Experimental details

1. Materials and General procedure for the synthesis of precursors

1,3,5-tris(4-aminophenyl)-benzene (TAPB) was purchased from J&K Scientific. 2,5-dioctyloxyterephthalaldehyde (OTPA) was purchased Changchun Third Party Pharmaceutical Technology Co., Ltd. 2,5-dihydroxyterephthalaldehyde was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. N,N-dimethylformamide (DMF) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ethyl 4-bromobutyrate was purchased from Tianjin Heowns OPDE Technologies, LLC. Methanol, NaOH and K_2CO_3 were purchased from Tianjin JiangTian Chemical Technology Co., Ltd. SiO_2/Si were purchased from China Electronics Technology Co., Ltd. The synthesis of the precursors 4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyric acid (FPBA) were carried out referring to reported procedure.[1,2]

1.1 Synthesis of diethyl-4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyrate.

A mixture of 2,5-dihydroxyterephthalaldehyde (200 mg, 1.2 mmol), N,N-dimethylformamide (DMF, 40 ml), ethyl 4-bromobutyrate (0.936 g, 4.8 mmol) and K_2CO_3 (0.664 g, 4.8 mmol) was heated at 75 ℃ for 12 h. Afterwards, the resulting solution was extracted 3 times with dichloromethane. What's more, the residue was purified by silica gel column chromatography, where petroleumether-ethyl acetate (5:1) is used as the eluent, and finally the yellow product can be obtained. (310.9 mg, 65.7%).^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 2H), 7.43 (s, 2H), 4.25 – 4.01 (m, 8H), 2.53 (t, J = 7.2 Hz, 4H), 2.29 – 2.05 (m, 4H), 1.26 (t, J = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.58, 173.06, 154.92, 129.40, 112.40, 68.60, 60.34, 30.66, 24.50, 14.55.

1.2 Synthesis of 4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyric acid.

Methanol (30 mL), water (6 mL), NaOH (0.096 g, 2.4 mmol) and diethyl-4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyrate (0.1183 g, 0.3 mmol) were added in a round bottom flask. Then the mixture was heated up to 50 ℃ for 12 h. After the completion of the reaction, the methanol solvent was removed by rotary evaporation and cooled to room temperature. Then, the solution was acidified to pH=1 using HCl (6 M). The resulting solid was collected by suction filtration, washed with water, and dried in vacuum. (0.0891 g, 87.9%). ^{1}H NMR (400 MHz, DMSO) δ 12.22 (s, 2H), 10.46 (s, 2H), 7.48 (s, 2H), 4.23 (t, *J* = 6.2 Hz, 4H), 2.50 (t, *J* = 7.2 Hz, 4H), 2.17 – 1.91 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 189.62, 174.64, 154.94, 129.40, 112.38, 68.73, 30.77, 24.57.

2. Synthesis of two-dimensional polymers

The two-dimensional polymer (2DP) films with density of carboxyl groups were prepared at the air-water interface via LB method. Stock solutions of OTPA and FPBA were prepared in DMF at concentrations of 2.6×10^{-6} mol/L and 3.0×10^{-6} mol/L, respectively. And the concentration of TAPB in chloroform is 2.8×10^{-6} mol/L. Then the mixture of TAPB, FPBA and OTPA (The specific volume is shown in Table.S1.) were added dropwise to the water subphase surface with a micro-syringe. Wait for 30 minutes to allow the solvent to evaporate, and then compressed to a surface pressure of 3 mN/m at a rate of 0.05 mm/s. Afterwards, 350 μL of acetic acid as a catalyst was gently added. The mixture was left to react for 12 h at room temperature. After the completion of the reaction, a continuous thin film was formed at the water−air interface, and the single layer 2DPs was horizontally or vertically transferred onto substrates with a rate of 0.02 mm/s.

Table.S1. The specific composition of the mixture in the synthesis of 2DPs.

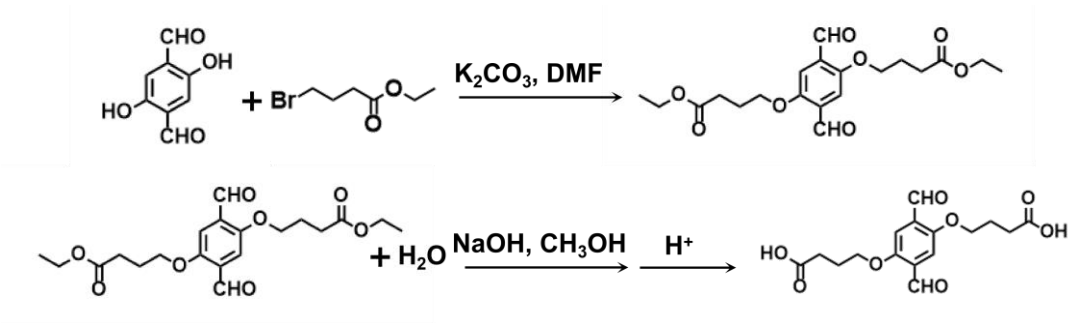
	V_{TAPB}/μL	V_{FPBA}/μL	V_{OTPA}/μL
$2DP_{TAPB+FPBA}$	49.2	70.8	/
2DP-75%	36.0	39.0	15.0
2DP-50%	27.4	19.8	22.8
2DP-25%	30.7	11.0	38.3
2DP-0%	22.5	/	37.5

