Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Nanoparticles in β-tricalcium phosphate substrate enhance modulation of structure and composition of octacalcium phosphate grown layer

Kazuo Onuma* and Mayumi Iijima

National Institute of Advanced Industrial Science and Technology

Central 6, 1-1-1 Higashi, Ibaragi 305-8566, Japan

*Corresponding author (k.onuma@aist.go.jp)

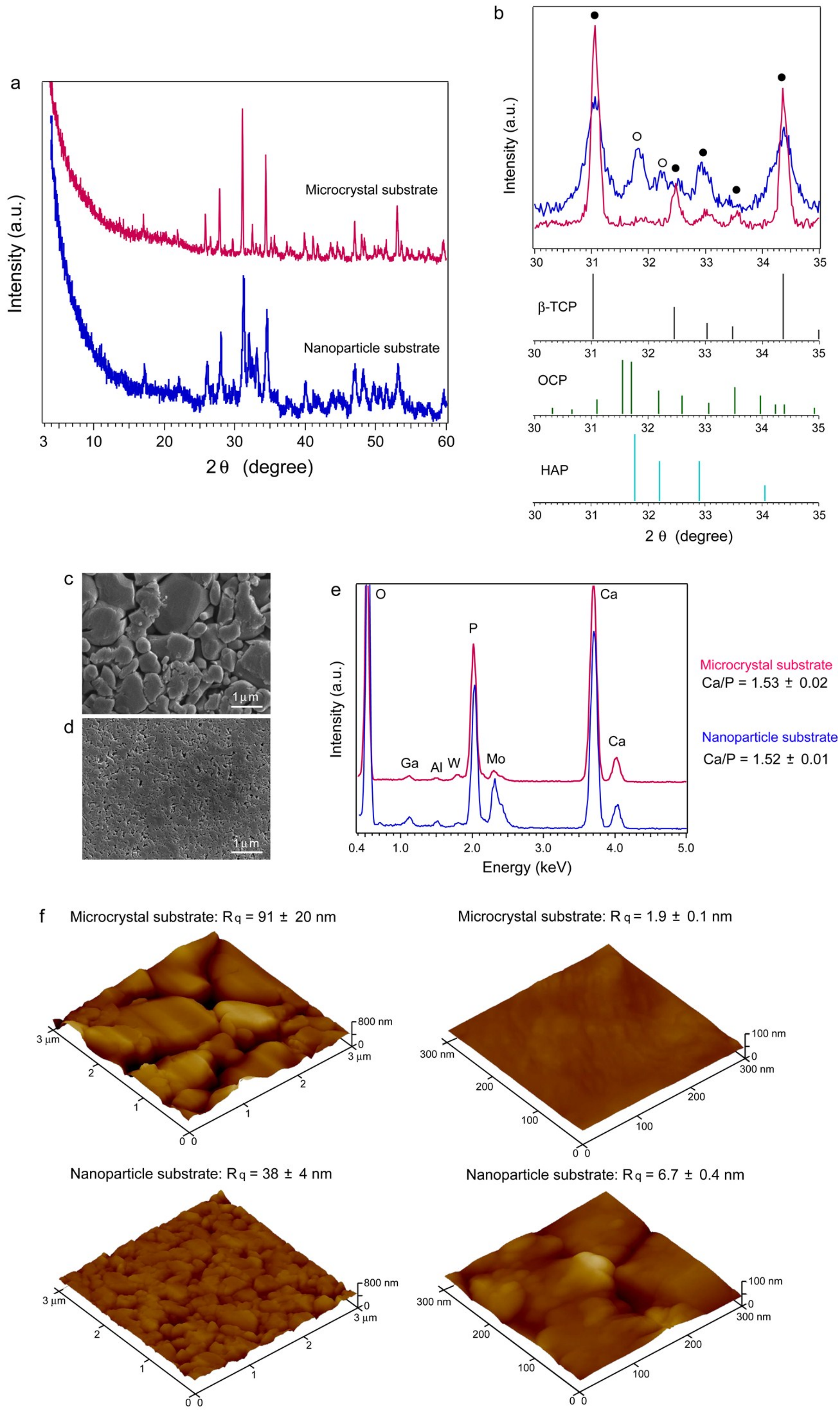

a
Microcrystal substrate
Nanoparticle substrate
Intensity (a.u.)
2θ (degree)
b
Intensity (a.u.)
β-TCP
OCP
HAP
2 θ (degree)
c
1μm
d
1μm
e
O
P
Ca
Ga
Al
W
Mo
Ca
Intensity (a.u.)
Energy (keV)
Microcrystal substrate
Ca/P = 1.53 ± 0.02
Nanoparticle substrate
Ca/P = 1.52 ± 0.01
f
Microcrystal substrate: Rq = 91 ± 20 nm
Microcrystal substrate: Rq = 1.9 ± 0.1 nm
Nanoparticle substrate: Rq = 38 ± 4 nm
Nanoparticle substrate: Rq = 6.7 ± 0.4 nm
800 nm
3 μm
300 nm
100 nm

