Supplementary Information

Mineralization for Micropatterned Growth of Carbonate Nanofibers

Jian-Hua Zhu[†], Ji-Ming Song[†], Shu-Hong Yu^{*†}, Wei-Qing Zhang[†], Jin-Xia Shi[‡]

Experimental sections

Octadecyltrichlorosilane (OTS) (Aldrich; 97%). Polyacrylate (Mn=5100 g/mol, Mw/Mn = 3) were purchased from Fluka. On average (on the basis of Mn), a single chain of sodium polyacrylate comprises 50-60 acrylate subunits. PEG₂₀₀-*co*-P(2-[4-dihydroxyphosphoryl]-2-oxabutyl acrylate ethyl ester)₅₃₀ was synthesized as literature.¹ Other agents were of analytic grade and used as received.

Poly (dimethylsiloxane) (PDMS) stamps with alternating 24 μ m strips and of 12 ' 12 μ m square arrays (with 3 μ m relief line spacing) were used (Fig. S1). All substrates (glass bottle, small pieces of glass and silicon slices) were cleaned and sonicated in ethanol for 5 min, after being rinsed with distilled water. They were first cleaned in piranha solution² (7: 3 concentrated H₂SO₄: 30% H₂O₂) for 30min, then rinsed with ultrapure water (Millipore Simplicity, ρ = 18.2 MΩ·cm⁻¹), and blown dry with nitrogen (99.999%).

A solution of OTS in *n*-hexane (1mM) was used as the "ink" for μ -CP. After applying the "ink" (by cotton Q-tip), the PDMS stamp was dried in a stream of nitrogen gas for 1 min and then brought it to contact with the surface of hydrophilic glass sides or silicon slide for an interval of 30s. Then the substrate was heated to 80°C for 45 min.

The mineralization of CaCO₃ was carried out by a gas diffusion technique as described by Addadi et al.³ The mineralization of CaCO₃ was carried out in a glass bottle with a volume of 15 mL, which was put into a closed desiccator. In a typical procedure, the substrate was placed in a glass bottle with the patterned side faced downwards to avoid the big sediment, containing 10 ml of 1 mM CaCl₂ solution. For synthesis of BaCO₃ nanofibers, 50 mg polymer was added into 5mM BaCl₂ solution.

The PH value of solution was adjusted by NaOH to 5.0. The bottle was then placed in a desiccator. Three small glass bottles of crushed ammonium carbonate covered with Parafilm were put at the bottom of the desiccator, each of which was punched with three needle holes. The reaction was performed at different temperature, respectively. The substrate was taken out to stop the reaction at different mineralization period and rinsed with distilled water and anhydrous ethanol several times to remove other impurities, then dried at the room temperature for characterization. The CaCO₃ fibers were also collected for further characterization.

X-ray power diffraction (XRD) analyses were carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu K α aradiation ($\lambda = 1.54056$ Å). Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL JEM 2011 microscope at an accelerating voltage of 200kV. High-resolution transmission electron microscope (HRTEM) photographs and selected area electron diffraction (SAED) patterns were performed on a JEOL JEM 2011 microscope at an accelerating voltage of 200 kV. Selected samples with mineral films on the Si (001) slices were measured for SEM microscopy on a JEOL JSM 6700 instrument equipped with an electron dispersion spectrum (EDS) system. The atomic ratios of the samples were determined using the EDS software which calculates their relative counts in the EDS peaks from at least five average areas within the samples. The optical images were taken by optical microscope GALEM/CTV microscope with CCD on them.



Fig. S1 Optical images of PDMS stamps used in our experiments. Dark blue regions

are concave, bright blue regions are protruding.



Fig. S2 (a, c, d) Light microscopic images of liquid mineral precursors formed on hydrophilic glass substrate after different reaction time. (a) 2 day, (c) 2.5 days. (d) 3days. (b) polarized light microscopic images of droplet-like precursor. ($[Ca^{2+}] = 10$ mM, $[PAA] = 0.13 \text{ g} \cdot \text{L}^{-1}$, $25 \pm 1^{\circ}\text{C}$, for 2 days).



