

Supporting Information

A rapid, green and versatile route to synthesize metal carbonate superstructures *via* the combination of regenerated silk fibroin and compressed CO₂

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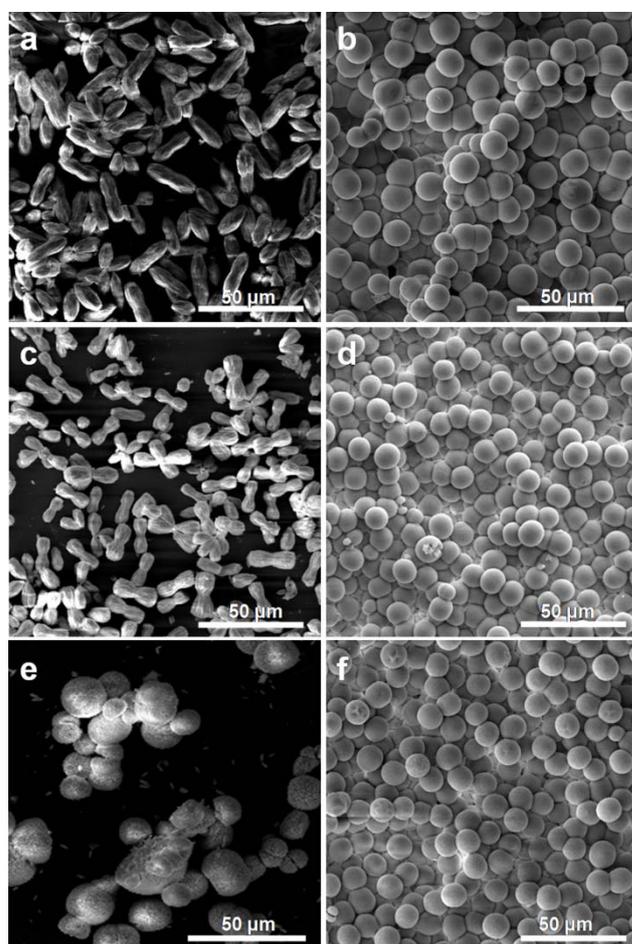


Fig. S1 SEM images of BaCO₃ particles prepared in different concentration RSF solution with 5.0 MPa compressed CO₂ at 60 °C after 60 min mineralization: (a) 0.01 wt %; (b) 0.1 wt %; (c) 0.5 wt %; (d) 1 wt %; (e) 1.5 wt % and (f) 3 wt %.