3. Mineralization

A 1:1 mixture of 2.5×10^{-3} mol/L $Ca(NO_3) \cdot 4H_2O$ and 1.5×10^{-3} mol/L $(NH_4)_2HPO_4$ solution was used as the mineralization solution. The mineralization was carried out in centrifuge tubes with the 2DPs on SiO_2/Si horizontally fixed on the bottom of the tubes, and immersed in an oil bath at 37°C.

4. Characterization

NMR spectra were recorded with a 400-MHz spectrometer for ^{1}H NMR and a 101-MHz instrument for ^{13}C NMR using TMS as an internal standard. Chemical shifts (δ) are reported relative to TMS (^{1}H NMR), $CDCl_3$ or DMSO-d6 (^{13}C NMR). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). AFM images were performed with the Bruker Dimension Icon AFM instrument, using tapping mode. Attenuated Total Reflectance FTIR (ATR-FTIR) spectra of 2DP films and precursors were conducted using the Bruker vertex 70. Raman spectra of samples were taken by Thermo Fisher Scientific DER2Xi. X-ray photoelectron spectroscopy (XPS) were carried out with a Thermo Fisher Scientific ESCALAB 250Xi. Hitachi SEM SU8010 field emission scanning electron microscope (FESEM) was used to characterize the morphology and section profile of the mineralized hydroxyapatite. Cross sectional SEM images at 20~30 randomly chosen points on the surface were collected. The data were presented with an average values and its standard deviation, shown as mean ± S.D.



Scheme S1. Synthetic routes of the precursor FPBA.

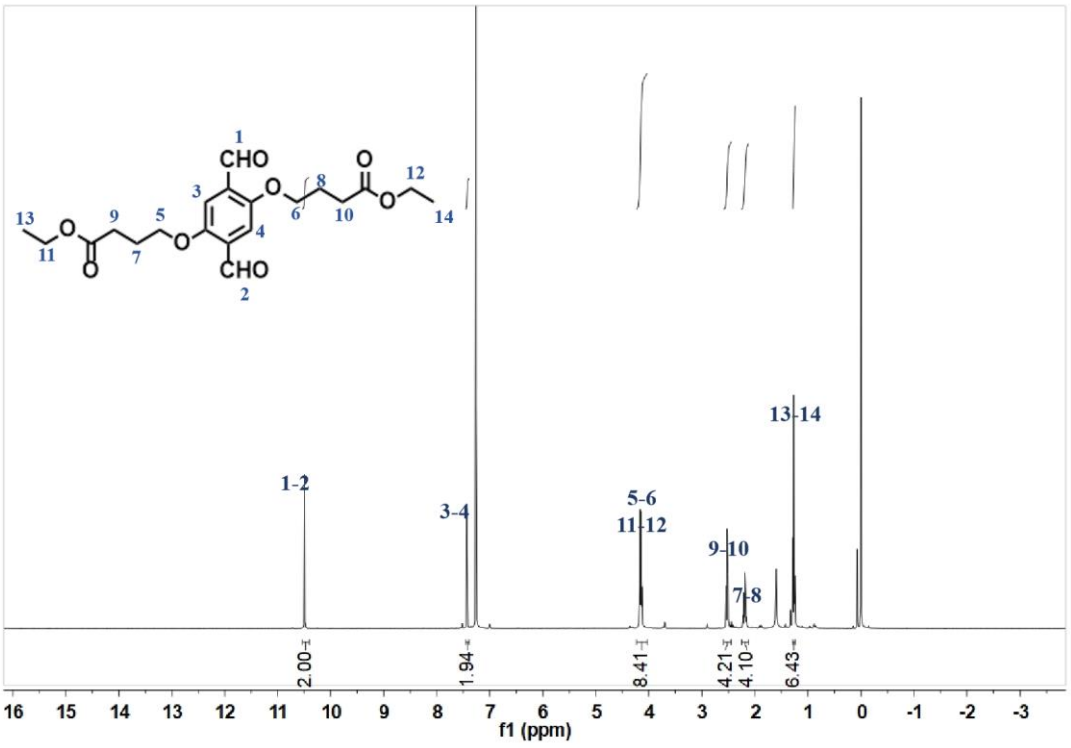


Fig. S1. ^{1}H NMR spectrum of diethyl-4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyrate in $CDCl_3$.

