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## **Morphology control of BaCO<sub>3</sub> by template and polymer-inorganic precursor**

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### **EXPERIMENTAL**

#### **1. Materials**

Poly(allylamine hydrochloride) (PAH, Mw = 58 000 g mol<sup>-1</sup>), poly(sodium 4-styrene-sulfonate) (PSS, Mw = 70 000 g mol<sup>-1</sup>) and branched poly(ethylene imine) (PEI, Mw = 25 000 g mol<sup>-1</sup>) were purchased from Sigma-Aldrich Co., LLC. Sodium chloride (NaCl), ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>), barium chloride (BaCl<sub>2</sub>), glutaraldehyde (GA, 25% in H<sub>2</sub>O), sodium chloride (NaCl), N,N-dimethylformamide (DMF) and ethanol were all purchased from Sinopharm Chemical Reagents Co., Ltd. They were all analytical grade reagents and directly used without further purification. Pure water with a resistivity of 18.2 MΩ cm<sup>-1</sup> at 25 °C was used in all experiments. Polycarbonate track-etched (PC) membranes from Whatman have the pore diameter and length of 400 nm and 10 μm, respectively.

#### **2. Methods**

##### **2.1 Layer-by-layer (LbL) self-assembly of (PSS/PAH)<sub>1.5</sub>**

Polyelectrolyte molecules were assembled on the inner pore walls of PC membranes as template for nanorods. The membranes were pretreated with positively charged PEI. The first layer was deposited by immersing a pretreated PC membranes in a PSS solution (1 mg mL<sup>-1</sup> in 0.5 M NaCl aqueous solution) for 30 min followed by rinsing with pure water for 5 min. Then, the second layer was deposited by immersing PC/PSS in a PAH solution (1 mg mL<sup>-1</sup> in 0.5 M NaCl aqueous solution) for 30 min followed by rinsing with pure water. After 1.5 deposition cycles, the (PSS/PAH)<sub>1.5</sub> polyelectrolyte layers forming on the inner walls of pores were formed, and then the PC/(PSS/PAH)<sub>1.5</sub> membranes were immersed in 25 % GA solution as cross-linking agent to enhance the structural stability of (PSS/PAH)<sub>1.5</sub> layers, for 30 min at room temperature, and kept in a drying oven at 40 °C for 30 min followed by rinsing with ethanol for 5 min. Afterwards, the PC/(PSS/PAH)<sub>1.5</sub> membranes were air dried at room temperature and stored in a sealed container. PAH and PSS deposited on PC planar surfaces instead of on inner walls of the membrane were removed by wetting grind at room temperature. In control experiment, the polyelectrolyte layers on the surface of PC membranes were not removed.

##### **2.2 BaCO<sub>3</sub> NRs prepared in pore channels of PC/(PSS/PAH)<sub>1.5</sub> membranes**

BaCO<sub>3</sub> nanorods (NRs) were prepared in the absence or presence of PSS in the cylindrical pore

channels of PC/(PSS/PAH)<sub>1.5</sub> membranes in a solution of 10 mM Ba<sup>2+</sup>, with 1.0 mg mL<sup>-1</sup> PSS, respectively. PSS was added to a 10 mM BaCl<sub>2</sub> solution under stirring to give PSS concentrations of 1 mg mL<sup>-1</sup>, followed by stirring overnight. The PC/(PSS/PAH)<sub>1.5</sub> membranes were transferred to a beaker containing 50 mL of BaCl<sub>2</sub> solution in the presence of PSS where it was degassed under vacuum (10 KPa, 30 min) to remove air in pores. Subsequently, the PC/(PSS/PAH)<sub>1.5</sub> membranes were exposed to decomposed gases (CO<sub>2</sub> and NH<sub>3</sub>) of solid (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in a sealed container. In order to lower down diffusion, the beakers containing PC/(PSS/PAH)<sub>1.5</sub> membranes in BaCl<sub>2</sub> and solid (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> were both covered with a Parafilm punched with needle holes of 0.7 mm in diameter. 6 d were maintained to allow complete crystallization of BaCO<sub>3</sub> in the pores of PC/(PSS/PAH)<sub>1.5</sub> membranes. Then, PC was dissolved by 20 mL of DMF under stirring for 30 min. The BaCO<sub>3</sub>@(PSS/PAH)<sub>1.5</sub> NRs were purified by several steps of washing and centrifugation (2000 rpm, 340 g, 5 min) with pure water.