Fig. S1 Characterizations of β-TCP microcrystal and nanoparticle substrates before immersion in solution. (a) XRD patterns of microcrystal (magenta) and nanoparticle (blue) substrates at wide 2θ range. Relatively broad peak-width in nanoparticle substrate is attributed to smaller crystallites of particles than those in microcrystal substrate. (b) XRD patterns of microcrystal (magenta) and nanoparticle (blue) substrates at 2θ = 30–35°. Open circles correspond to peaks of β-TCP and closed circles in nanoparticle substrate correspond to OCP or HAP. Ideal XRD patterns of β-TCP (black), OCP (green), and HAP (light blue) were presented as reference. Surface SEM images of (c) microcrystal and (d) nanoparticle substrates. (e) STEM-EDS spectrum measured for FIB-prepared microcrystal (magenta curve) and nanoparticle (blue curve) substrates. Mo is attributed to TEM grid mesh. Ga and W were present in ion source and sample cup. Al is attributed to equipment-specific factors. (f) AFM images of substrate surfaces and average RMS roughness (R_q value) at 3 μm square (left) and 300 nm square (right).

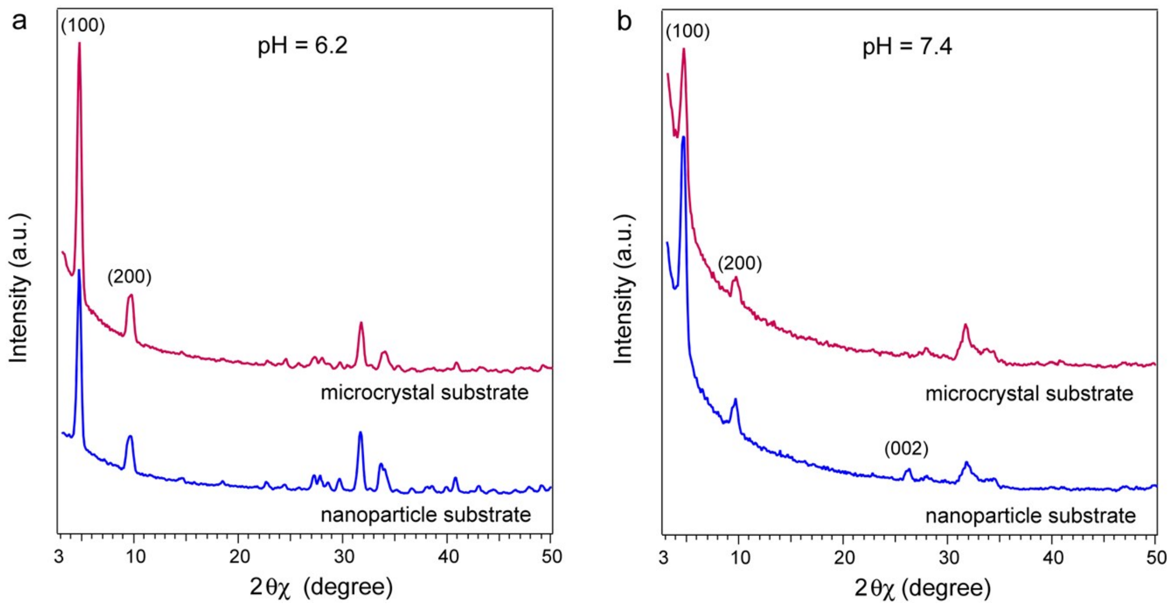


Fig. S2 Thin-film XRD measurement of grown materials depending on solution pH and substrate particle size after 20-h immersion. (a) XRD patterns of materials grown on microcrystal (magenta) and nanoparticle (blue) substrates at pH of 6.2. (b) XRD patterns of materials grown on microcrystal (magenta) and nanoparticle (blue) substrates at pH of 7.4.