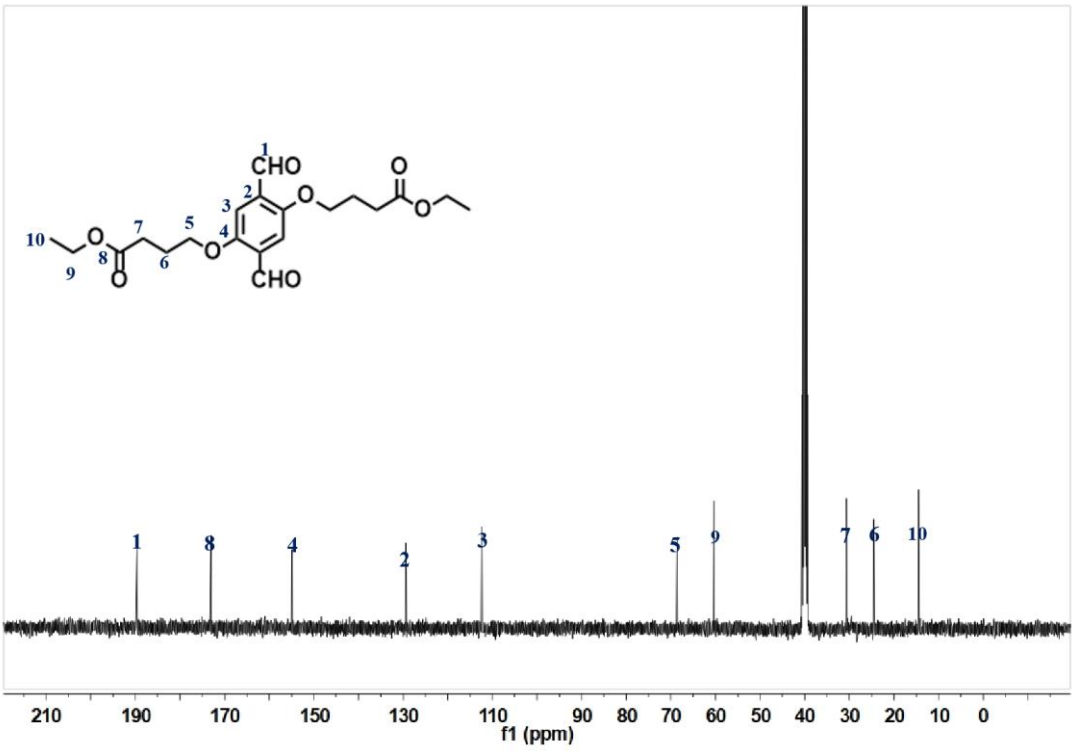


Fig. S2. ^{13}C NMR spectrum of diethyl-4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyrate in $CDCl_3$.

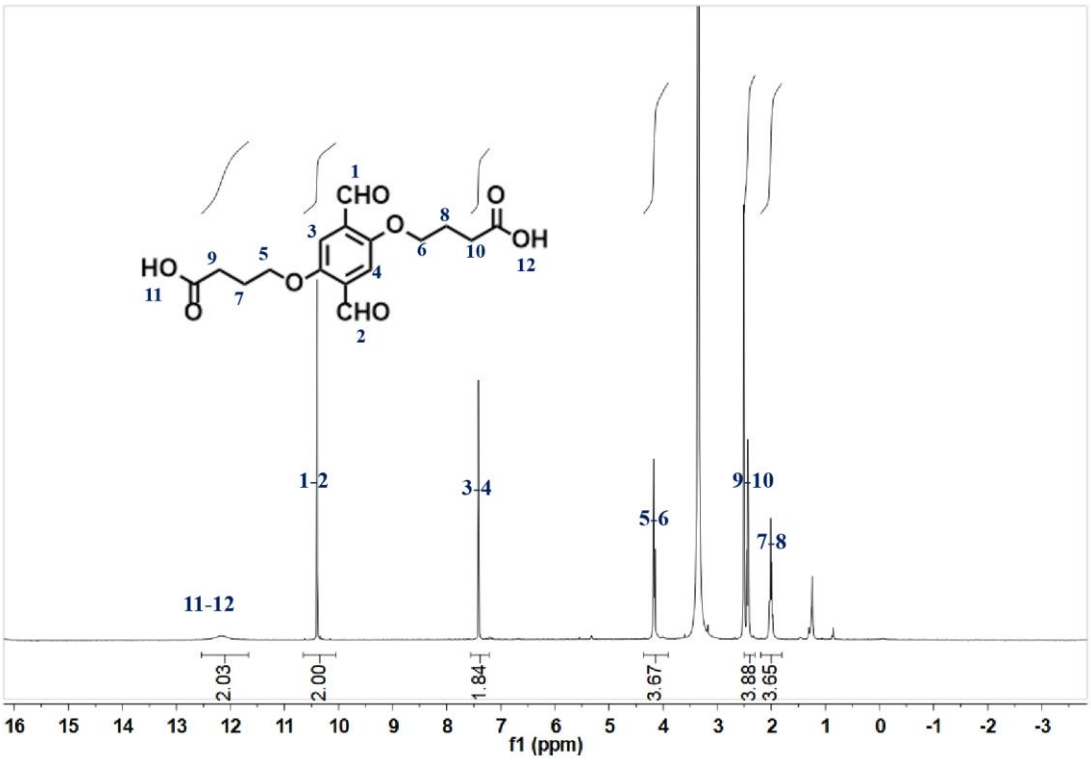


Fig. S3. [1]H NMR spectrum of 4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyric acid (FPBA) in DMSO-d6.