In control experiment, to explain the effect of (PSS/PAH)<sub>1.5</sub> polyelectrolyte layers, we prepared BaCO<sub>3</sub> with the same procedure as described above except in free PC membranes, which were not modified by polyelectrolyte layers.

### **2.3 Effect of blocking one end of PC membrane pores**

The PC/(PSS/PAH)<sub>1.5</sub> membranes were gently pressed against a piece of Parafilm which was back-supported by a clean glass slide. The slide was then heated to 40-50 °C in a drying oven for 45 min. After cooling to room temperature, the glass slide was separated from the membrane, leaving the Parafilm sticking on PC membrane. The blocked membranes were then transferred to a beaker containing 50 mL of BaCl<sub>2</sub> solution in presence of PSS, and degassed under vacuum (10 KPa, 30 min) to remove air in pores. BaCO<sub>3</sub> microcrystals were prepared with the same procedure described as section 2.2.

### **2.4 BaCO<sub>3</sub> crystallized in bulk solution**

BaCO<sub>3</sub> microcrystals crystallized in the absence or presence of PSS in bulk solutions. Solutions were prepared as follows: the concentration of BaCl<sub>2</sub> in the absence of PSS was 10 mM. In the presence of PSS, PSS was added to a 10, 50 or 100 mM BaCl<sub>2</sub> solution under stirring to give PSS concentrations of 0.1, 0.5 and 1 mg mL<sup>-1</sup>, followed by stirring overnight. 15 mL of solution in the presence of PSS was added into 25 mL of beaker. The beaker was then covered with a Parafilm punched with needle holes of 0.7 mm in diameter, and placed in a sealed container. An equal glass beaker containing 10 g of crushed ammonium carbonate was also covered with a Parafilm punched with needle holes of 0.7 mm in diameter and placed in the sealed container. After 6 d of reaction time, the precipitates were purified by several steps of washing and centrifugation (1000 rpm, 85 g, 5 min) with pure water. For comparison, to explain the effect of PSS, we prepared BaCO<sub>3</sub> crystals in bulk solutions with the same procedure described above except the absence of PSS.

### **2.5 BaCO<sub>3</sub> crystallized in bulk at early stages**

BaCO<sub>3</sub> crystals at early stages were prepared in a beaker containing 15 mL mixture solution of 10 mM Ba<sup>2+</sup>, with 1.0 mg mL<sup>-1</sup> PSS. The beaker was then covered with a Parafilm punched with needle holes of 0.7 mm in diameter, and placed in a sealed container. An equal glass beaker containing 10 g of crushed (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> was also covered with a Parafilm punched with needle holes of 0.7 mm in diameter and placed in the sealed container. When the solution became slightly turbid, 10 μL of the solution was pipetted out, placed into a freshly cleaned glass cell, which was covered with coverslips and examined with polarized light microscopy (PLM).

