

**Two Anti-acidification Pathways for the Dissolution Process of
Aragonite in Acidified Artificial Seawater with Different Additives:
Bonded with Bicarbonate and Hydrogen Ions**

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1. Materials and methods

1.1 Materials

CaCl₂ (GR, ≥99.99%), Na₂CO₃ (GR, ≥99.99%), NaHCO₃ (GR, ≥99.99%), Na₂SiO₃·9H₂O (AR, ≥98%), polyacrylic acid (PAA) (*M_w* = 2100), NH₄HCO₃ (AR, ≥99.0%), NaCl (GR, ≥99.8%), were all used without further purification. Pure water was obtained using a Milli-Q Advantage A10 water purification system. Acidified artificial seawater was prepared to match the salinity of natural seawater by dissolving 35.5 g of NaCl in 1 L of pure water.

1.2 Preparation of aragonite

A 20 mM CaCl₂ solution was prepared by mixing water with ethanol in a 1:1 volume ratio. 20 mL of CaCl₂ (20 mM) solution was placed in a petri dish and transferred to a desiccator containing 10 g NH₄HCO₃ at room temperature. After 6 h, the precipitates were washed three times with ultrapure water and centrifuged at 6000 rpm for 3 min. The final precipitates were transferred to an oven at 70°C until thoroughly dry.

1.3 Preparation of ACC, PAA@ACC, and Si@ACC

ACC was prepared by mixing 100 mL of CaCl₂ (10 mM) with 100 mL of Na₂CO₃ (10 mM) at room temperature. PAA@ACC and Si@ACC were prepared by adding PAA (0.2 mM) and Na₂SiO₃ (6 mM) to the carbonate solution, respectively, prior to mixing. The mixed solution was immediately filtered through a 0.45 μm PTFE filter, and the precipitates were washed three times with ethanol and transferred to a vacuum freeze-drying oven for 12 h.

1.4 Aragonite dissolution kinetics

The experimental temperature was maintained at 25 ± 0.5°C using a central air conditioning system. The pH, electric conductivity (EC), and calcium ion concentration of the solutions were recorded every 20s using a multifunction parameter meter (Mettler-Toledo, SevenExcellence S470). The pH of the solution was controlled using an automatic potentiometric titrator (Leici, ZDJ-4A). A three-point pH calibration was performed at pH 4.01, 6.86, and 9.18 using standard buffers before each experiment. In the dissolution experiment, 10 mg of aragonite and 1 mL of PAA (5 mM) or 1 mL of Na₂SiO₃ (0.1 M) were added to 100 mL of ultrapure water and titrated with HCl (0.01 M) to

maintain the pH at 7. The pH, EC, and volume of HCl were recorded during dissolution. The dissolution experiment of aragonite in acidified artificial seawater was conducted at specific pH values (7.0, 7.4, and 7.8) for 2 h, and the volume of HCl (0.01 M) needed to maintain constant pH was recorded. At least three independent experiments were conducted at each pH to ensure reproducibility. The dissolved aragonite was filtered using a 0.45 μm PTFE membrane, rinsed with ethanol, and transferred to a vacuum freezer overnight.

1.5 Dissolution kinetics of ACC, PAA@ACC, and Si@ACC

After the dissolution experiment under the above conditions, precipitates were removed from the aqueous solution at different time intervals (1, 2, 3, 5, 10, and 20 min). The reaction was immediately terminated by adding excess anhydrous ethanol, followed by vacuum extraction through a 0.45 μm PTFE membrane filter, rinsing with ethanol, and subsequent drying in a vacuum freezer overnight. To prevent the phase transition of ACC in air, the dried samples were obtained for subsequent characterization.

1.6 Titration experiment

In a titration experiment, 20 mM CaCl_2 solution was continuously dosed into 25 mL of 10 mM carbonate buffer solution at a constant rate of 0.9 mL/h using a syringe pump, with the pH maintained at 9.75 by an automatic potentiometric titrator. Before titration, PAA (0.2 mM) and Na_2SiO_3 (6 mM) were added to the carbonate buffer solution. The concentration of free calcium ions was monitored using a calcium ion-selective electrode, which was calibrated before each experiment.

