Supporting Information

Photothermal conversion enabled temperature modulation for the growth of complex polymorphic architectures of calcium carbonate

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1. Supplementary figures

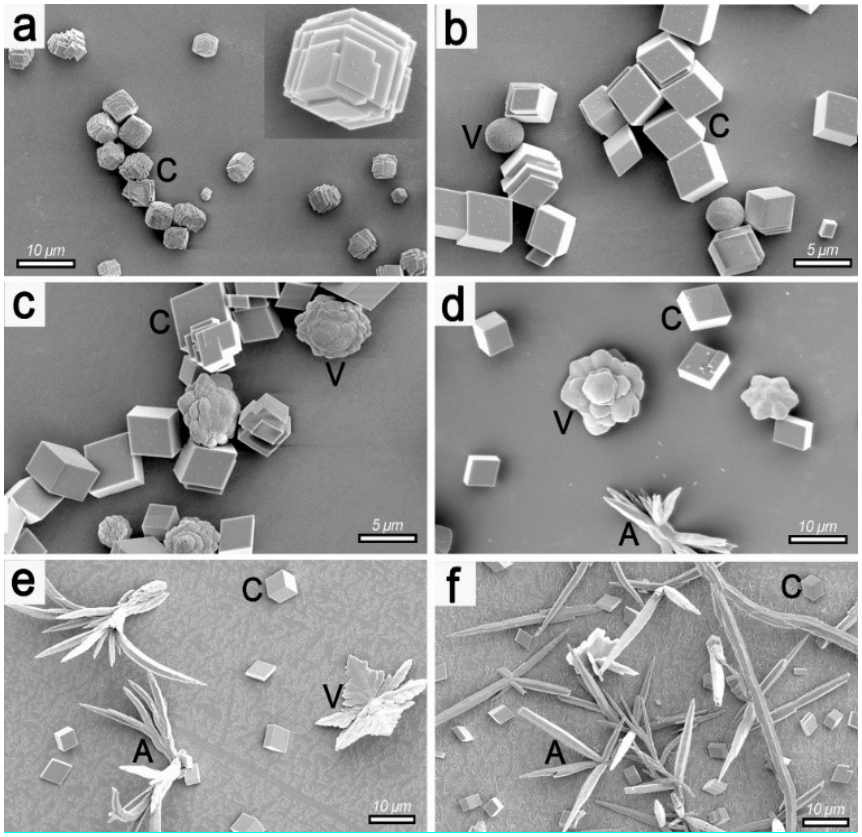

Figure S1. SEM images of different forms of $CaCO_3$ obtained at different temperatures. The reaction temperatures in (a)-(f) correspond to 5 °C, 25 °C, 35 °C, 45 °C, 55 °C, and 70 °C, respectively. Here C = calcite, A = aragonite, V = vaterite.

