

Supporting information

1, 1'-Ferrocenedicarboxylic acid/tetrahydrofuran induced precipitation of calcium carbonate with multi-level structure in water

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Experimental section

Materials: 1, 1'-ferrocenedicarboxylic acid ($C_{12}H_{10}FeO_4$, >98.0%), anhydrous calcium chloride ($CaCl_2$, analytical grade) and anhydrous ammonium carbonate ($(NH_4)_2CO_3$, analytical grade) were provided by Shanghai Aladdin Biochemical Technology Co., Ltd., China. Anhydrous tetrahydrofuran (C_4H_8O , analytical grade) was purchased from Chengdu Chron Chemical Reagent Co., Ltd., China.

With the goal of studying the precipitation of $CaCO_3$ in various organic solvents in the presence of FA, we mainly focused on its diverse behaviors. The total settling time was appropriate 6 hours.

Precipitation of $CaCO_3$: 0.1 M solutions of $CaCl_2$ in water were prepared stirring the previously dried salts 2 hours and dispersing with sonication for 30 minutes. Varied solutions of FA in THF (as reported in Table 1) was added into $CaCl_2$ solution under vigorous stirring. The color of the mixed solution gradually deepened and finally turned into brown-black. The solutions were filtered with 0.45 μm filters. A vial containing $(NH_4)_2CO_3$ (0.1057 g) was hung on the inner wall of the beaker where the mixed solution is located. Then the beaker was sealed twice by the sealing film. After precipitation for 6 hours, the solutions were centrifuged at 4500 g for 10 minutes. The samples were washed twice with THF, then the precipitate was collected by a centrifuge and dried in a vacuum drying oven at 60 $^{\circ}C$ for 24 hours.

Characterization: Powder XRD measurement was carried out using an X-ray diffractometer (SHIMADZU XRD-6100) with Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$) at 40 kV and 30 mA. Sample morphology was determined using an SEM (Prisma E, Thermo Fisher Scientific, China) and TEM (JEM-2100 Plus, JEOL Ltd., Japan). High-resolution mass spectra are recorded on a Shimadzu LCMS-IT-TOF instrument in the ESI mode. The absorption spectra in the middle IR range (4000–400 cm^{-1}) are recorded using a Nicolet Fourier-Transform IS10 instrument (Thermo Scientific, USA). The FTIR spectra are recorded at a resolution of 2 cm^{-1} and with an average of 16 scans per sample.