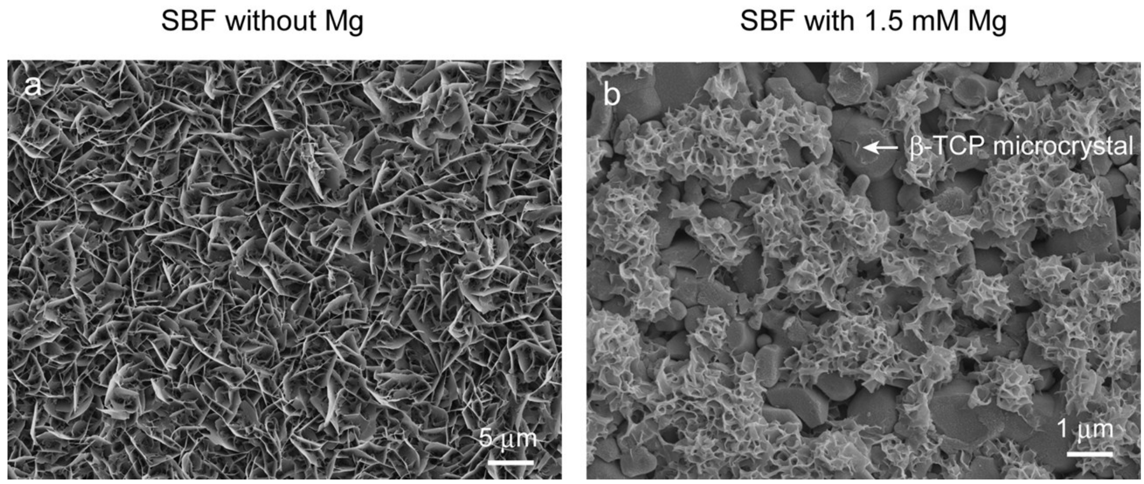


Fig. S3 Grown materials on β-TCP microcrystal substrate after 20-h immersion in SBF without and with Mg. (a) Without Mg. OCP plates grew on substrate. (b) With 1.5-mM Mg. Fewer agglomerates with smaller plates grew on substrate.

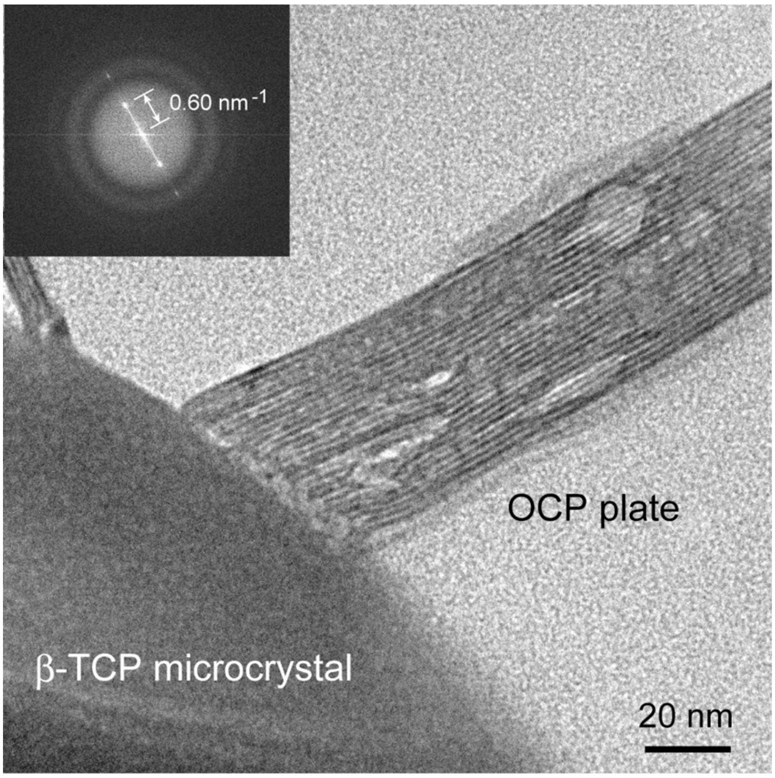


Fig. S4 HR-TEM image of area around interface between OCP plate and β-TCP microcrystal in initial growth stage. Lattice fringes parallel to elongated direction of plate were directly connected to surface of microcrystal. This fringe pattern is typical of OCP crystal and corresponds to [100]. FFT image of plate (superimposed at upper left) shows that average spacing of lattice fringe was 1.67 nm.