## **3. Characterization**

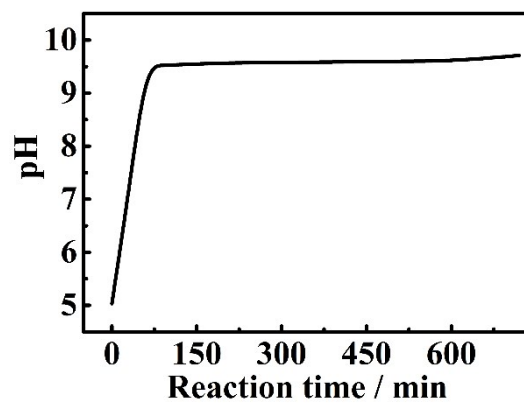
Scanning electron microscopy (SEM) measurement was carried out on a JSM-6700 (JEOL, Japan) instrument under an operating voltage of 5 kV and operating distance of 5 mm. The SEM species were prepared by dropping 5  $\mu\text{L}$  of  $\text{BaCO}_3@(\text{PSS}/\text{PAH})_{1.5}$  NRs suspensions on silicon wafers followed by air drying, and then sputtered with platinum. The elemental mapping was obtained from energy dispersive X-ray spectrometer (EDS) attached to SEM. X-ray diffraction (XRD) patterns were collected through a D8 Advance X-ray diffractometer (Bruker, Germany) operated at 40 mA and 40 kV with the Cu ( $K\alpha$ ) radiation ( $\lambda = 1.54184 \text{ \AA}$ ) in an angular range of 15–60° at an interval of 0.02° and a scanning rate of 4°/min. The instrumental line broadening was evaluated by measuring the XRD spectrum of annealing Si powder and the instrumental peak broadening was taken out by using Jade software. Transmission electron microscopy (TEM) images were obtained through a JEM-1011 TEM (JEOL, Japan) with an acceleration voltage of 200 kV. High resolution TEM (HRTEM) images and selected area electron diffraction (SAED) were obtained on a JEOL-2100F TEM (JEOL, Japan) with an acceleration voltage of 200 kV. The TEM species were prepared by 5  $\mu\text{L}$  of  $\text{BaCO}_3@(\text{PSS}/\text{PAH})_{1.5}$  NRs suspensions on copper grids followed by air drying. Raman spectra were obtained using the LabRAM HR 800 system (Horiba JY, France) excited with the laser of 633 nm. To characterize specific surface of  $\text{BaCO}_3$  NRs, 4 pieces of PC membranes for NRs were used to meet the mass requirement of BET measurement. pH of mixture solution was obtained by PHS-3C pH meter (Shanghai INESA Scientific Instrument Co., Ltd, China). Zeta potential of  $\text{BaCO}_3@(\text{PSS}/\text{PAH})_{1.5}$  NRs was obtained by Zetasizer Nano ZS (Malvern Instruments Ltd., England).

#### 4. Calculation on thickness of $\text{BaCO}_3$ microcrystals in NRs

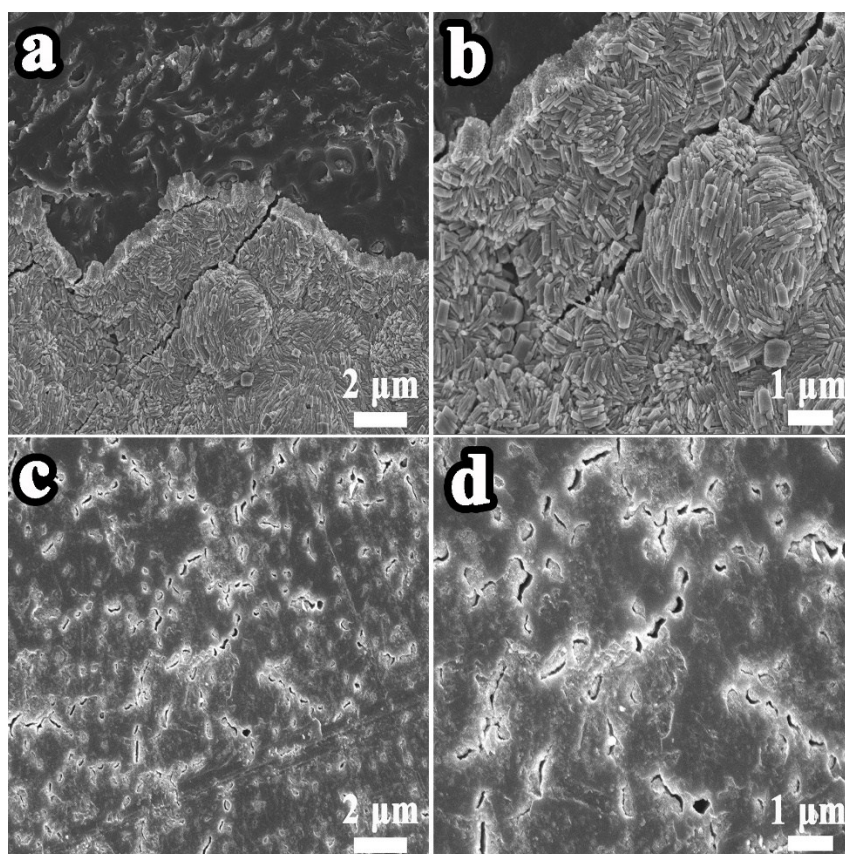
The average thickness of  $\text{BaCO}_3$  NRs in the direction perpendicular to (111) face is calculated by using Debye-Scherrer's formula<sup>1</sup>,

