Supporting information

Enhanced Biomineralization of Shape Memory Composite Scaffold from Citrate Functionalized Amorphous Calcium Phosphate for Bone Repair

Kun Luo¹, Li Wang^{1,2*}, Jiajing Tang³, Xiyang Zeng¹, Xiaohu Chen¹, Peicong Zhang¹, Shiyi Zhou¹, Junfeng Li¹, Yi Zuo³

¹ College of Materials, Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, P. R. China

² College of Chemistry, Sichuan University, Chengdu 610064, China

³ Research center for nano-biomaterials, Analytical & Testing Center, Sichuan University, Chengdu 610064, China

*Corresponding author, E-mail addresses: wangli18@cdut.edu.cn



Fig. S1. DTG curve of porous PUsCCACP scaffolds with different CCACP content.



Fig. S2. DTA curve of porous PUsCCACP scaffolds with different CCACP content.



Fig. S3. DSC thermograms of 2nd heating run for PUsCCACP scaffolds.

 Table. S1 The parameter of crystal structure and thermal for scaffolds with varied CCACP content.

| Sample | ^a Xc (%) | ^a Lc (nm) | <i>^bT</i> m (°C) | $\Delta H m (J \cdot g^{-1})$ | <i>T</i> c (°C) | $\Delta Hc (J \cdot g^{-1})$ |
|------------|---------------------|----------------------|-----------------------------|-------------------------------|-----------------|------------------------------|
| PUsCCACP0 | 53.22% | 6.27 | 42.05 | 67.87 | 11.1 | 46.52 |
| PUsCCACP10 | 50.19% | 6.22 | 40.76 | 62.03 | 17.91 | 47.21 |
| PUsCCACP20 | 47.00% | 6.20 | 39.55 | 51.11 | 18.12 | 42.27 |
| PUsCCACP30 | 43.13% | 3.71 | 39.19 | 22.59 | 21.83 | 17.21 |
| PUsCCACP40 | 40.50% | 1.31 | 40.19 | 31.66 | 22.34 | 22.86 |

 ${}^{a}X_{c}$ and L_{c} represent crystallinity and crystallites size of scaffolds which determined by the results of X-ray diffractometer.

^b Thermodynamic parameters were determined from the second cycle.



Fig. S4. Bar chart with compressive strength for PUsCCACP scaffold with various CCACP content at stain of 60% (n=5).



Fig. S5. SEM images of PUsCCACP scaffolds with various CCACP content

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|------------------|---|--|--|
| "Porosity (% | Density (g/cm3 | ^b Stress | Modulus |
|) |) | (Mpa) | (Mpa) |
| 81.83±0.73 | 0.19±0.01 | 1.22 ± 0.14 | 20.16 ± 4.36 |
| 77.88 ± 1.07 | 0.26 ± 0.02 | 3.52 ± 0.16 | 99.33 ± 17.56 |
| 70.77 ± 1.77 | 0.38 ± 0.03 | 5.37 ± 0.42 | 123.33 ± 10.74 |
| 69.27±2.23 | 0.40 ± 0.02 | 6.57 ± 0.26 | 148.40 ± 8.08 |
| | * Porosity (%) 81.83±0.73 77.88±1.07 70.77±1.77 69.27±2.23 | aPorosity (% Density (g/cm3) 3) 81.83±0.73 0.19±0.01 77.88±1.07 0.26±0.02 70.77±1.77 0.38±0.03 69.27±2.23 0.40±0.02 | aPorosity (% Density (g/cm3) bStress)) (Mpa) 81.83±0.73 0.19±0.01 1.22±0.14 77.88±1.07 0.26±0.02 3.52±0.16 70.77±1.77 0.38±0.03 5.37±0.42 69.27±2.23 0.40±0.02 6.57±0.26 |

Table. S2 Physical and mechanical properties of scaffolds with different CCACP

^a Essential parameter of scaffolds were evaluated by ceramic bulk density tester which based on the Archimedes principle.

^b Mechanical date were determined by tensile testing of independent sample (n = 3).



Fig. S6. Visual demonstration of shape-memory for PUsCCACP scaffolds with different CCACP content at 40 °C.

 Table. S3. The shape fixed rate and shape recovered rate of PUsCCACP scaffolds with different CCACP content.

| Sample | ^a <i>R</i> _f (%) | ^a R _r (%) |
|------------|--|--|
| PUsCCACP0 | 97.41 ± 0.93 | 97.63 ± 1.02 |
| PUsCCACP10 | 97.04 ± 0.29 | 98.19 ± 1.09 |
| PUsCCACP20 | 98.15 ± 0.46 | 98.11 ± 0.74 |
| PUsCCACP30 | 97.04 ± 0.55 | 97.07 ± 1.00 |
| PUsCCACP40 | 96.59 ± 0.28 | 97.96 ± 0.76 |

^a Determined from the shape recovery bending test.



Fig. S7. SEM micrographs and EDS mapping for PUsCCACP scaffolds prior to SBF immersion (scale bar: 10 μm).



Fig. S8. SEM images of porous PUsCCACP scaffolds with different CCACP content soaking in SBF.

 Table. S4. Mass remnant (%) and CCACP remnant (%) of scaffolds with different CCACP content.

| Sample | ^a Mass loss (%) | ^b Mass remnant (%) | CCACP remanant (%) | | | |
|------------|----------------------------|-------------------------------|---------------------------|--|--|--|
| PUsCCACP0 | 4.05 ± 0.23 | 95.95 ± 0.23 | | | | |
| PUsCCACP10 | 10.28 ± 0.29 | 89.72 ± 0.29 | 3.77 ± 0.29 | | | |
| PUsCCACP20 | 13.40 ± 0.58 | 86.60 ± 0.58 | 10.66 ± 0.58 | | | |
| PUsCCACP30 | 18.39 ± 0.47 | 81.61 ± 0.47 | 15.66 ± 0.47 | | | |
| PUsCCACP40 | 20.34 ± 0.45 | 79.66 ± 0.45 | 23.71 ± 0.45 | | | |

^a Mass loss was confirmed by the in vitro degradation test.

^b Mass remnant was calculated by the following formula:

Mass remnant (%) = $(1-^{a}Mass loss) \times 100$ %

^c CCACP remnant was calculated by the following formula:

CCACP remnant (%) = [Original CCACP content - (aMass loss – pure scaffold mass loss)] \times 100 %

Note: Pure scaffold mass loss was set as 4.05 % which was the mass loss of PUsCCACP0 scaffold.



Fig. S9. The adhesion behaviors of MG63 cells after culturing on PUsCCACP scaffolds with different CCACP content.

Video S1. Bending recovery experiments of PUsCCACP20.Video S2. Compression recovery experiments of PUsCCACP20.Video S3. PUsCCACP20 scaffold was recovered at 37 °C in water bath.