1.7 Characterization

Powder X-ray Diffraction (XRD) patterns were recorded using a Rigaku Smartlab 9000 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$, Generator: 40 kV, 15 mA). Fourier transform infrared (FT-IR) spectra of the samples were recorded using the Bruker Vertex 70v instrument equipped with an attenuated total reflection (ATR) accessory, the spectra were recorded in the range of 400 to 4000 cm^{-1} with a spectral resolution of 2 cm^{-1} and 64 scans were accumulated for background correction and sample characterization. Raman spectra of all samples and standards

were acquired using a Raman Vis-NIR spectrometer (Horiba LabRam HR Evolution) coupled with a 532 nm laser. Scanning electron microscope (SEM) images were obtained by a ZEISS Merlin. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of etched aragonite in the presence of PAA were obtained by a FEI Talos F200X electron microscope. Simultaneous thermogravimetric analysis and differential scanning calorimetry (TG/DSC) were performed using a Netzsch Model 449C instrument with its high temperature furnace. X-ray Photoelectron Spectroscopy (XPS) analyses were carried out on a PHI 5000 VersaProbe III spectrometer using monochromatic Al K(alpha) X-ray source, and spectra were charge-corrected to the main line of the C 1s spectrum (adventitious carbon) and set to binding energy of 284.8 eV.

2. Supplementary Figures

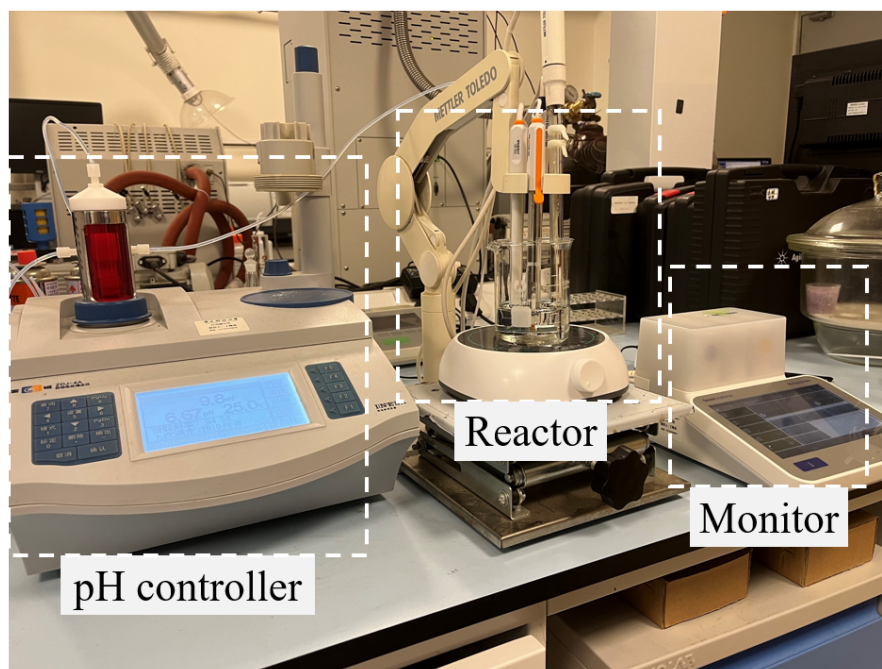


Fig. S1 The experimental setup is designed for in-situ monitoring the dissolution process of CaCO_3 .