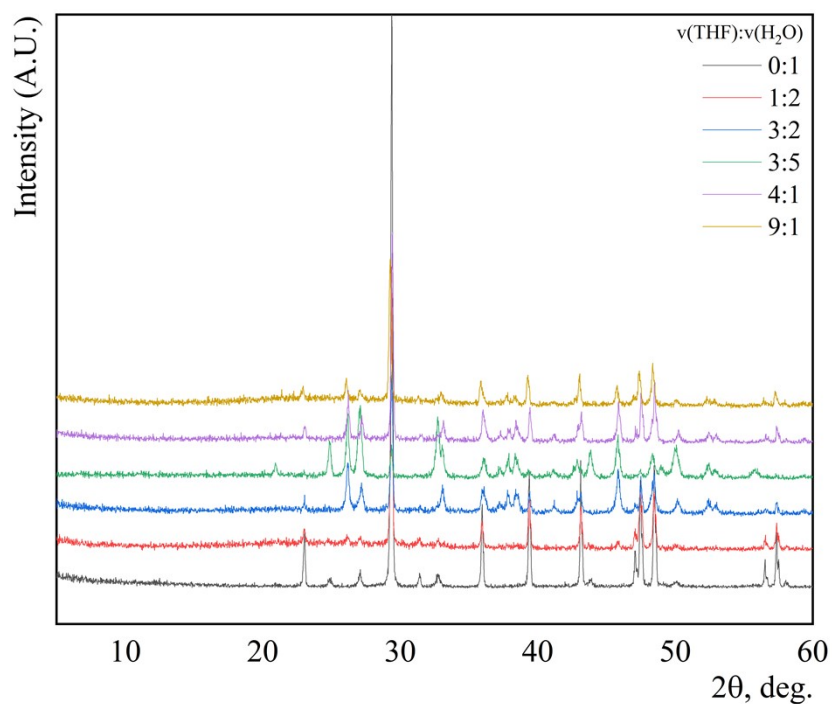


Figure S1 Influence of solvent ratios (H₂O-THF) on the precipitation of CaCO₃: XRD results of products of v(THF)=0 mL, v(H₂O)=100 mL; v(THF)=50 mL, v(H₂O)=100 mL; v(THF)=60 mL, v(H₂O)=100 mL; v(THF)=150 mL, v(H₂O)=100 mL; v(THF)=200 mL, v(H₂O)=50 mL; v(THF)=180 mL, v(H₂O)=20 mL.

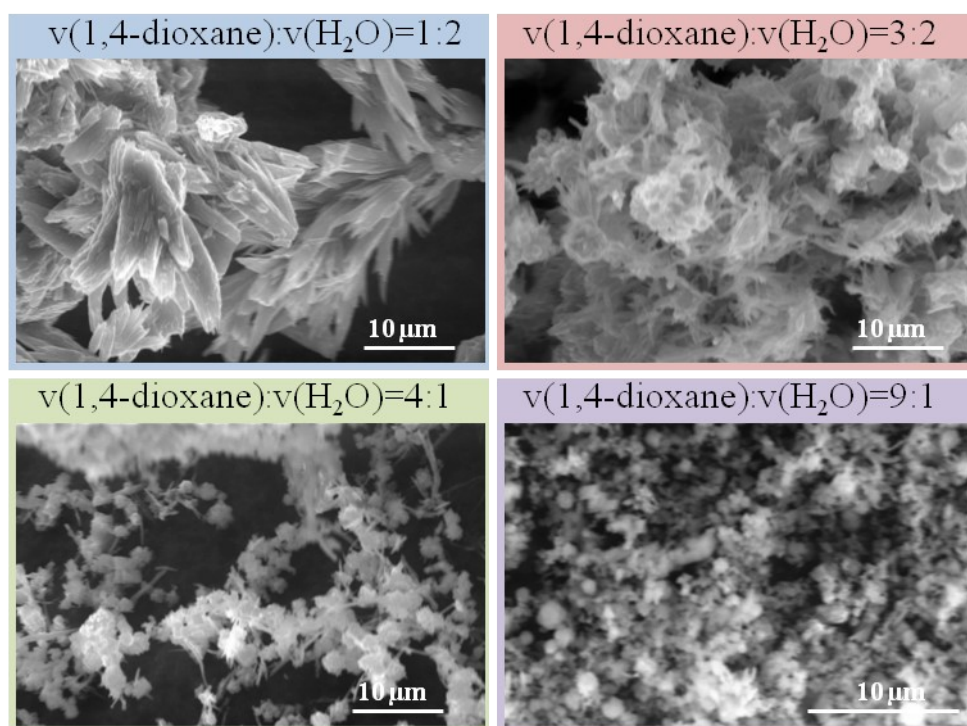


Figure S2 Influence of solvent ratios (H₂O -1,4-dioxane) on the precipitation of CaCO₃: SEM images of products of v(H₂O): v(1,4-dioxane)=1:1; v(H₂O): v(1,4-dioxane)=1:1.25; v(H₂O): v(1,4-dioxane)=1:1.5; v(H₂O): v(1,4-dioxane)=1:1.75.