Fig. S3 SEM images of droplet-like mineral precursor obtained on glass substrate without OTS films after mineralization for 2 days ($[Ca^{2+}] = 10 \text{ mM}$, $[PAA] = 0.13 \text{ g} \cdot \text{L}^{-1}$, $25 \pm 1^{\circ}\text{C}$).



Fig. S4 AFM image showing an array stamped OTS square field on a Si (001) substrate. The OTS domains exhibit a considerably larger degree of surface roughness than the Si surface background, with some OTS "pillars" taller than 100 nm.



Fig. S5 EDS analysis of liquid mineral precursor was measured by SEM equipped with EDS on Si (001) substrate. Sample was prepared in PAA solution for two days. The peaks of Ca and Cl indicate the existences of $CaCl_2$ in the liquid mineral precursor. The weight percentage of Cl is 5 wt% (within the error range of 2.5wt%). Si peak arises from the substrate. The weight percentage of C is 25wt% (within the error range of 5wt%), indicating the presence of PAA indeed in the liquid mineral precursor. The molar ratio of Ca: C: O is about 1: 29.8: 6.4.



Fig. S6 X-ray diffraction patterns of mineral films after mineralization at $25 \pm 1^{\circ}$ C for different times. (a) two days; (b) three days; (c) one week.



Fig. S7 FT-IR spectra of mineral films formed at $25 \pm 1^{\circ}$ C on the OTS-coated Si (001) substrate after mineralization for different times. (a) two days, (b) three days.

Note for Fig. S7:

The FTIR spectrum (Fig. S7a) shows broad peaks at 872 cm⁻¹ (v_2 , the carbonate out-ofplane bending) 1075cm⁻¹ (v_1 , the symmetric stretch in noncentrosymmetric structure), and splitting of the 1450 cm⁻¹ peak (v_3 , the asymmetric stretch), all of which show amorphous character of the liquid precursor. The band of H₂O is also observed in the precursor in form of hydrate. In addition, the water adsorption bands decrease in intensity as mineralization continues (Fig. S7b).



Fig. S8 SEM images showing different dissolving stages of underlying mineral films on the substrate. (a) Nanofibers and mineral films coexist on the substrate observed in early stage. (b-c) parts of mineral films begin to dissolve, where are marked by arrows. ($[Ca^{2+}] = 10 \text{ mM}$, $[PAA] = 0.13 \text{ g} \cdot \text{L}^{-1}$, T = 25 ± 1°C, three samples are obtained in the same bottle and the former are taken out a little earlier, for 5 days).





Fig. S9 EDS analysis of CaCO₃ nanofiber measured by SEM equipped with EDS on Si (001) substrate. (a) The spectrum was taken on the tip of the fiber. The atomic ratio of Ca: C: O is close to 1: 6: 5, and the percentage of carbon is about 35wt% (within the error% of 5%). (b) The spectrum was taken in the middle of nanofiber. The atomic ratio of Ca: C: O is about 1: 2.5: 3, and the percentage of carbon is about 32wt%. The higher percentage of C on the surface of fiber and on the tip of the fiber is possibly due to the PAA adsorbed onto the tip of nanofiber.



Fig. S10 (a) A typical calcite $CaCO_3$ nanofiber for HRTEM analysis. The long axis of the fiber has an offset of 26.3° from [006], the simulated morphology shows that the nanofiber at this location is oriented along [102] direction. (b)

The selected area electron diffraction (SAED) pattern by focusing the electron beam is along [100] zone axis. (c) A HRTEM image of the nanofiber in the marked area in (a).



Fig. S11 SEM images of micropatterned BaCO₃ mineral films at different time: (a-b) for 1 day; (c-d) for two days. Arrows point to the spherical mineral precursor.

References

- 1 T. X. Wang, A. W. Xu, H. Cölfen, Angew. Chem. Int. Ed., 2006, 45, 4451.
- 2 C. W. Kuo, J. Y. Shiu and P. L. Chen, Chem. Mater., 2003, 15, 2917.
- 3 S. Weiner, S. Albeck and L. Addadi, Chem. Eur. J., 1996, 2, 278.