$$K\lambda / \beta \cos \theta$$

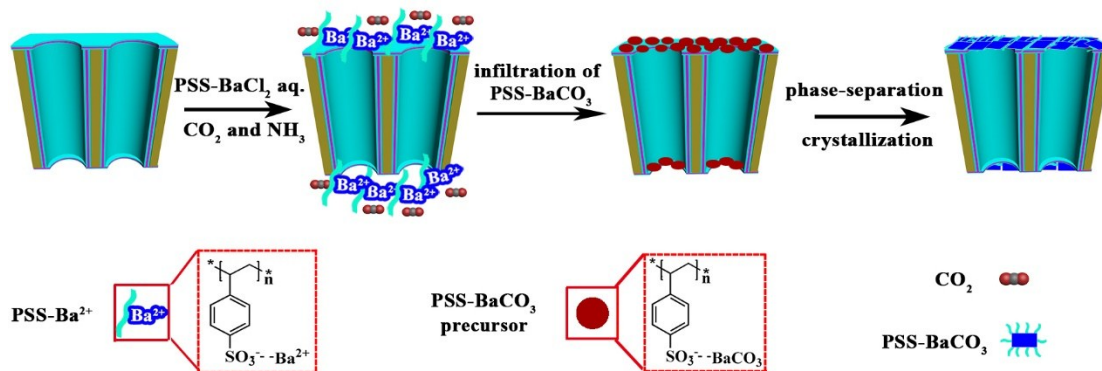
where  $\lambda$  is the wavelength of the X-ray (0.154 nm),  $\beta$  is the full width at half-maximum (radian),  $K$  is a dimensionless shape factor, with a value of 0.89 when  $\beta$  is the full width at half-maximum, and  $\theta$  is the diffraction angle (radian).



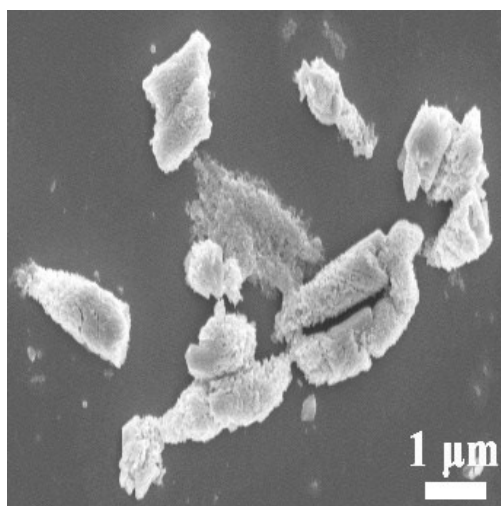
**Figure S1.** pH of the mixture solution of 10 mM Ba<sup>2+</sup> and 1 mg mL<sup>-1</sup> PSS exposed decomposed gases (CO<sub>2</sub> and NH<sub>3</sub>) of solid (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> at different reaction time.



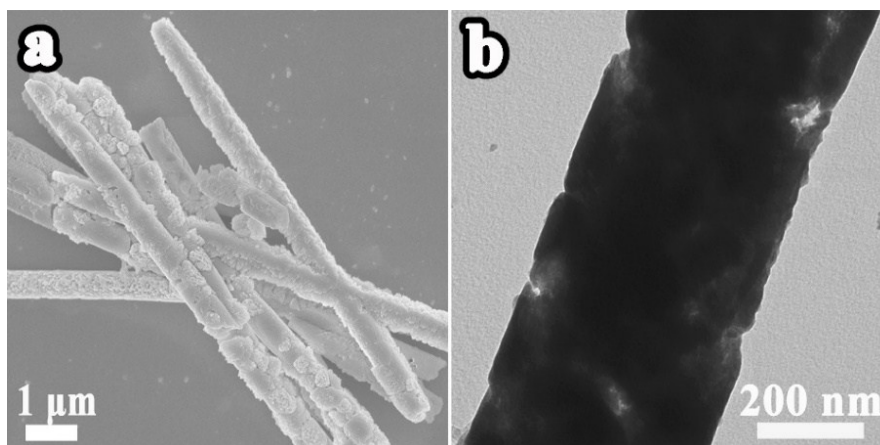
**Figure S2.** (a-b) SEM images of the surface of PC/(PSS/PAH)<sub>1.5</sub> membrane before the polyelectrolyte layers on the surface have been removed by wetting grind. (c-d) SEM images of surface of PC/(PSS/PAH)<sub>1.5</sub> membrane after the polyelectrolyte layers on the surface have been removed by wetting grind.