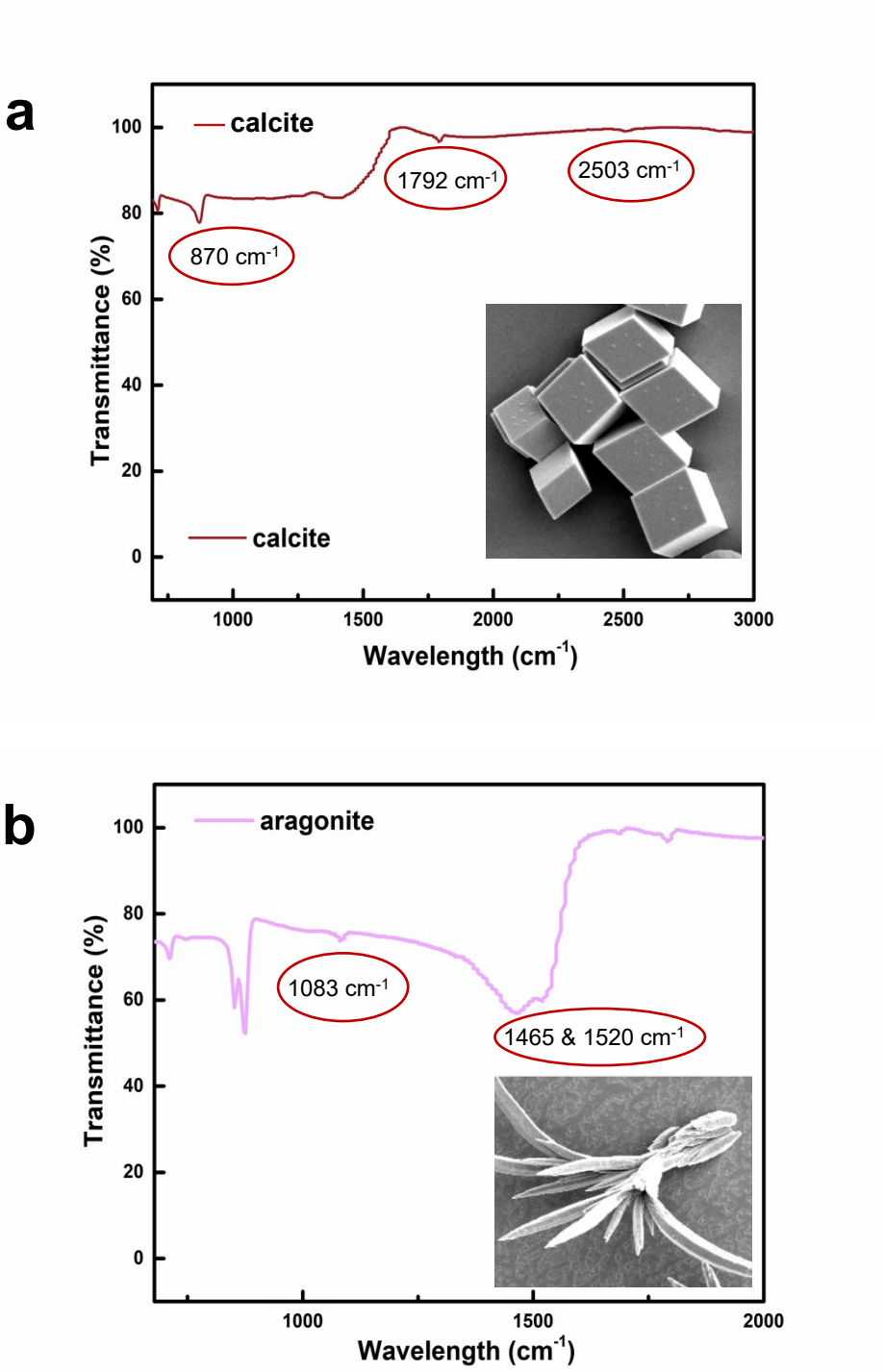

Figure S2. Infrared micro-spectra of calcite phase (a) and aragonite phase (b) that were obtained at 25 ℃ and 70 ℃, respectively. The inserts are the SEM images of the cubic-shaped calcite phase and branch-shaped aragonite phase, respectively. The corresponding peaks of calcite phase (870 cm^{-1}, 1792 cm^{-1}, and 2503 cm^{-1}) and aragonite phase (1083 cm^{-1} and 1520 cm^{-1}) are labelled with red circles.