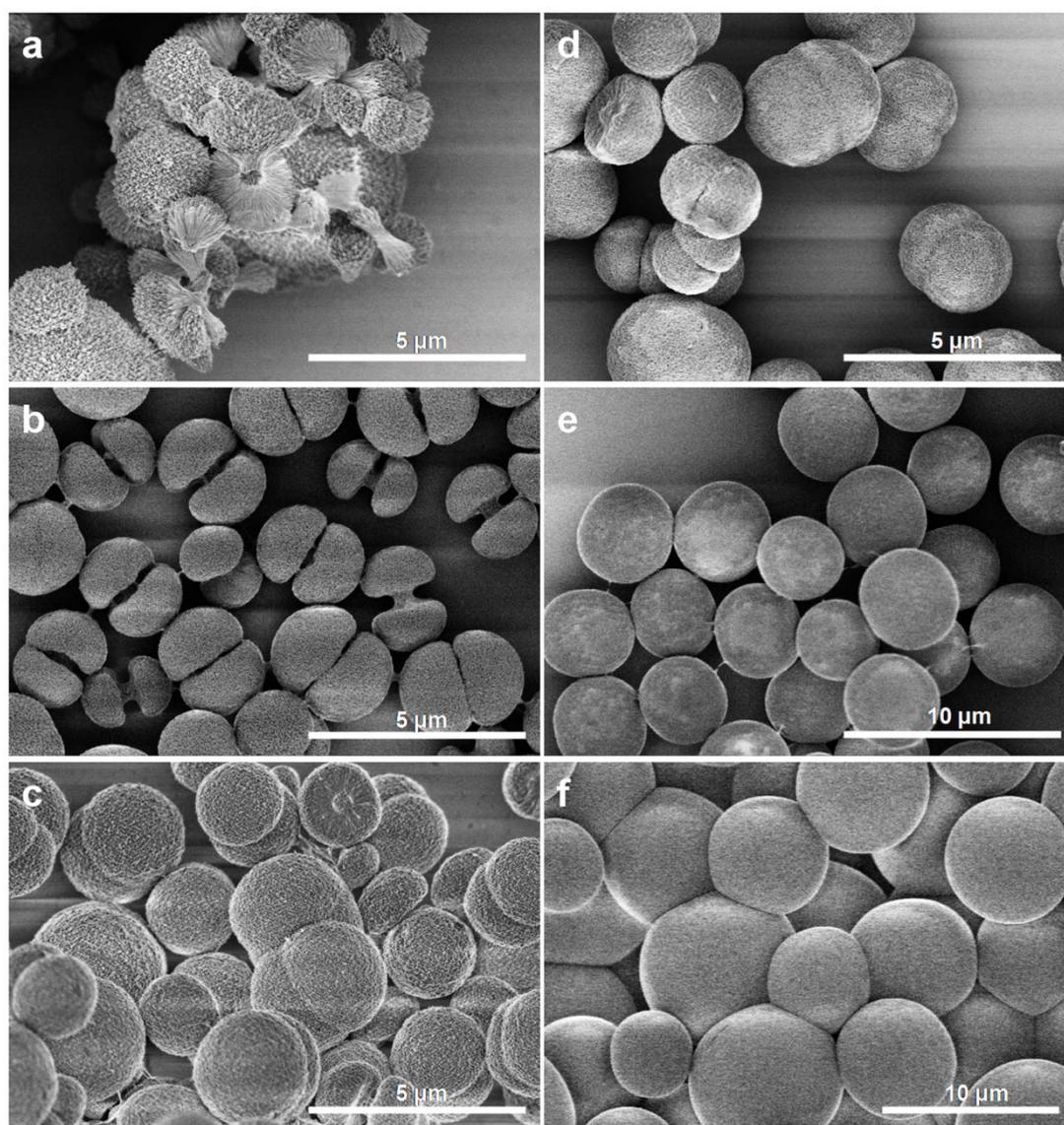


Fig. S2 FESEM images of SrCO₃ generated in different concentration RSF solution with 5.0 MPa compressed CO₂ at 60 °C after 60 min mineralization: (a) 0.01 wt %; (b) 0.1 wt %; (c) 0.5 wt %; (d) 1 wt %; (e) 1.5 wt % and (f) 3 wt %.

