) 5%; (f) 10%.

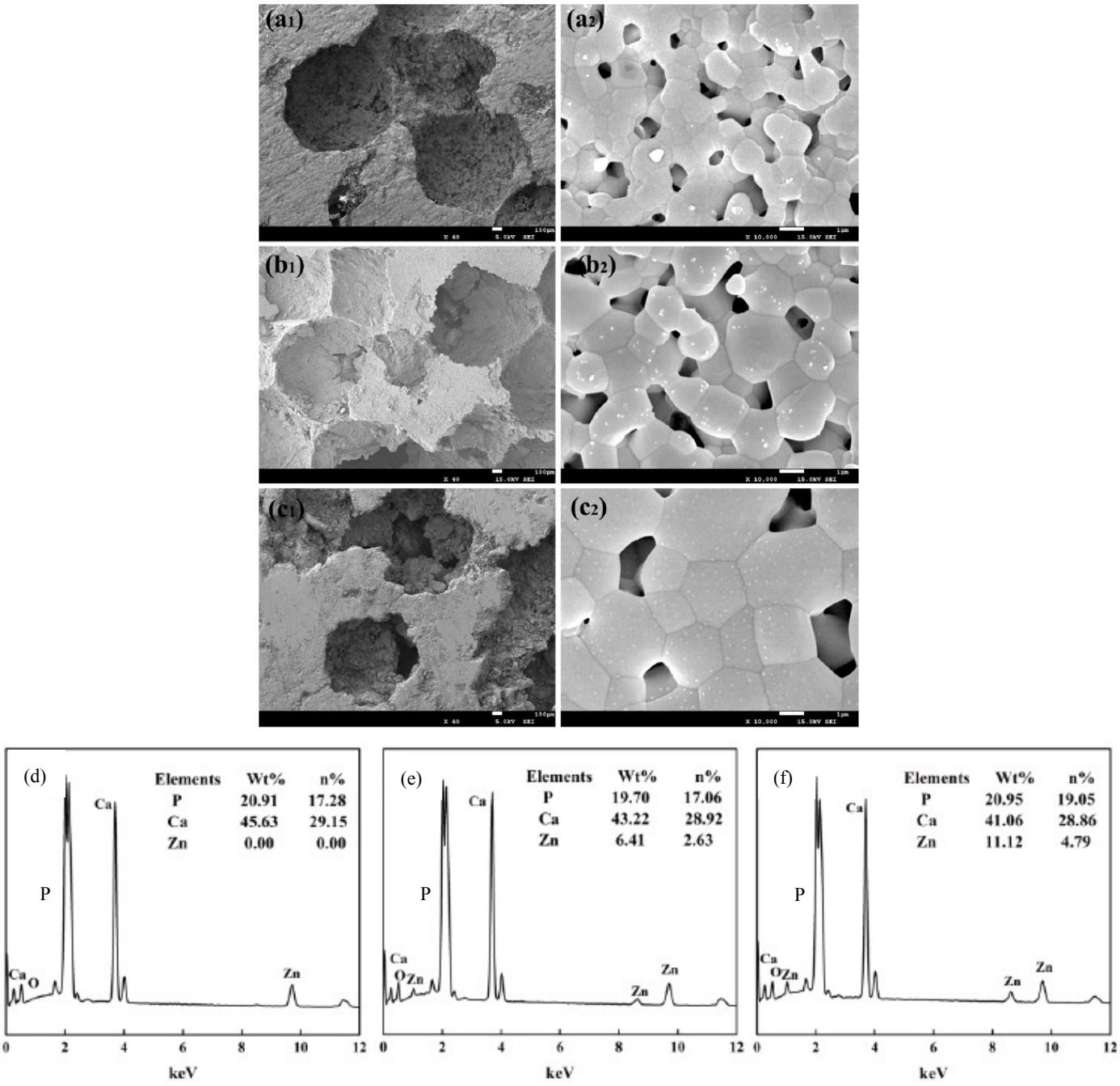

Figure S3. SEM images of Zn-TCP of (a1) (a2) 2%; (b1) (b2) 5%; (c1) (c2) 10%; EDS of Zn-TCP of (d) 2%; (e) 5%; (f) 10%.

3. TEM

The TEM images of the Fe/Zn-TCP materials are shown in Figure S4 and S5. The 2%, 5%, and 10% metal-content are indicated as (a), (b), and (c) for each kind of the metal-TCP sample, respectively. All the samples have tiny needle- or rod-like shape with the length of about 100 nm. It can be seen that the doping of Fe/Zn into the cell lattice has little influence on the microstructure and morphology of the TCP species.