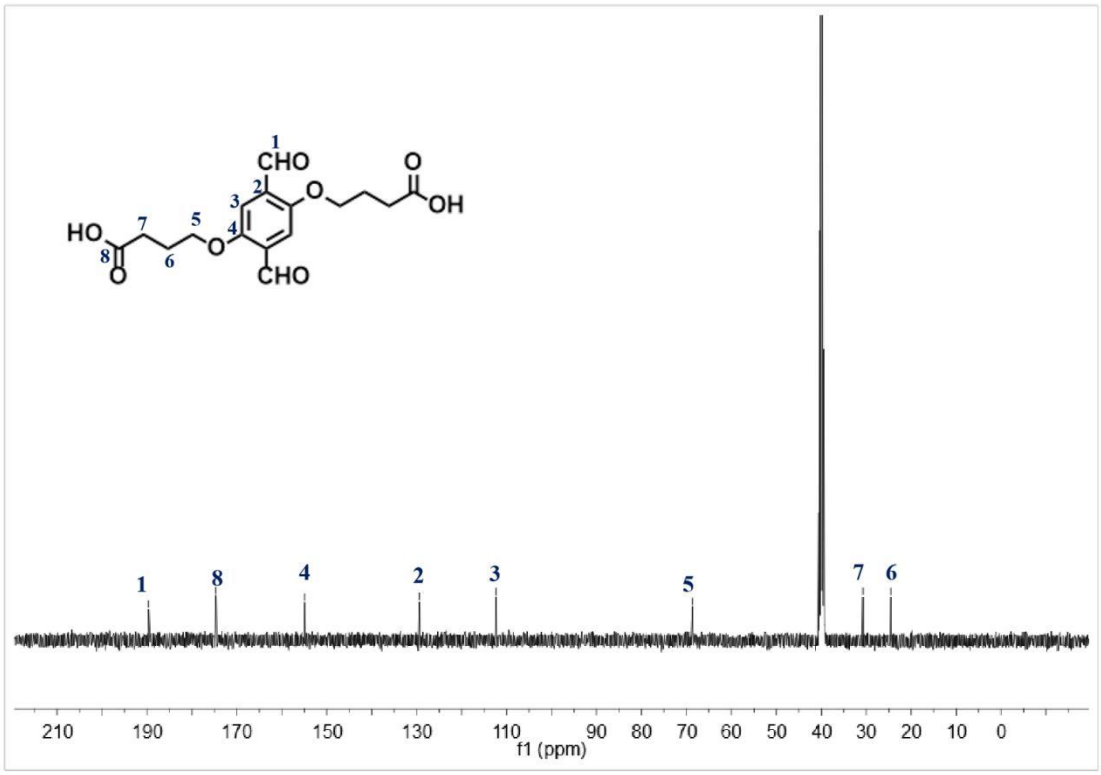


Fig. S4. [13]C NMR spectrum of 4,4'-((2,5-diformyl-1,4-phenylene)bis(oxy))dibutyric acid (FPBA) in DMSO-d6.

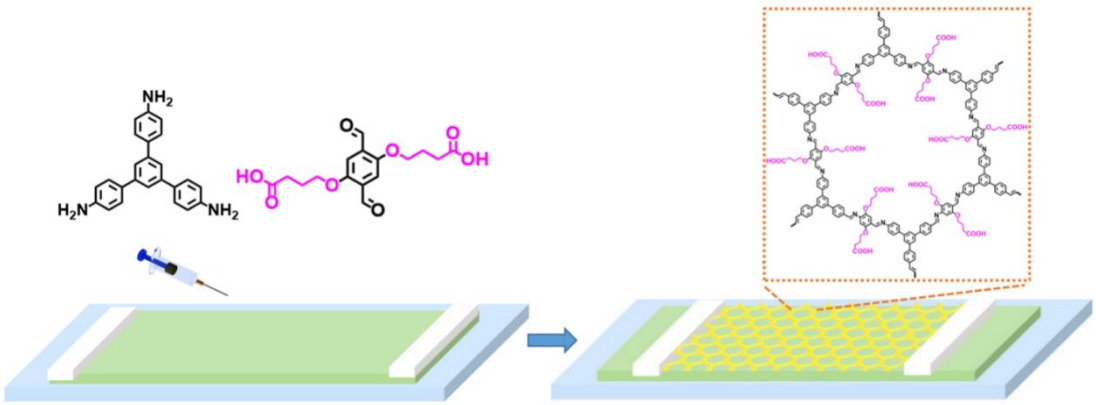


Fig. S5. A schematic illustration on the synthesis of $2DP_{TAPB+FPBA}$.