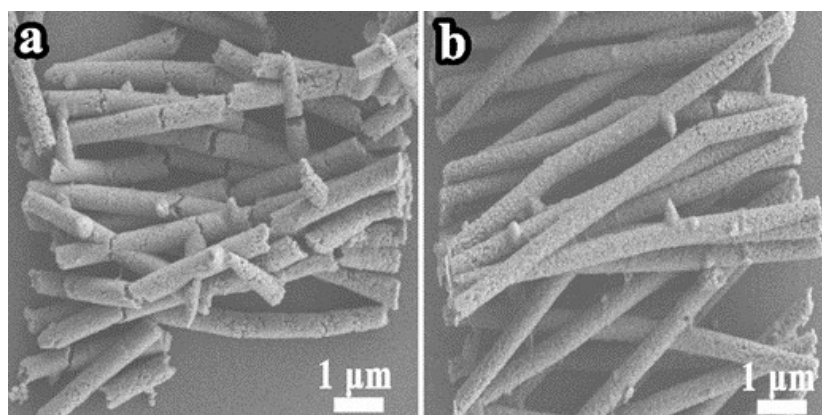
**Figure S3.** Schematic effect of polyelectrolyte layers on the surface of PC membrane on crystallization process of  $\text{BaCO}_3$ .



**Figure S4.** SEM image of  $\text{BaCO}_3$  crystals prepared in pore channels when one side of the PC/(PSS/PAH)<sub>1.5</sub> membranes is blocked.

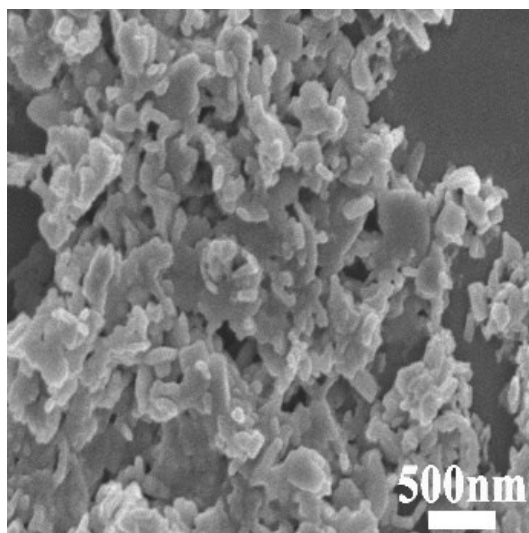


**Figure S5.** (a) SEM image and (b) TEM image of  $\text{BaCO}_3$  NRs prepared in free pore channels of PC membrane after reaction for 6 d from the solution of 10 mM  $\text{Ba}^{2+}$  with 1.0 mg mL<sup>-1</sup> PSS as well as  $\text{CO}_2$  from  $(\text{NH}_4)_2\text{CO}_3$ .