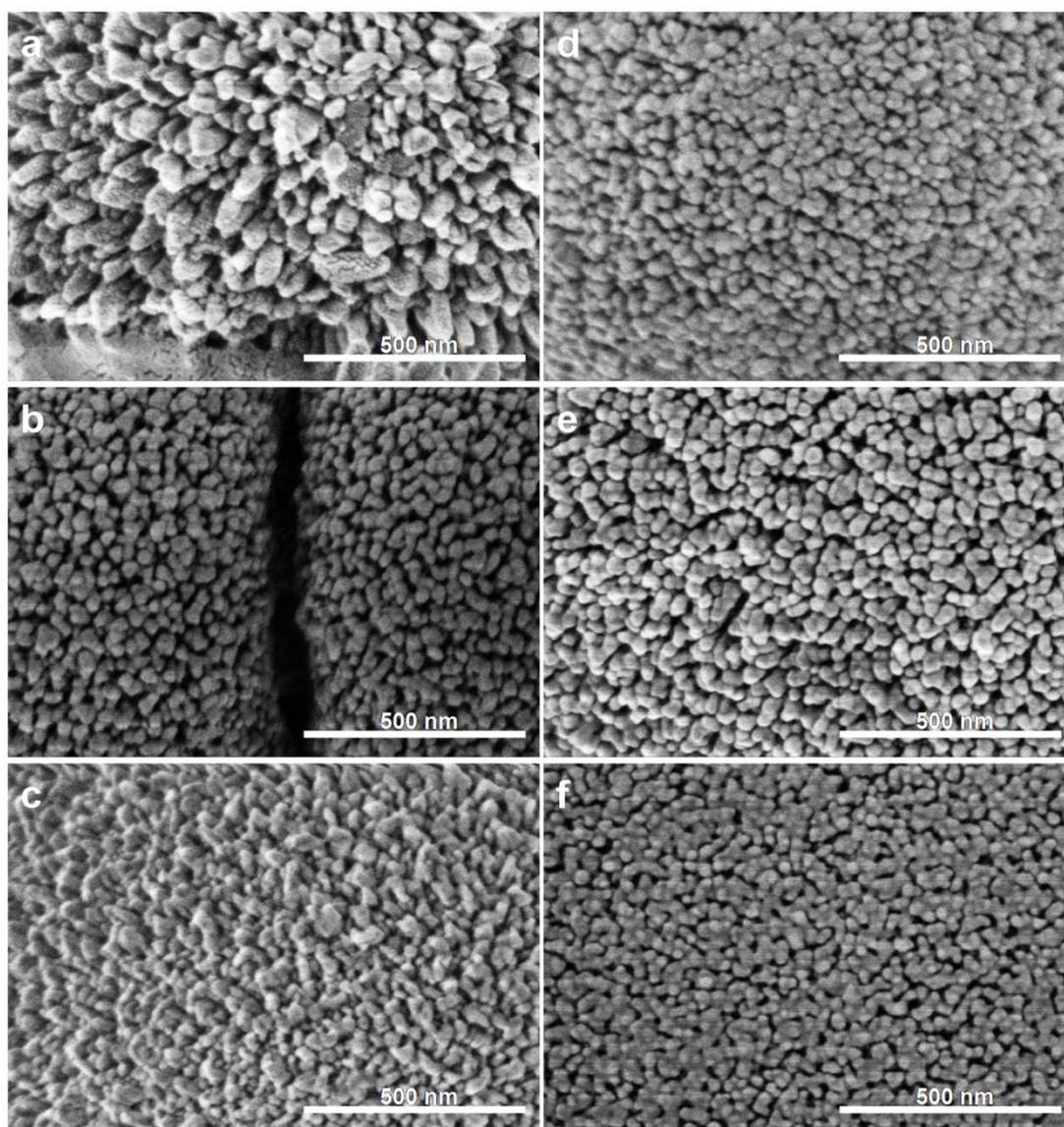


Fig. S3 FESEM images of SrCO₃ generated in different concentration RSF solution with 5.0 MPa compressed CO₂ at 60 °C after 60 min mineralization: (a) 0.01 wt %; (b) 0.1 wt %; (c) 0.5 wt %; (d) 1 wt %; (e) 1.5 wt % and (f) 3 wt %.

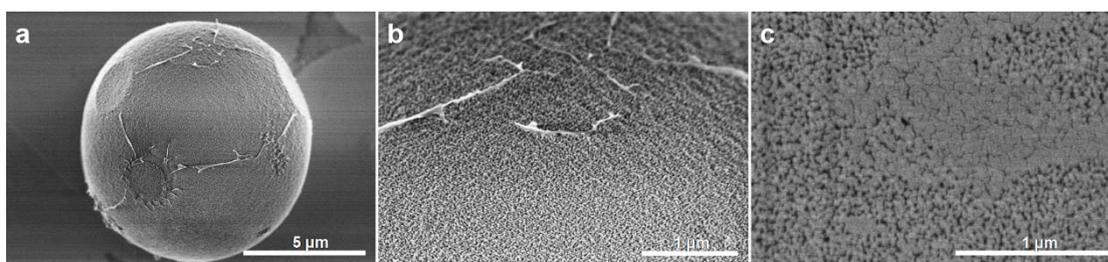


Fig. S4 FESEM images of SrCO₃ obtained in 3 wt% concentration RSF solution with 5.0 MPa compressed CO₂ at 60 °C: (a) panoramic image of SrCO₃; (b) and (c) enlarged image of (a). The fuzzy area in Fig. S4c are flexible RSF chains.

In Fig. S4a and b, the filiform on crystal surface is the bigger RSF which is well-assembled by many single RSF chains. It shows that most of these RSF chains are almost completely released from crystals. However, Fig. S4c shows many RSF chains which maintain flexible chain are still adsorb on crystal surface, it is not easy to remove them due to part of these chains are still intercalated into crystal.