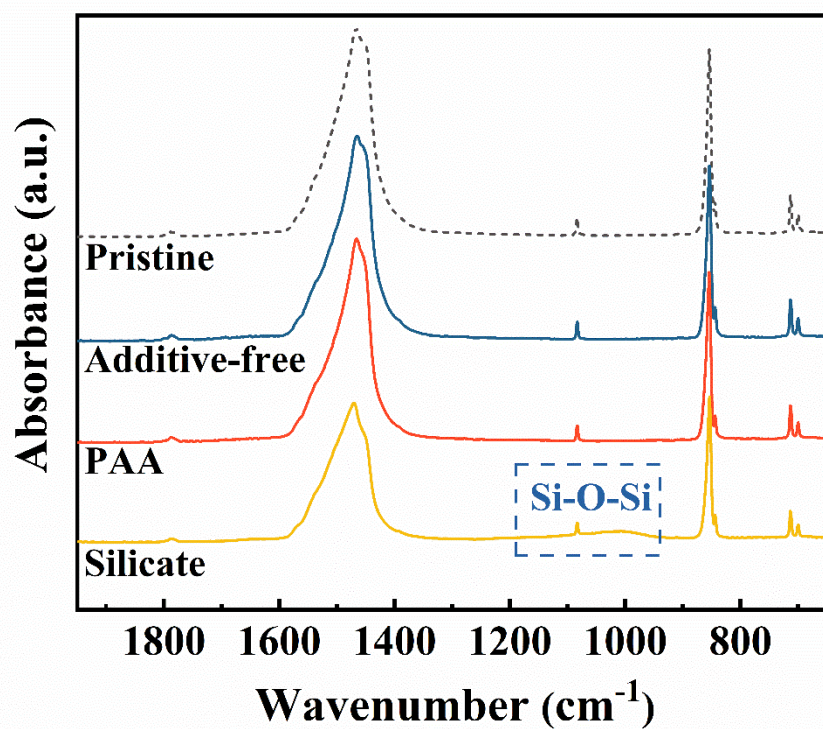


Fig. S2 ATR-FTIR spectra of aragonite immersed in acidified artificial seawater at pH 7 for 2 h.

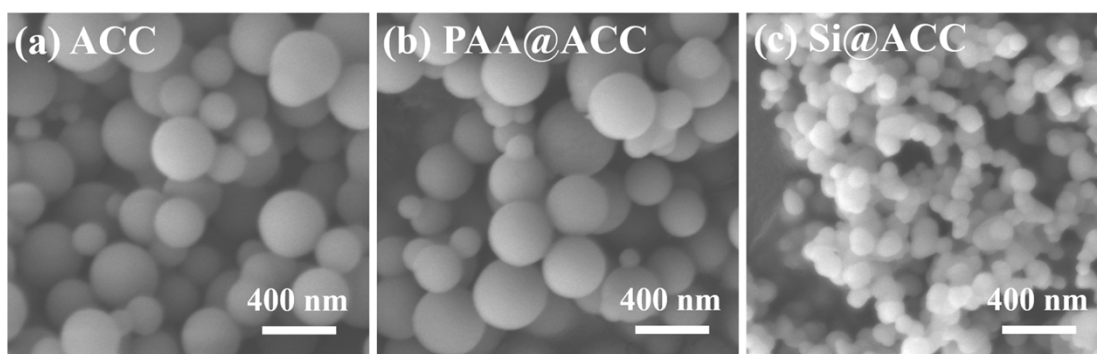


Fig. S3 SEM images of (a) ACC, (b) PAA@ACC, and (c) Si@ACC.