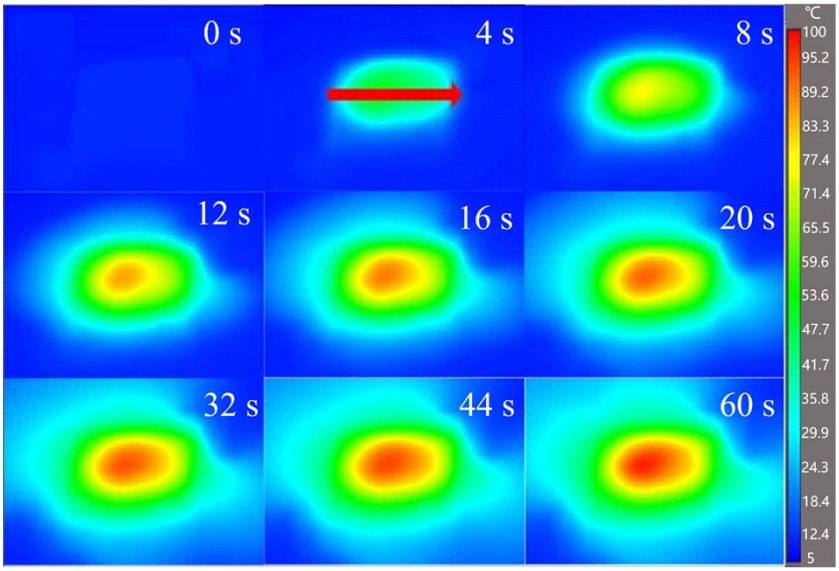

Figure S3. The IR images of cover glass at different times during the "cold-hot" temperature modulation process.

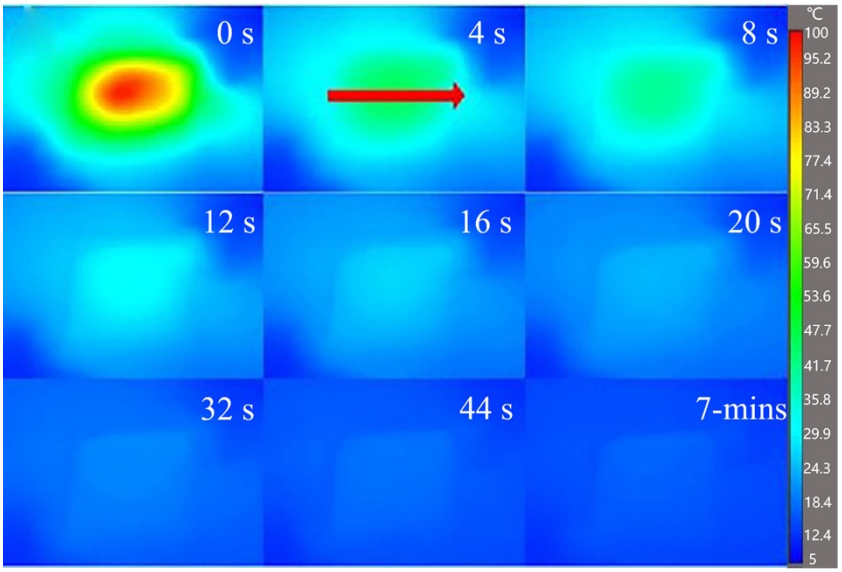

Figure S4. The IR images of cover glass at different times during the “hot-cold” temperature modulation process.