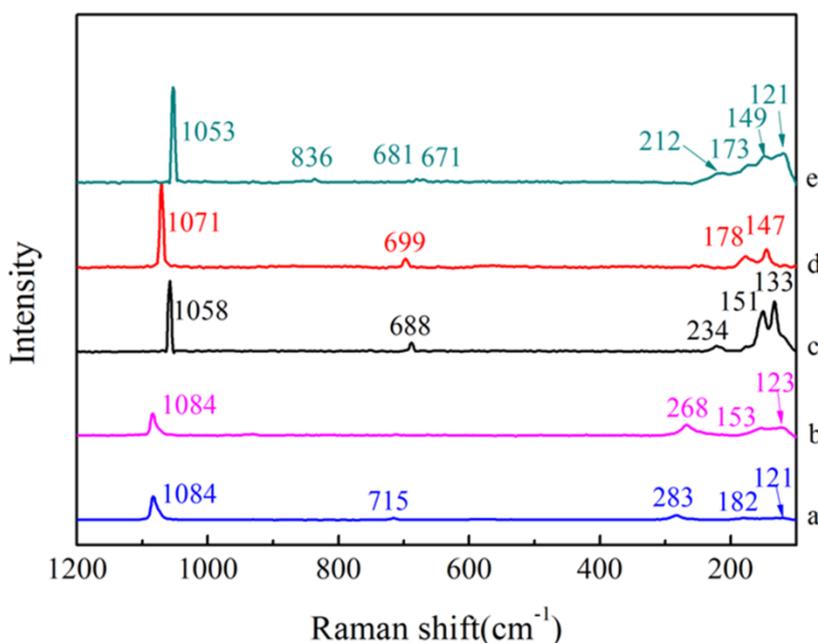


Fig. S5 Raman spectra of different metal carbonates crystallized in 1.5 wt% RSF solution at 60 °C with 5.0 MPa compressed CO₂ after 60 min mineralization: (a) MnCO₃; (b) CdCO₃; (c) BaCO₃; (d) SrCO₃ and (e) PbCO₃.

In Raman spectra of metal carbonates, the peaks range from 1000 to 1100 cm^{-1} are assigned to symmetric C-O stretching (ν_1) of CO_3^{2-} groups, while the peaks locate between 650 and 720 cm^{-1} are referred to in-plane bending (ν_4) of CO_3^{2-} groups, and the peaks seat between 800 and 850 cm^{-1} are attributed to out-plane bending (ν_2) of CO_3^{2-} groups, all of above peaks are assigned to internal mode of CO_3^{2-} groups, suggesting that the peaks are not significantly affected by different metal ions. As shown in Fig. S5, the metal ions only make peak position shift in these sections. Moreover, the peaks locate at 100 and 290 cm^{-1} are assigned to lattice vibration (external mode) of CO_3^{2-} groups.^{1,2} In the section, the peaks are associated with the metal ions and CO_3^{2-} groups along different axis and with rotation of CO_3^{2-} groups, so the peaks are evidently impacted with changing the metal ions. The Raman spectra of these metal carbonates are identified from other references,³⁻⁵ as shown in Fig. S5.