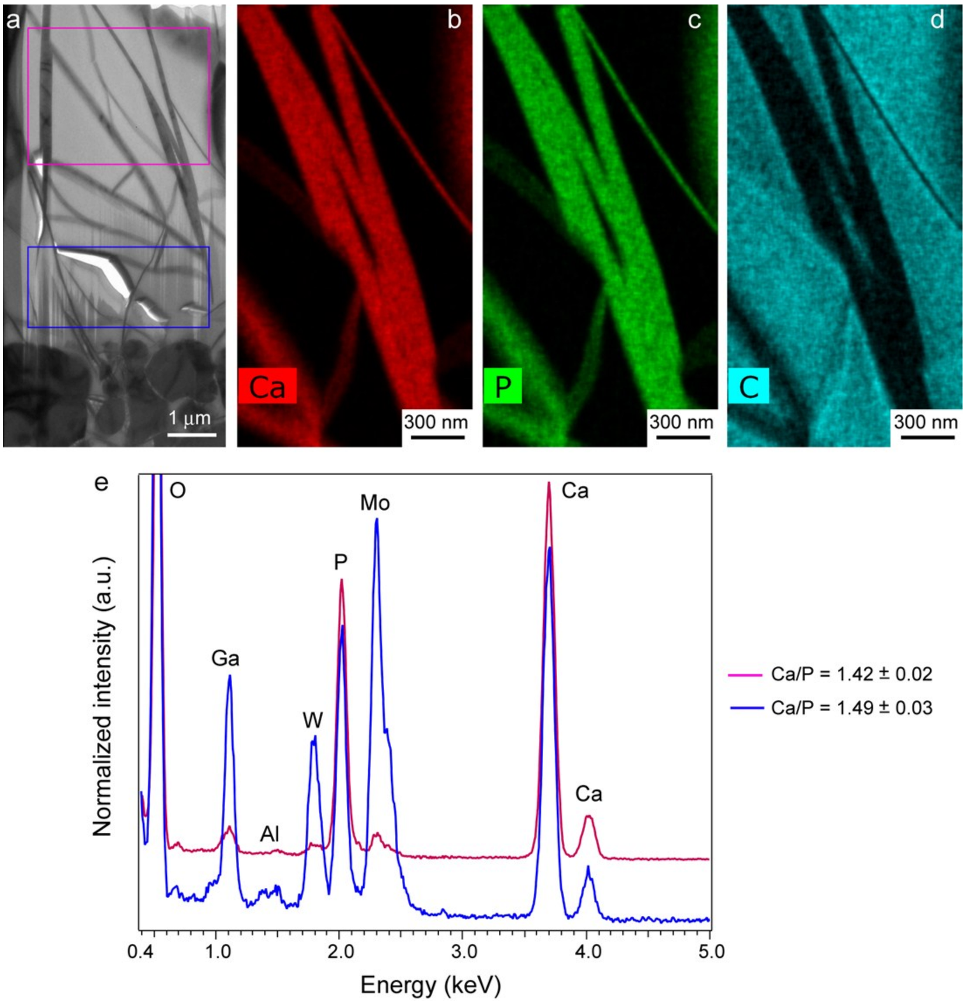
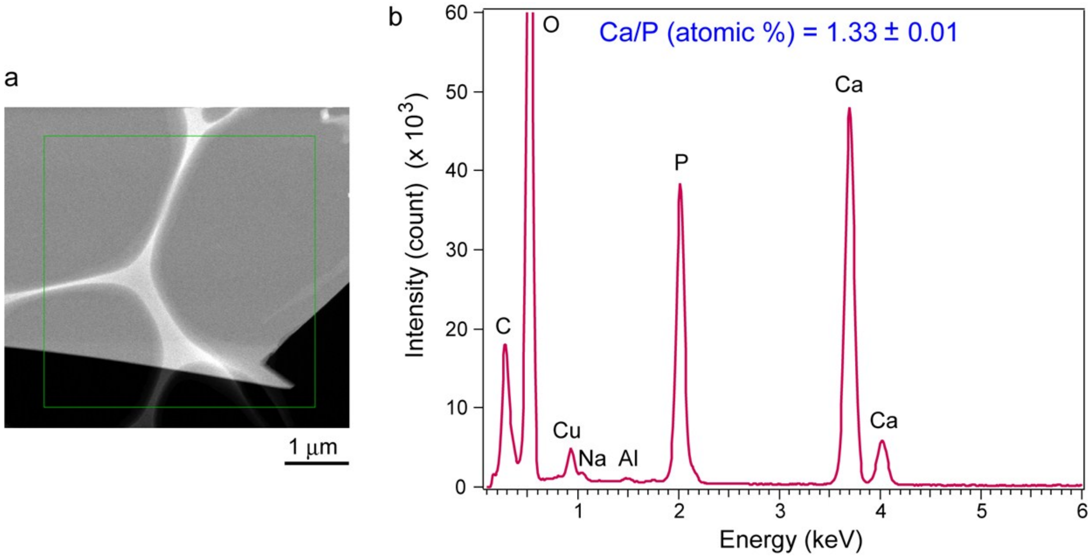


