

Supporting Online Material for

Heterostructured Calcium Carbonate Nanowires Controlled by the Cationic Polyelectrolyte

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1. Materials and Methods

CaCl₂ (99%) and ammonium carbonate were of analytical grade. They were purchased from Shanghai Chemical Reagent Company and used as received without further purification. Poly(allylamine hydrochloride) ($[-\text{CH}_2\text{CH}(\text{CH}_2\text{NH}_2\cdot\text{HCl})-]_n$, PAH, $M_w=15$ KDa) was bought from Aldrich accompany. Glass substrates (1.0×1.0 cm) were used after intensive cleaning with sulphuric-peroxide mixture (H₂SO₄: H₂O₂ = 4:1) and thorough rinsing with de-ionized water.

1.1 Mineralization

Typically, five glass substrates were put flatly in a glass Petri dish filled up with 10 mM CaCl₂ solution. The Petri dish was then placed in a closed desiccator containing a 10 mL vial of ammonium carbonate. After one-day reaction at room temperature (22 ± 1°C), the substrates were taken out and washed with water. Each substrate was transferred into a new glass vial containing 1mg PAH and 10mL water. After slow dissolution under atmospheric condition for 1 day at room temperature, more CaCl₂ (1-5mg) was supplemented into the solution and placed in a gas diffusion desiccator for continuous mineralization. The substrates were taken out followed by thorough washing with water and ethanol sequentially, and dried at room temperature before characterization.

1.2 Characterization

X-ray powder diffraction patterns were obtained on a Japan Rigaku D/Max-gA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178 \text{ \AA}$). The SEM images were taken on a field emission scanning electron microscope (JEOL JSM-6700F, 5-15kV). High-resolution transmission electron microscope photographs (HRTEM) and selected

area electron diffraction patterns were performed on a JEOL JEM 2011 microscope at an accelerating voltage of 200 kV. FTIR spectra were measured on a Nicolet 6700 FT-IR spectrometer from 4000 cm^{-1} to 400 cm^{-1} at room temperature. Optical images were taken on the Zeiss microscope (Axio Imager. M2m, German). Confocal laser scanning microscopy (CLSM) was taken on Zeiss LSM510 (German). Calcium concentrations were measured by ion selected electrode (ISE) (Mettler, Switzerland). Polymer concentrations were detected by High Performance Liquid Chromatography (HPLC) (Agilent 1260, German).

Fig. S1 a) A calcite crystal after one-day dissolution, the circle showing the region for EDX analysis. b) EDX pattern of the carbonate sample.

Fig. S2 a) SEM images of nanorods on an existing calcite crystal; b) a magnified image of nanoshoots. $[\text{PAH}] = 0.1\text{ g/L}$, $[\text{CaCl}_2] = 2\text{ mM}$. After 5 days.

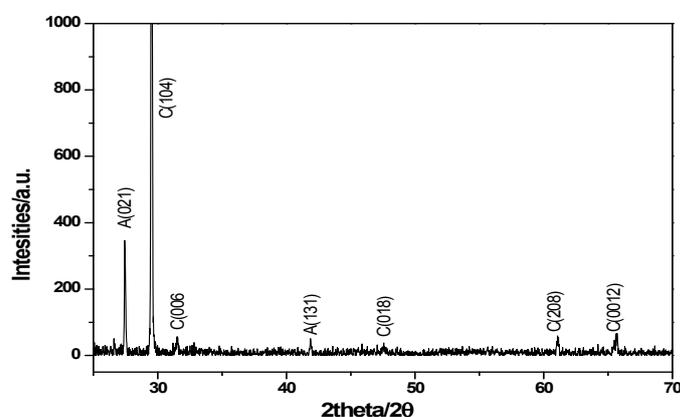


Fig. S3 XRD pattern of mineral sample after 4 days. The diffraction peaks of calcite crystallites

were labeled as “C” and “A” for the aragonite phase.

Fig. S4 SAED patterns of early CaCO_3 nanoshoots and rods taken in the square nanoregions. a) for 2-3 days; b) for 5 days.

Fig. S5 SEM images of calcite crystals covered with aragonite NWs. (a) after 7 days; (b) 14 days.

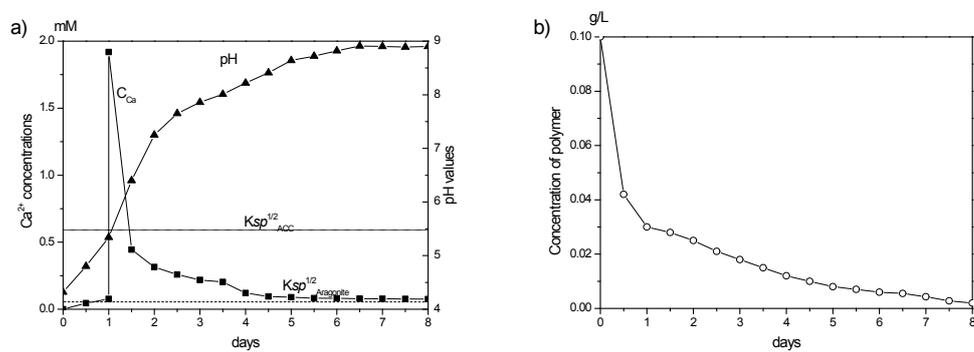


Fig. S6 (a) Concentration variations of calcium ions and changes of pH value during the mineralization; (b) Concentration changes of PAH.