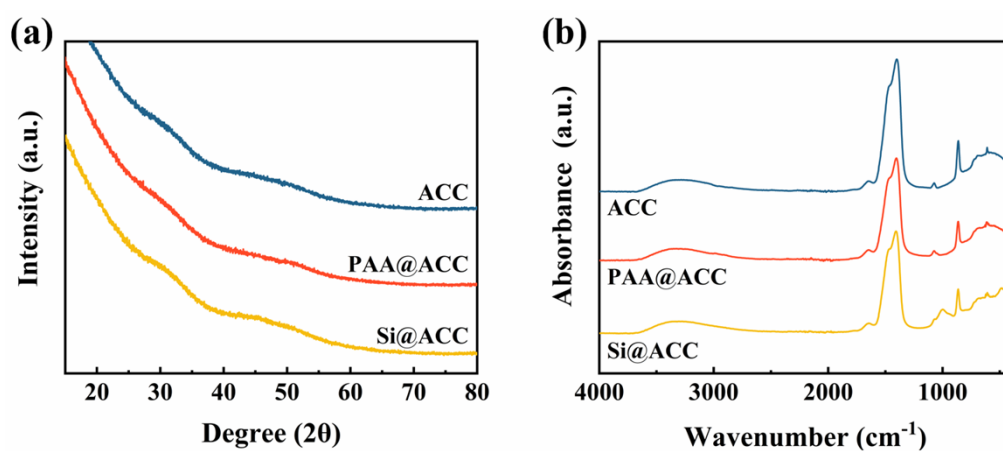


Fig. S4 (a) XRD patterns and (b) ATR-FTIR spectra of ACC, PAA@ACC, and Si@ACC.

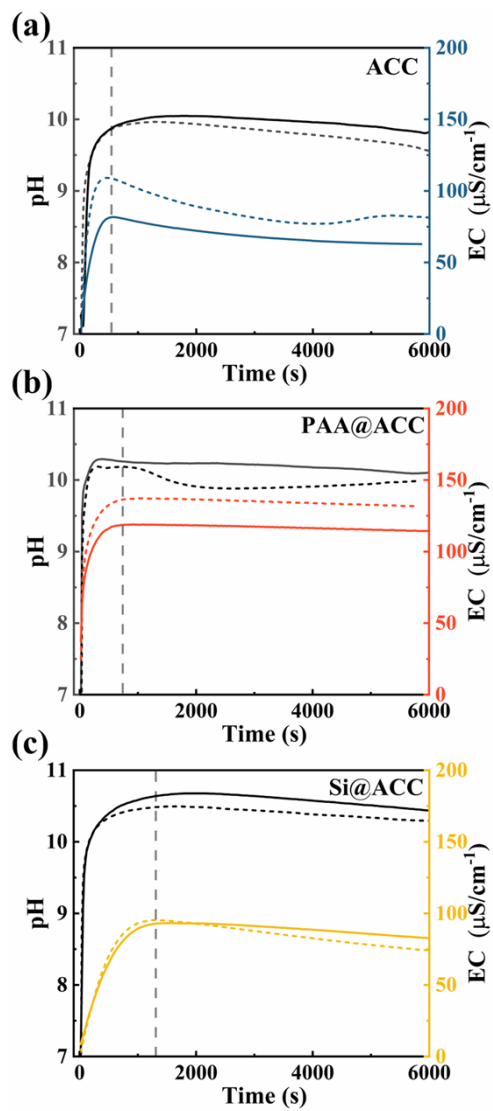


Fig. S5 Time-development of pH and EC for (a) ACC, (b) PAA@ACC, and (c) Si@ACC under acidified artificial seawater.