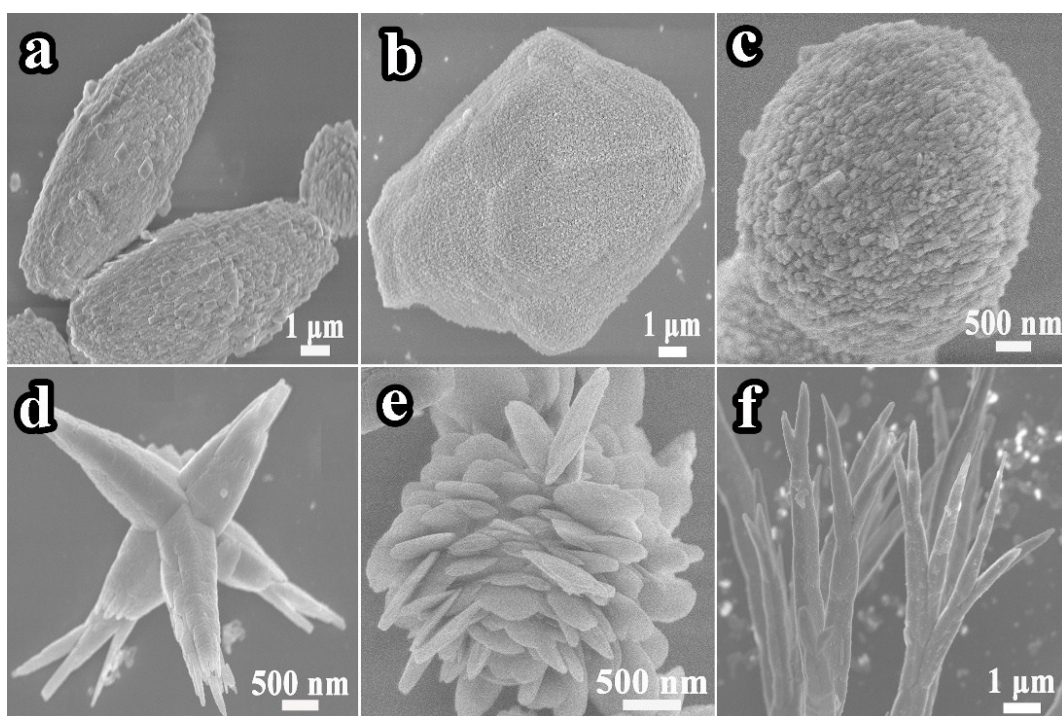


**Figure S6.** SEM images of (a)  $\text{BaCO}_3$  NRs and (b)  $\text{BaCO}_3@(\text{PSS}/\text{PAH})_{1.5}$  NRs prepared in pore channels of PC membrane after reaction for 6 d separated from the solution after centrifugation (2000 rpm, 340 g, 5 min).



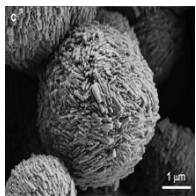
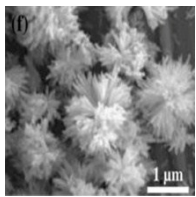
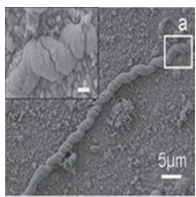
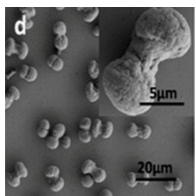
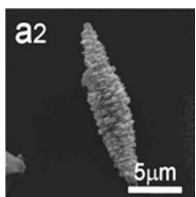
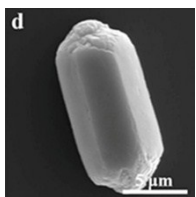
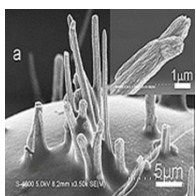


**Figure S7.** SEM image of BaCO<sub>3</sub> microcrystals prepared in pore channels of PC membrane from a solution of 10 mM Ba<sup>2+</sup> in the absence of PSS.

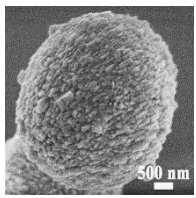
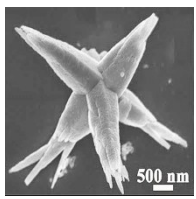
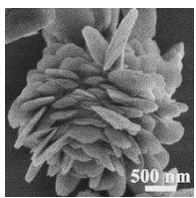
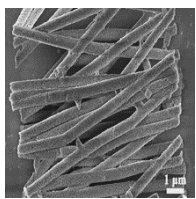