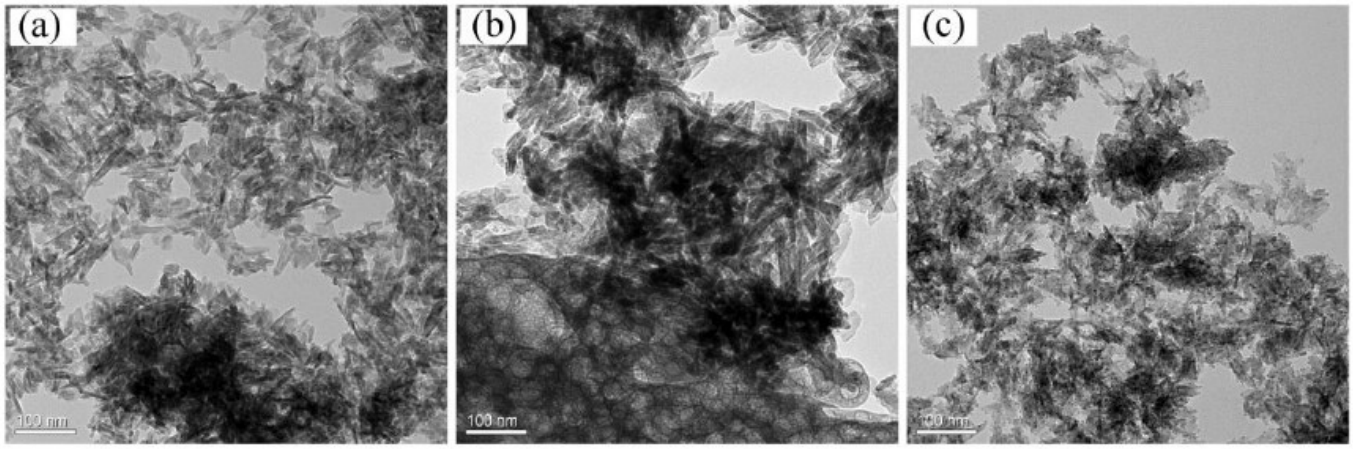

Figure S4. TEM images of Fe-TCP of (a) 2%; (b) 5%; (c) 10%.

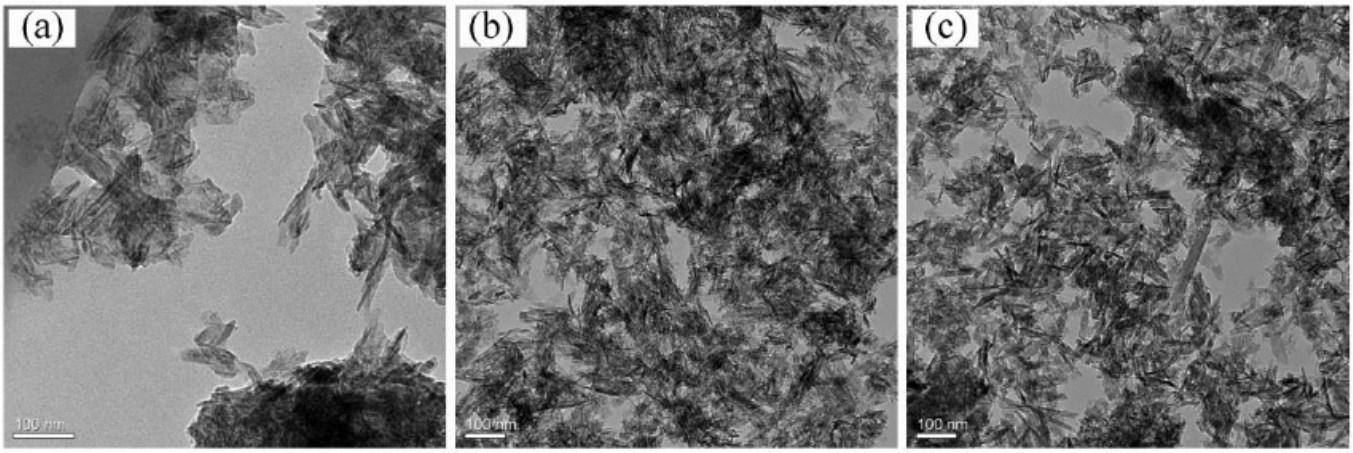

Figure S5. TEM images of Fe-TCP of (a) 2%; (b) 5%; (c) 10%.