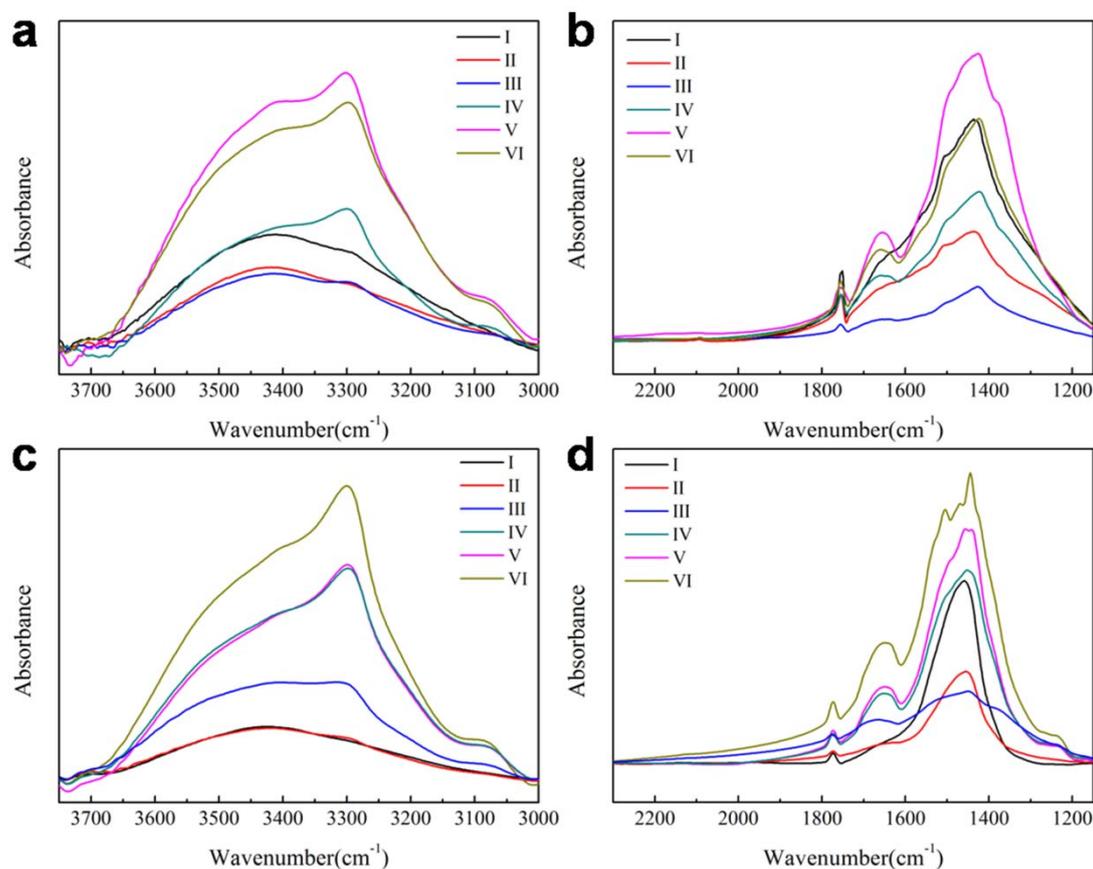


Fig. S6 FTIR spectra of BaCO_3 (a, b) and SrCO_3 (c, d) prepared with different RSF concentration: (I) 0.01 wt %; (II)

0.1 wt %; (III) 0.5 wt %; (III) 1 wt %; (IV) 1.5 wt % and (V) 3 wt %.

In FTIR spectra, the band at 1650 cm^{-1} and 3280 cm^{-1} are assigned to the amide I and the N-H stretching of RSF chains. When additive RSF is fewer than 0.1wt % intensity of RSF feature peak is very weak, with the increase of RSF concentration, the peak intensity is obviously improved, suggesting some RSF are residual in crystals during the crystallization.

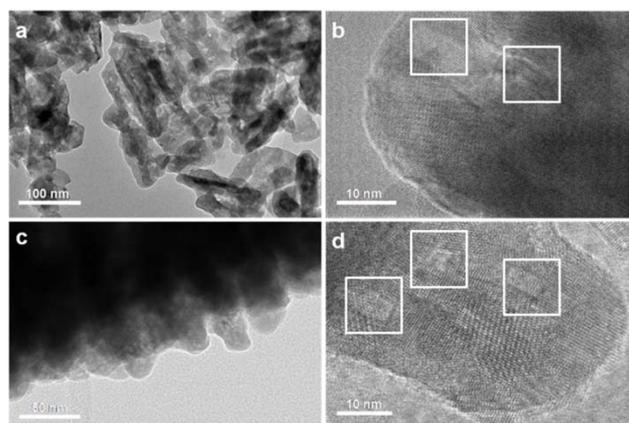


Fig. S7 TEM and HRTEM images of BaCO_3 (a, b) and SrCO_3 (c, d) obtained in different concentration RSF solution with 5.0 MPa compressed CO_2 at 60°C . The marked areas with square shape are the mesopores and defects.