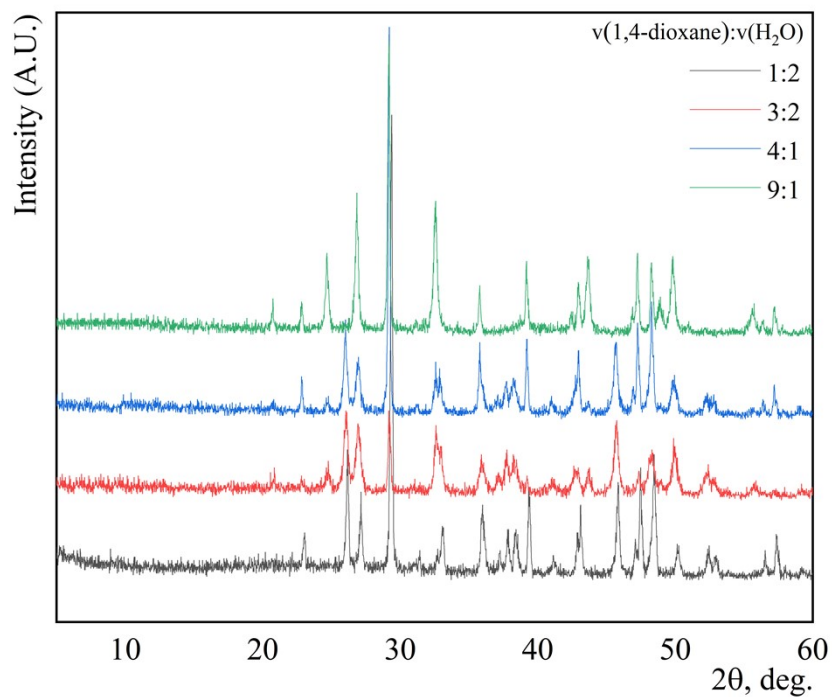


Figure S3 Influence of solvent ratios (H₂O -1,4-dioxane) on the precipitation of CaCO₃; XRD results of products of v(H₂O): v(1,4-dioxane)=1:1; v(H₂O): v(1,4-dioxane)=1:1.25; v(H₂O): v(1,4-dioxane)=1:1.5; v(H₂O): v(1,4-dioxane)=1:1.75.

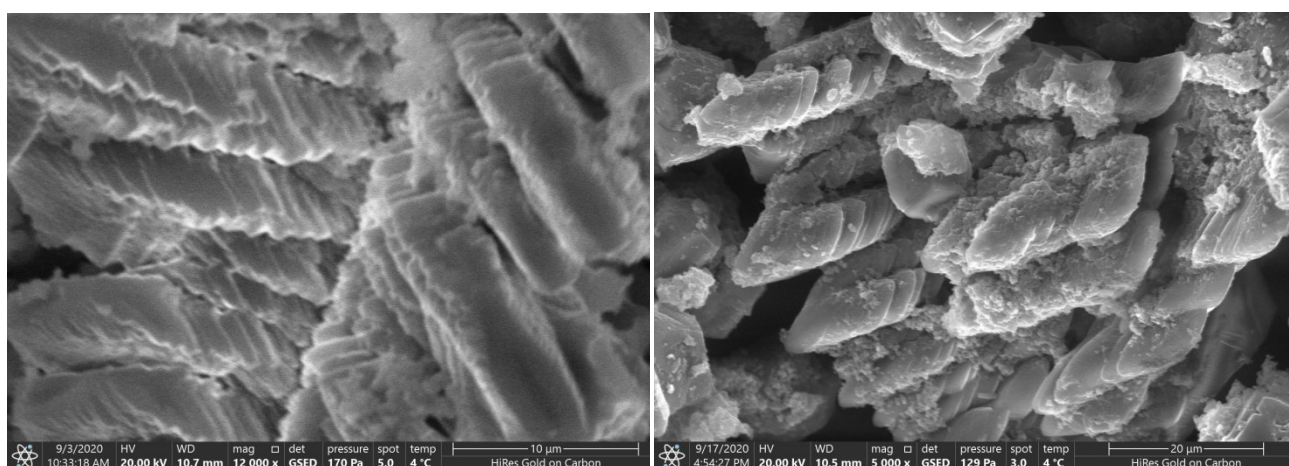


Figure S4 SEM analysis of the products from reaction c3 (Ca²⁺:FA=1:0.5) and c4 (Ca²⁺:FA=1:0.75) with the magnification of 12000 and 5000 times were performed.