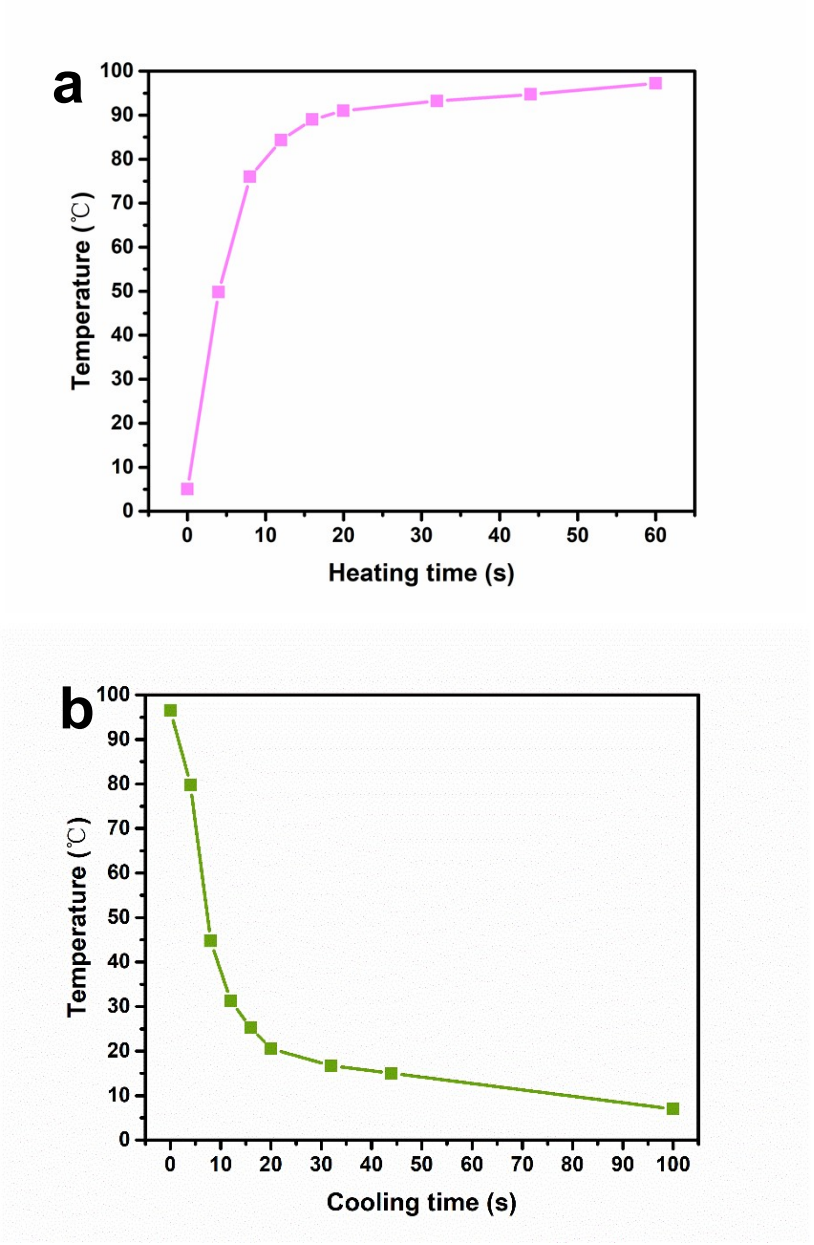

Figure S5. Time-dependent temperature change at the center of the illumination spot on the cover glass during (a) the heating period; (b) the cooling period.