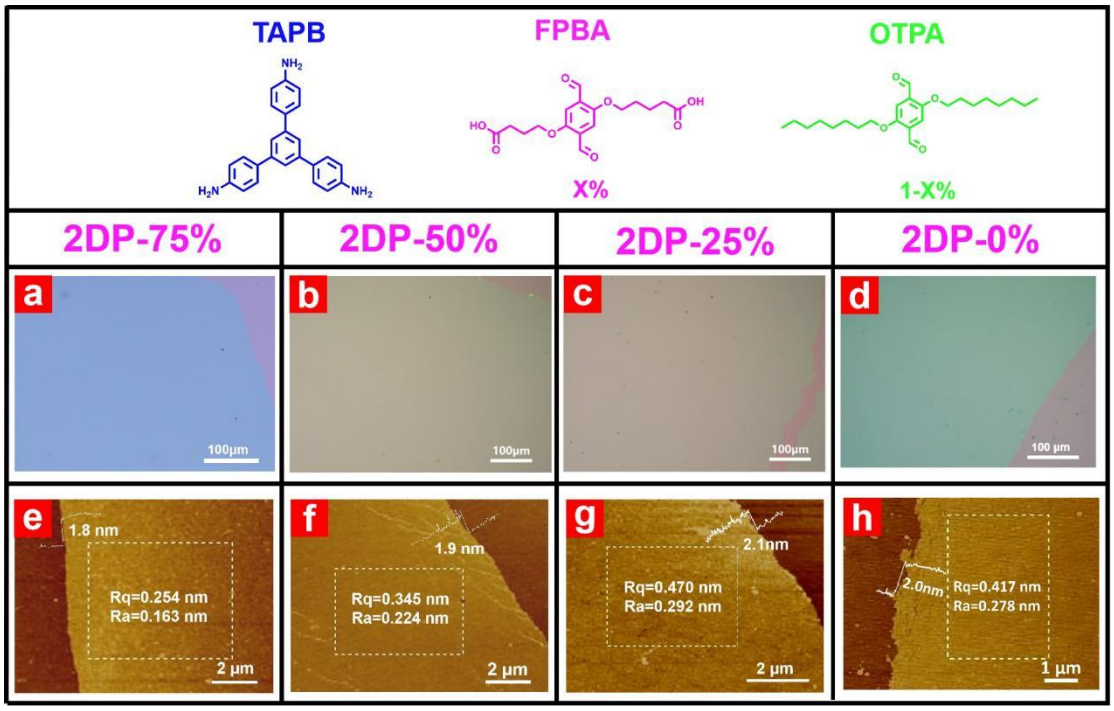


Fig. S6 (a)(b)(c)(d) OM and (e)(f)(g)(h) AFM images of the 2DP-75%, 2DP-50%, 2DP-25% and 2DP-0% on SiO_2/Si.

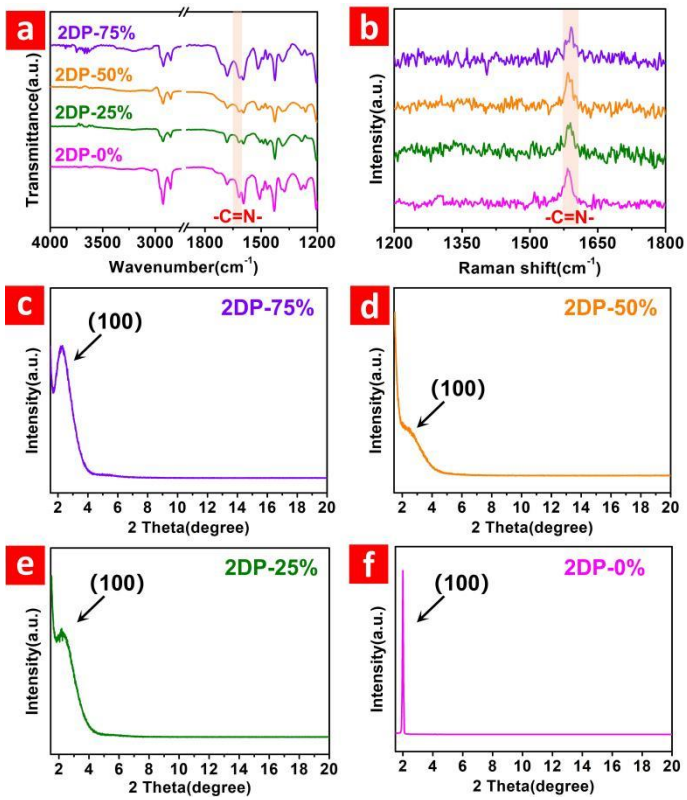


Fig. S7. (a) FT-IR spectra, (b) Raman spectra of 2DPs with different carboxyl density and XRD patterns of the (c) 2DP-75%, (d) 2DP-50%, (e) 2DP-25% and (f)2DP-0%.(Purple: 2DP-75%, Orange: 2DP-50%, Green: 2DP-25%, Pink: 2DP-0%)