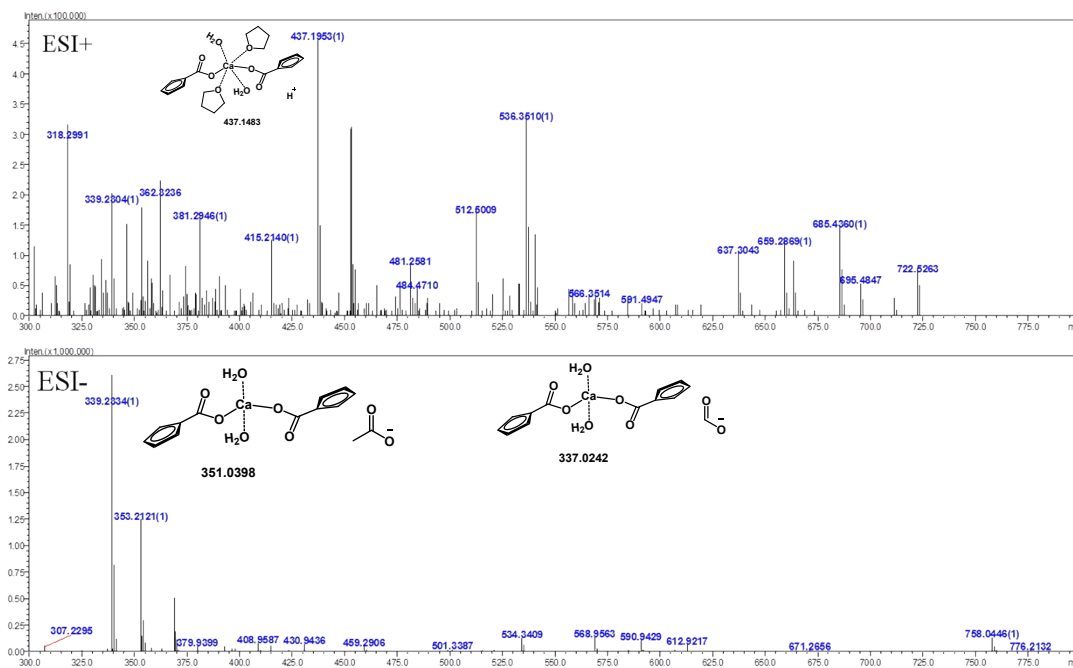


Figure S5 The original HRMS results of volume ratio of solvent ($\text{H}_2\text{O}:\text{THF}=1:10$), CaCl_2 (1 mM) and FA (2 mM) in the ESI mode.

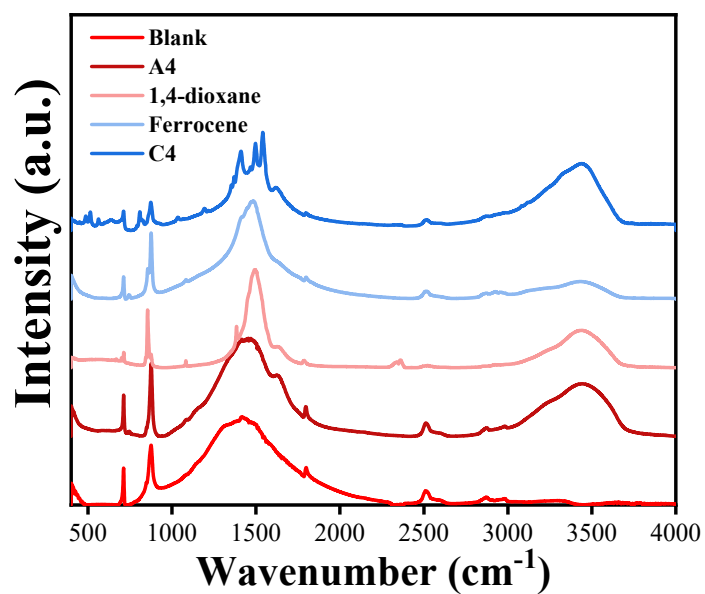


Figure S6 Complete FTIR spectrum of fig. 3D.