Fig. S7a and c shows the subunits of BaCO_3 and SrCO_3 are needle-like. The HRTEM images indicate the both crystals have well-crystallized structure (Fig. S7b and d); however, many defects can be seen in these TEM images. These defects probably result from the intercalation of RSF chains into crystals to destroy the orderly crystallization process of crystals.

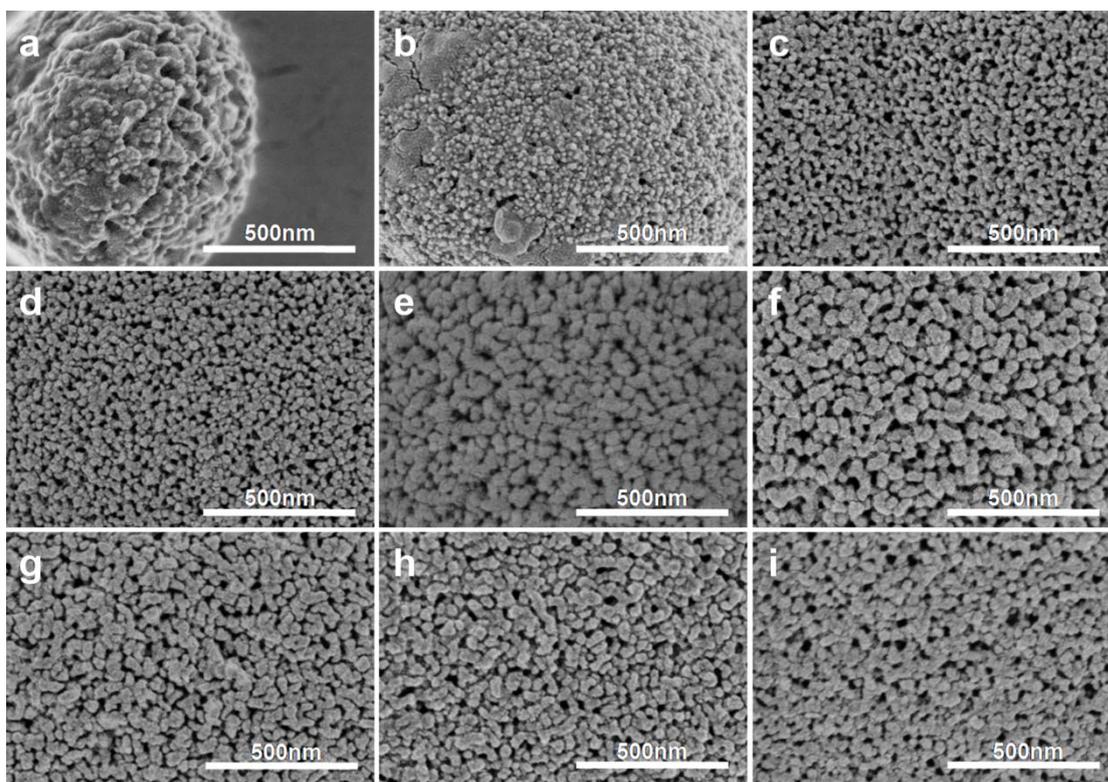


Fig. S8 Enlarged FE-SEM images of BaCO_3 crystal prepared after different mineralization time in 1.5 wt % RSF solution at 60 °C with 5.0 MPa compressed CO_2 at 60 °C: (a) 5 min; (b) 8 min; (c) 10 min; (d) 13 min; (e) 15 min; (f) 20 min; (g) 25 min; (h) 45 min and (i) 60 min.