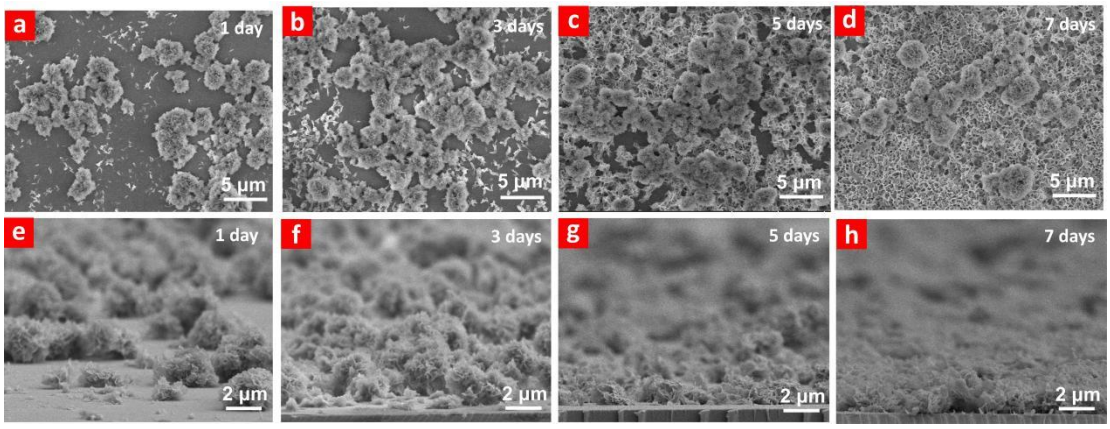


Fig. S8. SEM images show the surface morphology and cross section of 2DP-75% surface after (a)(e)1 day, (b)(f) 3 days, (c)(g) 5 days, and (d)(h) 7 days of biomineralization.

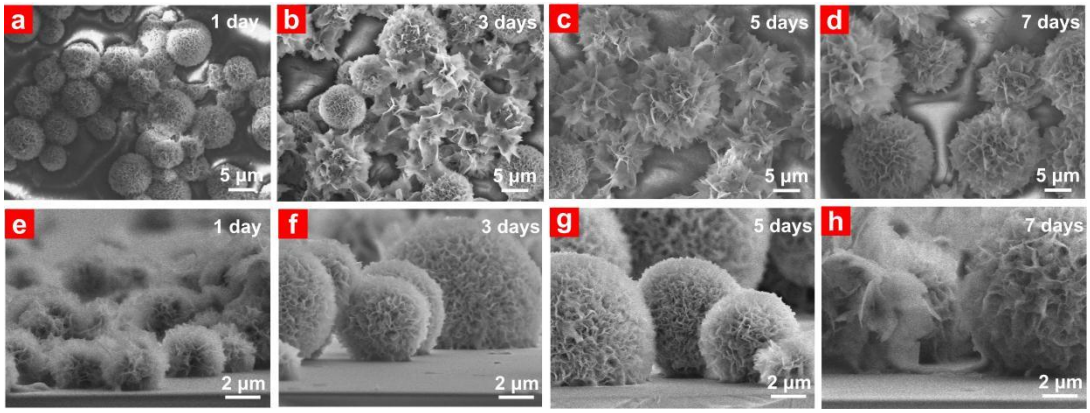


Fig. S9. SEM images show the surface morphology and cross section of 2DP-50% surface after (a)(e)1 day, (b)(f) 3 days, (c)(g) 5 days, and (d)(h) 7 days of biomineralization.

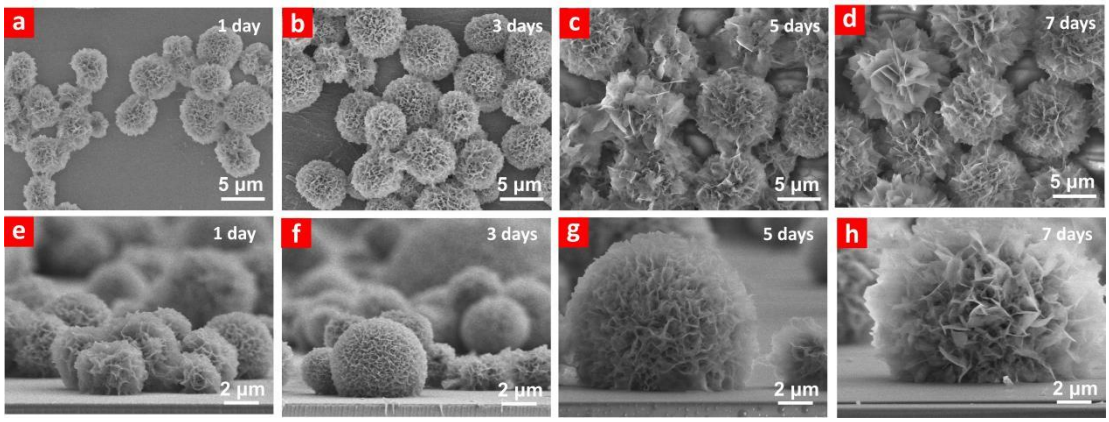


Fig. S10. SEM images show the surface morphology and cross section of 2DP-25% surface after (a)(e)1 day, (b)(f) 3 days, (c)(g) 5 days, and (d)(h) 7 days of biomineralization.