Fig. S7 a) SEM image of NWs on calcite substrate; b) the relevant TEM image. White arrows points to calcite NWs and others aragonite. After 10-14 days, $[\text{PAH}] = 0.25\text{g/L}$, $[\text{CaCl}_2] = 2\text{mM}$.

Fig. S8 a-b) SEM images of calcite crystals covered with long NWs after 10-14 days. c) Long NWs grown from the rough surface of an almost dissolved calcite crystal. d) TEM image of the NWs and inset is its SAED pattern. [PAH] = 0.5g/L, [CaCl₂] = 5mM.

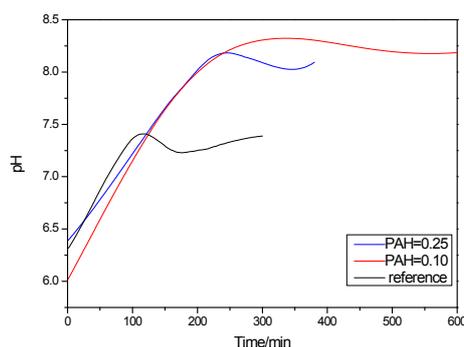


Fig. S9 pH evolution versus time for Ca(HCO₃)₂ solution crystallization according to the Kitano method.

Notes: pH evolution versus time for Ca(HCO₃)₂ solution crystallization. The crystallization according to the Kitano method¹ and other literature² was performed as follows: A supersaturated CaCO₃ solution was prepared by bubbling CO₂ gas into a 100mL solution containing 0.25g BaCO₃ for 60min to shift the CaCO₃/Ca(HCO₃)₂ equilibrium toward the more water-soluble Ca(HCO₃)₂. The surplus BaCO₃ particles were subsequently filtered off from the solution. Then, CO₂ was continuously bubbled through for another 30 min to dissolve remaining BaCO₃ precipitation. Then 50ml saturated Ca(HCO₃)₂ solution was transferred to a 100mL beaker and the pH evolution was measured under constantly stirring (1000rpm) using a Mettler Toledo Delta 302 pH instrument. The pH values were recorded in time intervals of one minute automatically by computer. The solution pH increases because of constant release of CO₂ from the solution. A sharp drop of the pH value indicates the CaCO₃ nucleation. Experiments reveal that PAH could effectively inhibit the nucleation of CaCO₃. Comparing the start of nucleation in the experiments without (113min) and with (235min and 326min) polymer shows that the nucleation is significantly

inhibited in the presence of the polymer.

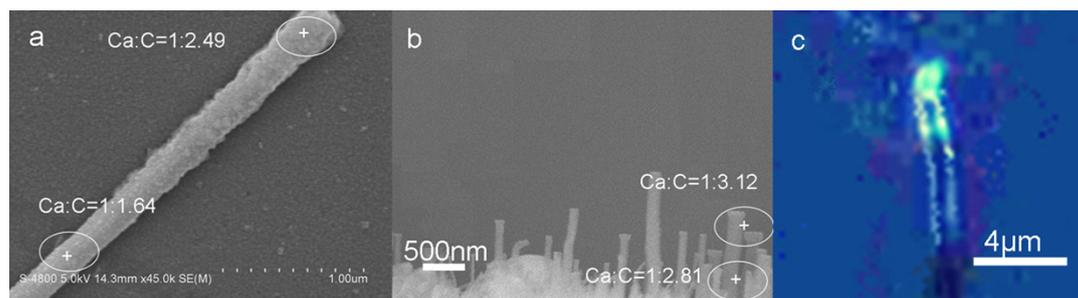
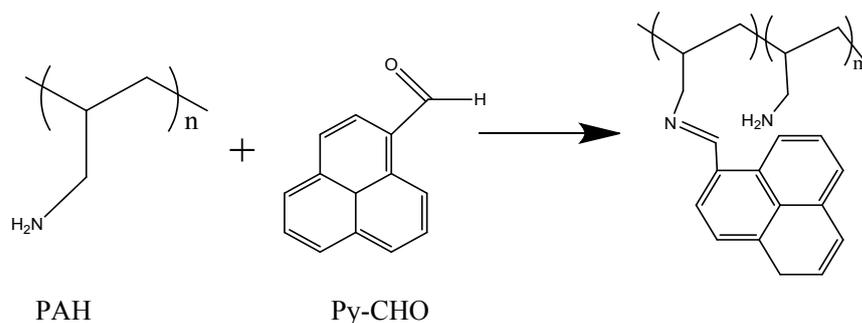


Fig. S10 EDX analysis of different aragonite NWs. The mole ratios (Ca/C) in the circular nanoregions were marked. (C) Confocal laser scanning microscopy (CLSC) image of NWs treated with fluorescent molecules.

Note: 1-pyrenecarboxaldehyde (Py-CHO) was used to treat with NWs. As PAH molecules contain $-NH_2$ groups at their side chains, they will react with $-CHO$ forming Schiff base. PAH will accumulate onto the tips NWs, so does the Py-CHO molecules. The CLSC image shows that at the end of NW the fluorescent signal is enhanced, which implies that more PAH molecules radually accumulate at the end.



1 Y. Kitano, K. Park, D. W. Hood, *J. Geophys Res.*, 1962, **67**, 4873.

2 A. W. Xu, W. F. Dong, M. Antonietti, H. Cölfen, *Adv. Funct. Mater.*, 2008, **18**, 1307.