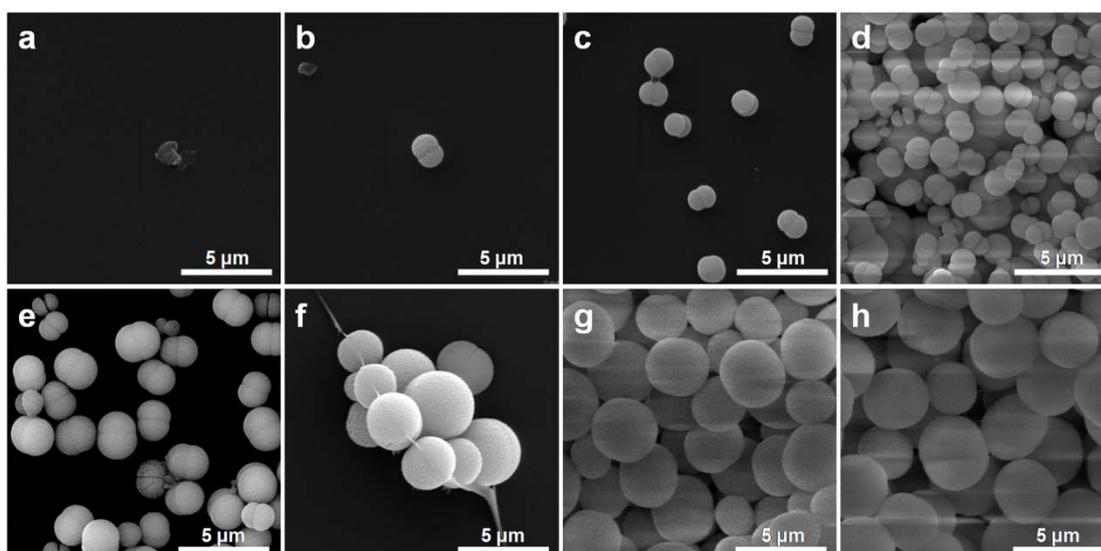


Fig. S9 SEM images of SrCO_3 crystal prepared after different mineralization time in 1.5 wt % RSF solution at 60 °C with 5.0 MPa compressed CO_2 at 60 °C: (a) 10 min; (b) 15 min; (c) 18 min; (d) 20 min; (e) 30 min; (f) 45 min; (g) 60 min and (h) 90 min.