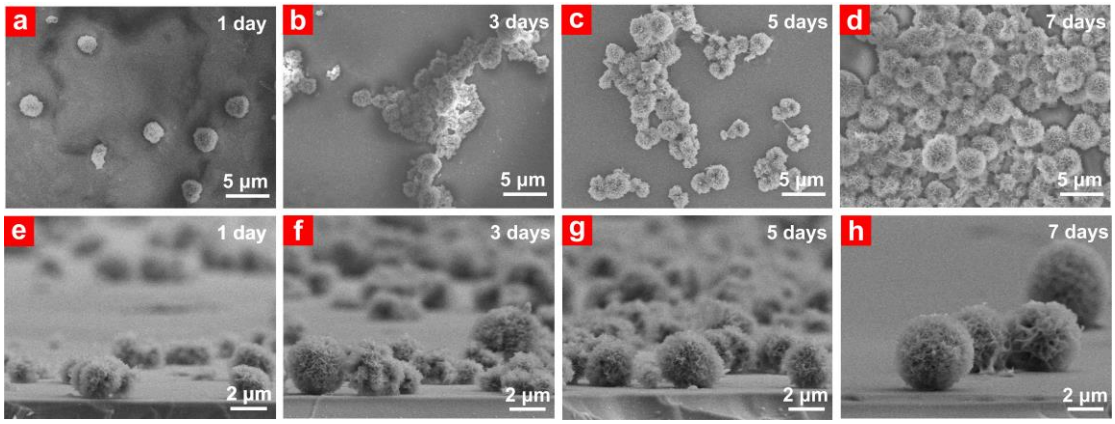


Fig. S11. SEM images show the surface morphology and cross section of $2DP_{TAPB+OTPA}$ surface after (a)(e)1 day, (b)(f) 3 days, (c)(g) 5 days, and (d)(h) 7 days of biomineralization.

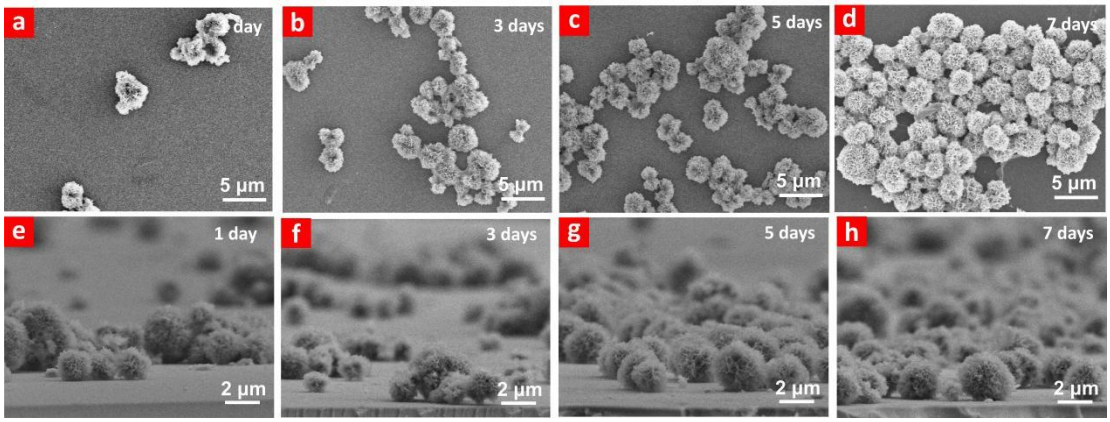


Fig. S12. SEM images show the surface morphology and cross section of glass substrate after (a)(e)1 day, (b)(f) 3 days, (c)(g) 5 days, and (d)(h) 7 days of biomineralization.