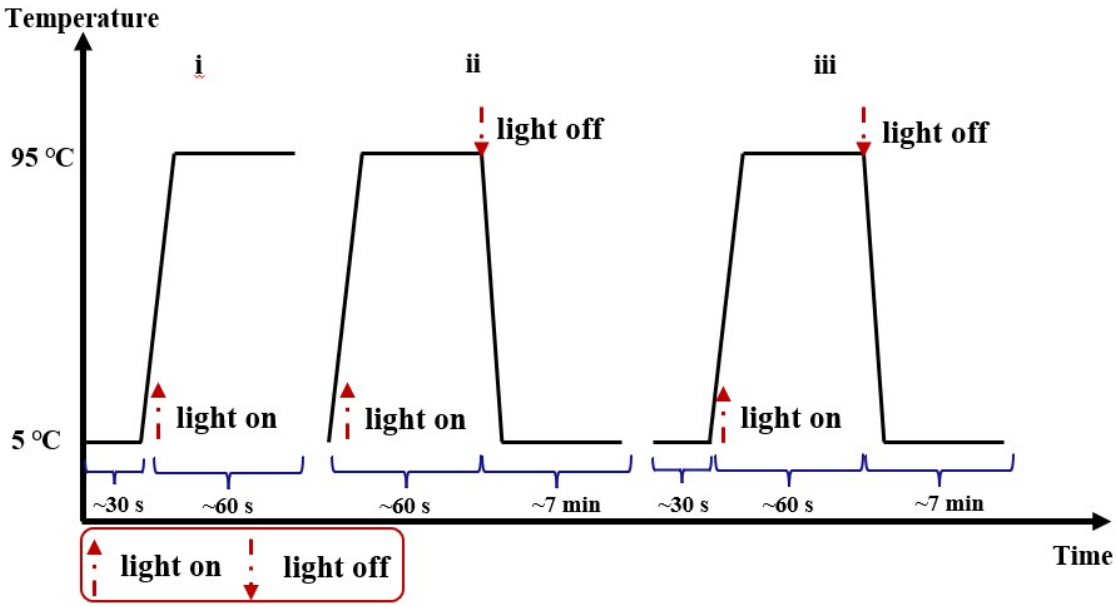

Figure S6. Illustration of the different temperature modulation processes for the growth of multi-polymorphic $CaCO_3$ structures: i) the "cold-hot" temperature modulation; ii) the "hot-cold" temperature modulation; iii) the three-step "cold-hot-cold" temperature modulation. The starting time of "on" and "off" of the light illumination is marked with red arrows.

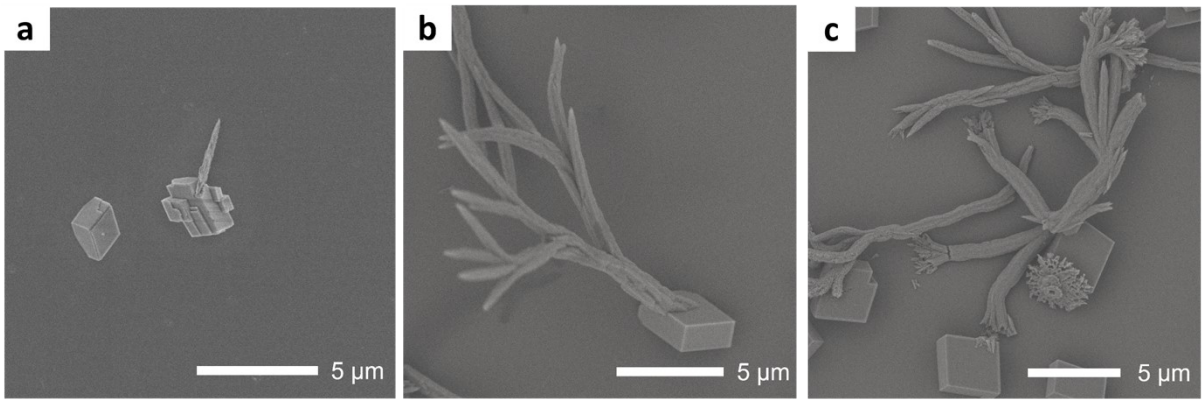

Figure S7. SEM images of multi-polymorphic $CaCO_3$ structures under the "cold-hot" temperature modulation. (a) Growth of $CaCO_3$ at cold condition for 30 sec followed by 30-sec at hot condition. (b) Growth of $CaCO_3$ at cold condition for 30 sec followed by 60-sec at hot condition. (c) Growth of $CaCO_3$ at cold condition for 30 sec followed by 90-sec at hot condition.