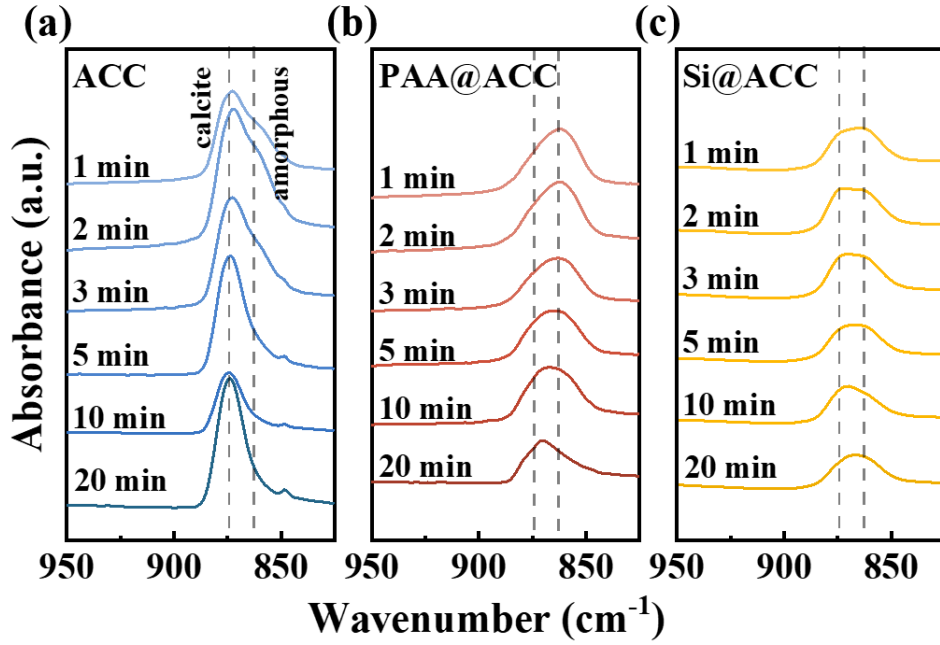


Fig. S6 ATR-FTIR spectra for (a) ACC, (b) PAA@ACC, and (c) Si@ACC after immersed in aqueous solution at different periods.

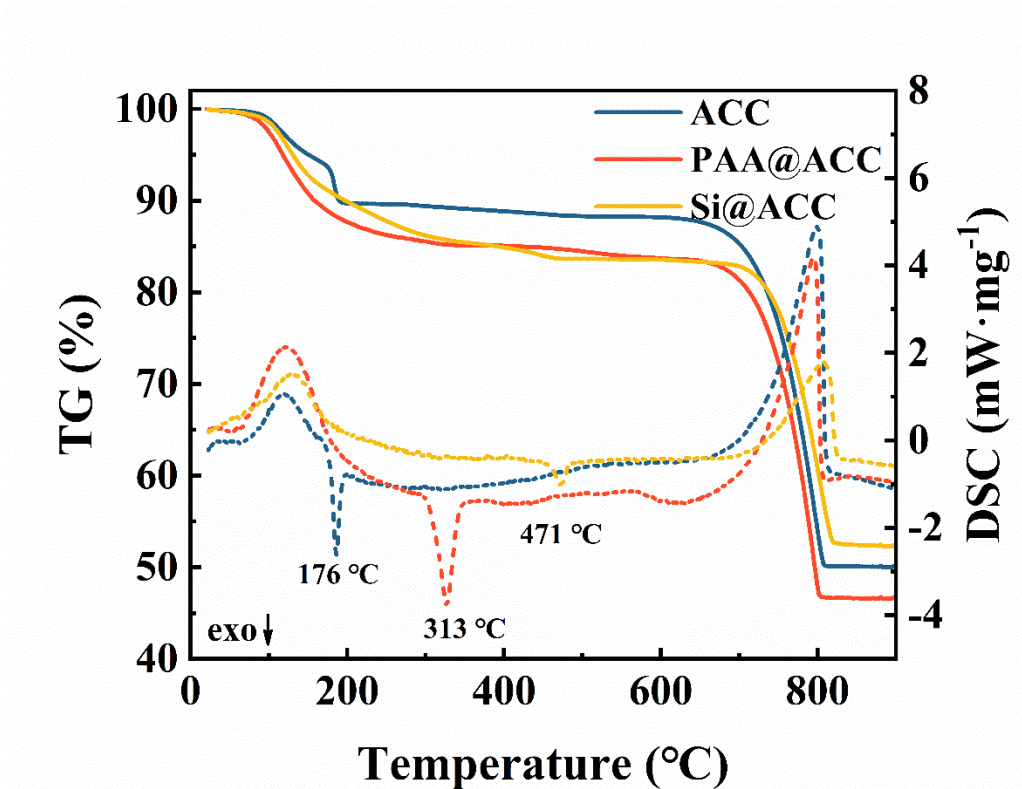


Fig. S7 TGA (solid lines) and DSC (dotted lines) curves for ACC, PAA@ACC, and Si@ACC.