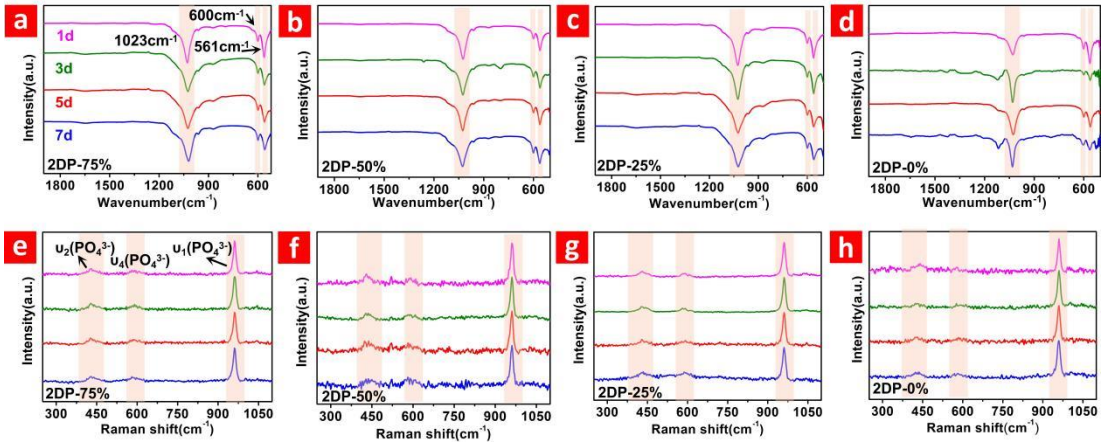


Fig. S13. (a)(b)(c)(d) FT-IR spectra, (e)(f)(g)(h) Raman spectra of the 2DP-75%, 2DP-50%, 2DP-25% and $2DP_{TAPB+OTPA}$ after 1, 3, 5, 7 days of mineralization. (Blue: 1 day, Red: 3 days, Green: 5 days, Pink: 7 days).

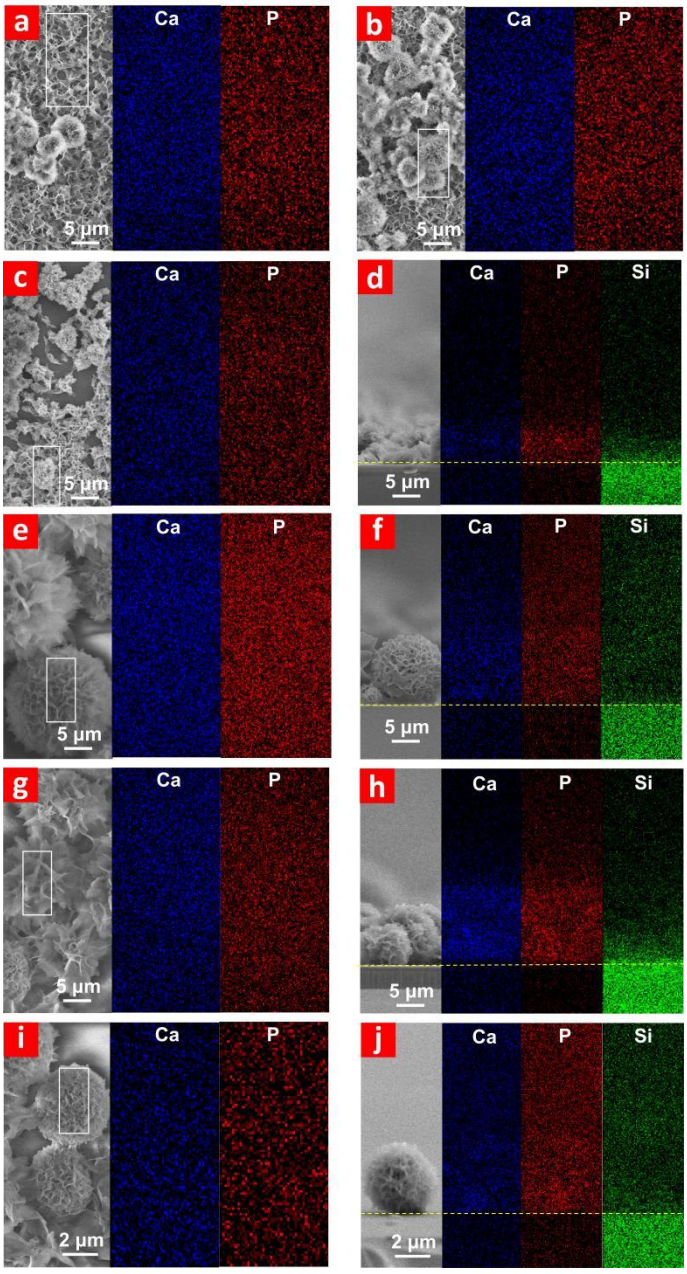


Fig. S14. The element mapping of HAp crystals both on the continuous layer (a) and spheres (b) of 2DP-100%, and both from top view and cross section of (c)(d) 2DP-75%, (e)(f) 2DP-50%, (g)(h) 2DP-25%, (i)(j) 2DP-0% after 5 days of biomineralization

[1] Wang, W.; He, Y.; Xu, P.; You, Q.; Xiai, H.; Xiang, H. Synthesis and biological evaluation of isoflavone amide derivatives with antihyperlipidemic and preadipocyte antiproliferative activities. *Bioorg. Med. Chem.* 2015, 23, 4428.

[2] Lei, K.; Li, P.; Yang, X. F.; Wang, S. B.; Wang, X. K.; Hua, X. W.; Sun, B.; Ji, L. S.; Xu, X. H. Design and synthesis of novel 4-hydroxyl-3-(2-phenoxyacetyl) -pyran-2-one derivatives for use as herbicides and evaluation of their mode of action. *J. Agric. Food Chem.* 2019, 67, 10489– 10497.