Fig. S5 STEM-EDS analysis of grown materials on β-TCP microcrystal substrate. (a) Low-magnification TEM image using sample prepared using FIB technique. Magenta and blue rectangles correspond to measured areas. Elemental mappings of (b) calcium, (c) phosphate, and (d) carbon. (e) STEM-EDS spectrum of late growth stage (magenta curve corresponds to magenta rectangular area in (a)) and initial growth stage (blue curve corresponds to blue rectangular area). Mo is attributed to TEM grid mesh. Ga and W were present in ion source and sample cup, and were re-deposited in void areas during sample preparation. Al is attributed to equipment-specific factors.



c

Crystal No.	Ca/P atomic % ratio (±0.01)
1	1.33
2	1.38
3	1.37
4	1.33
5	1.35
Average	Ca/P (atomic %) = 1.35 ± 0.02

Fig. S6 STEM-EDS analysis for OCP crystals at ~70 µm from grown layer-substrate interface.

(a) Low-magnification TEM (STEM-HAADF mode) image of OCP crystal. Green rectangle indicates measured area. (b) STEM-EDS spectrum. Ca/P atomic % ratio was 1.33±0.01. (c) Table showing measured Ca/P ratios for different five OCP crystals. Average Ca/P ratio and its standard deviation was 1.35±0.02.