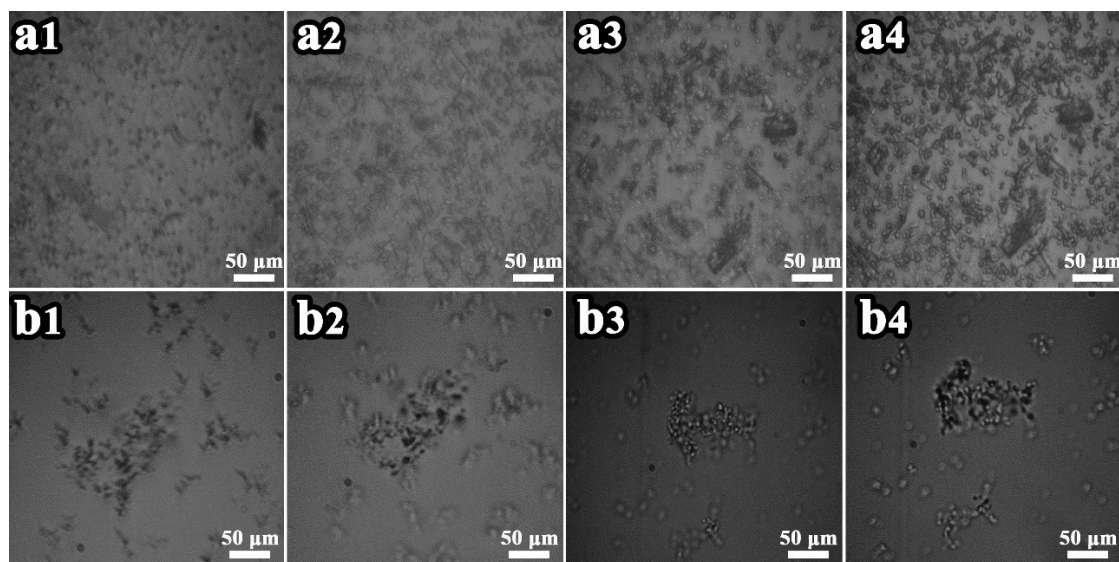
**Figure S8.** SEM images of BaCO<sub>3</sub> crystals prepared in bulk solution after reaction for 3 d at room temperature. (a-c) 10 mM Ba<sup>2+</sup> with 0.1, 0.5, and 1.0 mg mL<sup>-1</sup> PSS, respectively; (d-e) 50 and 100 mM Ba<sup>2+</sup>, respectively, with 1.0 mg mL<sup>-1</sup> PSS. (f) SEM image of BaCO<sub>3</sub> crystals prepared in bulk solution containing 10 mM Ba<sup>2+</sup> without PSS after reaction for 6 h at room temperature;

**Table S1** Morphology of BaCO<sub>3</sub> prepared in bulk solution in the presence of additive involving CO<sub>2</sub> decomposed from solid (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>

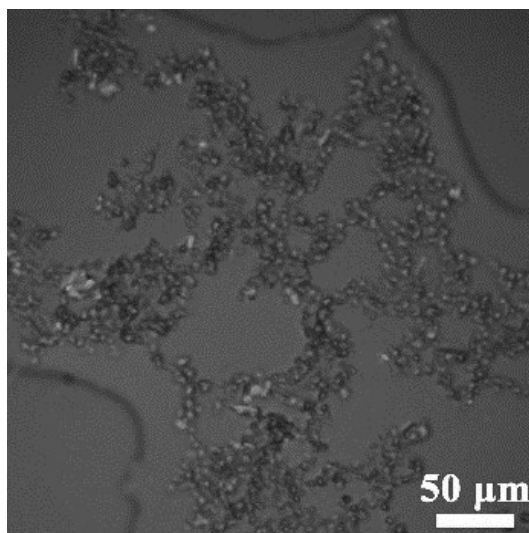
Additive		Ba <sup>2+</sup> concentration (mM)	Morphology	Ref.
Sample	concentration (mg mL <sup>-1</sup> )			
poly(sodium 4-styrenesulfonate) (PSS)	1.0	10		2
cetyltrimethyl ammonium bromide (CTAB)	9.1	50		3
polyethyleneglycol- <i>b</i> -[(2-[4- dihydroxy phosphoryl]-2- oxabutyl) acrylate ethyl ester] (PEG- <i>b</i> -DHPOBAEE)	0.5	5.0		4
carboxymethyl cellulose	1.0	10		5
PEO <sub>70</sub> -PPO <sub>20</sub> -PEO <sub>70</sub> (P <sub>123</sub> )	20	20		6
poly(2- methacryloyloxyethylphosphory lcholine)	15	10		7
poly(allylamine hydrochloride) (PAH)	0.5	10		8



PSS		10		This work
PSS	1.0	50		
		100		
PSS as additive, PC@(PSS/PAH) <sub>1.5</sub> membrane as template	1.0	10		



**Figure S9.** PLM images (with gypsum  $\lambda$ -plate) of  $\text{BaCO}_3$  collected at different polarizer positions after (a1, b1) 30 min, (a2, b2) 1 h, (a3, b3) 2 h, (a4, b4) 3 h of reaction, respectively.



**Figure S10.** PLM image of BaCO<sub>3</sub> NRs prepared in pore channels of PC membrane after reaction for 1 d.

## References and notes

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