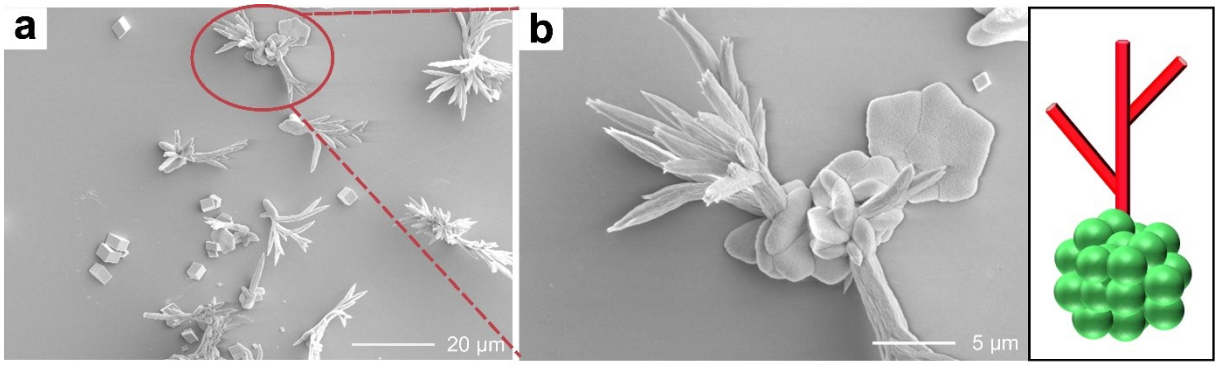

Figure S8. SEM images of bi-polymorphic A@V $CaCO_3$ structures (a) and the enlarged image of A@V structure (b) under the "cold-hot" temperature modulation. Note: the schematic on the right in (b) shows the bi-polymorphic structure. The red branch-shaped components represent aragonite phase, the green flower-shaped components represent vaterite phase.

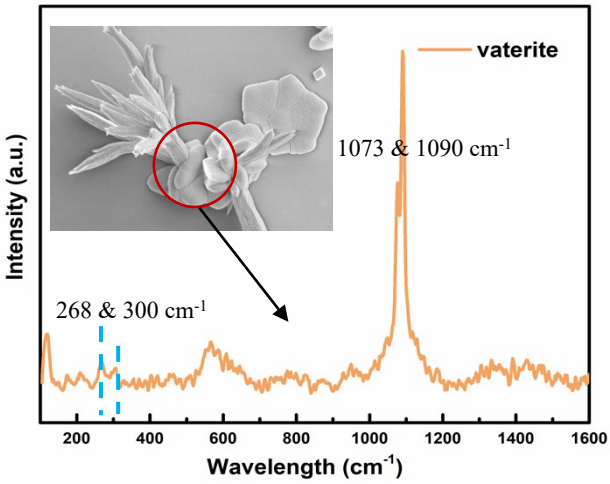

Figure S9. Raman micro-spectroscopy study confirmed the vaterite phase on the A@V structures under the "cold-hot" temperature modulation. The insert is the SEM image of the A@V $CaCO_3$ structure.

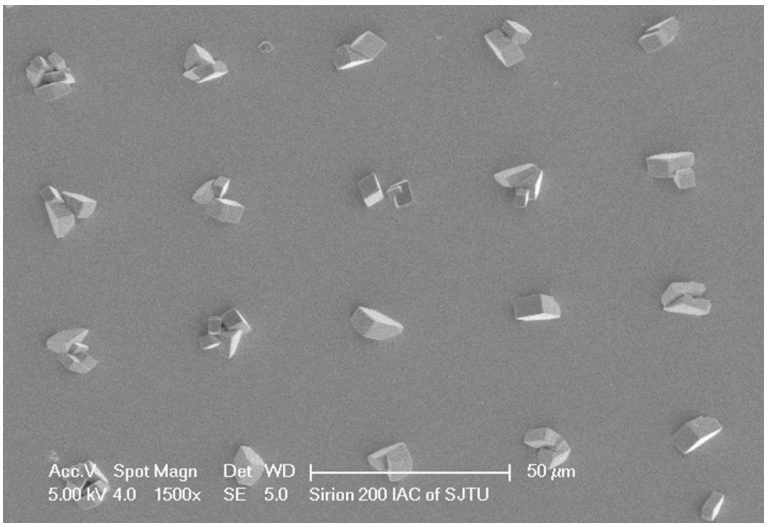

Figure S10. SEM image of the single-phase calcite arrays that grow at low-temperature condition on the chemically modified substrate.

2. Supplementary movies

Movie S1. Experimental operation of “cold-hot” temperature modulation process.

Movie S2. Experimental operation of “hot-cold” temperature modulation process.

Movie S3. Experimental operation of “cold-hot-cold” temperature modulation process.