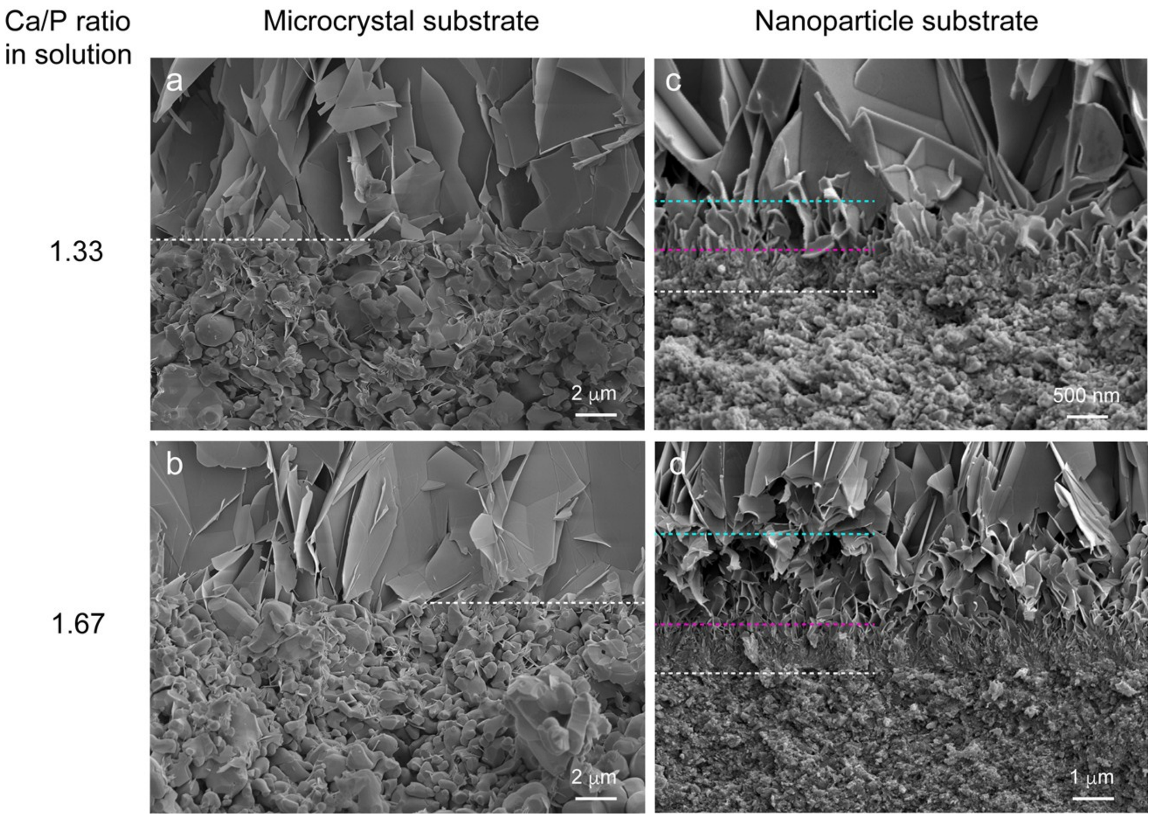


Fig. S7 Cross-sectional SEM images after 20-h immersion at pH of 6.2 depending of Ca/P molar ratio in solution and substrate particle size. (a) OCP layer grown on microcrystal substrate in solution at Ca/P = 1.33. White dotted line indicates boundary between substrate and grown layer. (b) OCP layer grown on microcrystal substrate in solution at Ca/P = 1.67. (c) OCP layer grown on nanoparticle substrate in solution at Ca/P = 1.33. White dotted, magenta dotted, and blue dotted lines indicate boundary between substrate and bush-like region, bush-like and irregularly shaped plate regions, and irregularly shaped plate and polyhedral plate regions, respectively. (d) OCP layer grown on nanoparticle substrate in solution at Ca/P = 1.67.

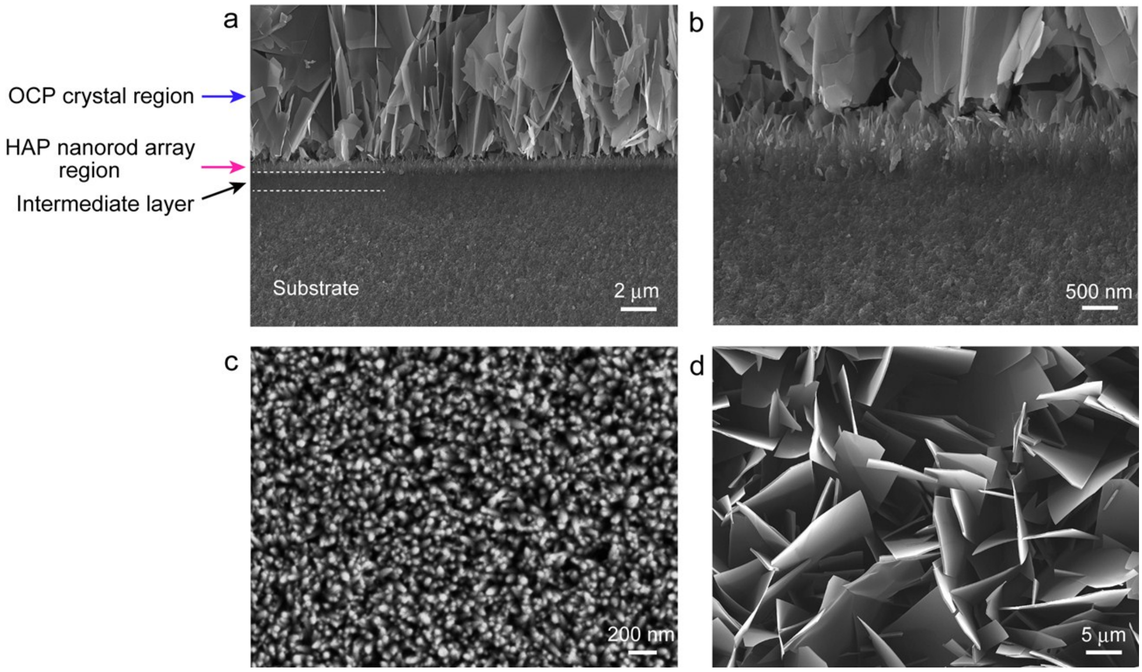


Fig. S8 Cross-sectional and surface SEM images after immersion of ACP substrate in calcium phosphate solution at pH of 6.2. (a) Cross-sectional SEM image of ACP substrate after immersion. Substrate was first immersed to solution with 3.96 mM Ca^{2+}, 3.94 mM PO_4^{3-}, and 0.526 mM (10 ppm) F^- for 30 min, and then immersed in the same solution without F^- for ~20 h. (b) Magnified image of (a). (c) Surface image after 30 min. HAP nanorod array had formed on surface. This sample differs from that in (a), (b), and (d). (d) Surface image after ~20 h. Surface is covered with OCP plates.