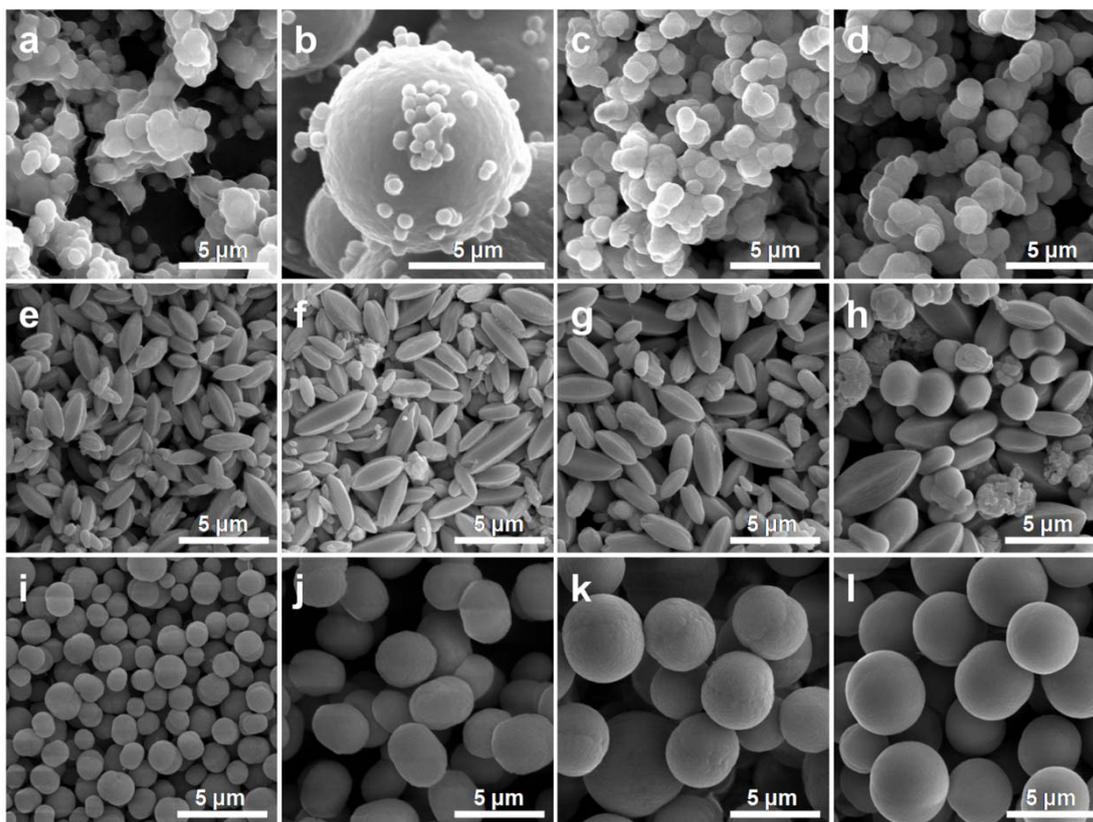


Fig. S10 SEM images of MnCO_3 (top), PbCO_3 (middle) and CdCO_3 (bottom) obtained in different RSF solution at 60 °C for 60 min with 5.0 MPa compressed CO_2 : (a, e, i) 0.1 wt%; (b, f, j) 0.5 wt%; (c, g, k) 1 wt% and (d, h, l) 1.5 wt %.

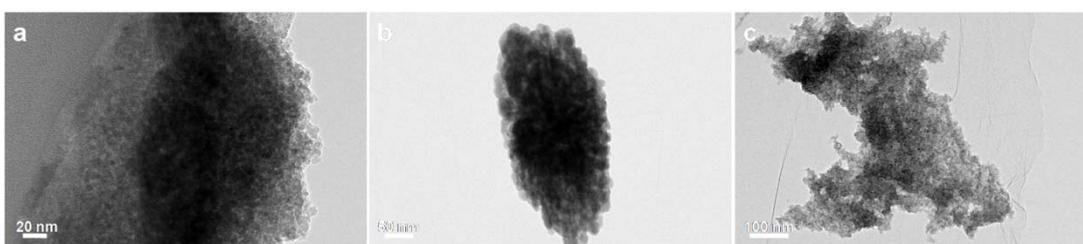


Fig. S11 TEM images of cross section of metal carbonates prepared in 1.5 wt % RSF solution at 60 °C for 60 min with 5.0 MPa compressed CO_2 : (a) MnCO_3 ; (b) PbCO_3 and (c) CdCO_3 .

TEM images show the MnCO_3 and CdCO_3 particles are formed by the random aggregation of spherical nanoparticles (Fig. S11a and c); however, the PbCO_3 particles are formed by the orderly

assemble of needle-like subunits which is similar to BaCO_3 and SrCO_3 crystals (Fig. S11b).

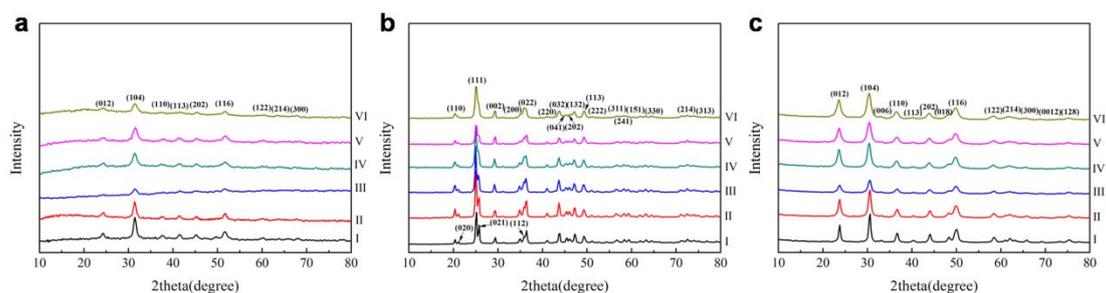


Fig. S12 XRD patterns of MnCO_3 (a), PbCO_3 (b) and CdCO_3 (c) prepared in different RSF solution at 60 °C for 60 min with 5.0 MPa compressed CO_2 : (I) 0 wt%; (II) 0.1 wt%; (III) 0.5 wt%; (IV) 1 wt%; (V) 1.5 wt% and (VI) 3 wt%. The parameters of crystal are referenced to JCPDF (86-0173), (76-2056) and (42-1342).

Fig. S12a and c show the independence of polymorph of MnCO_3 and PbCO_3 particles on RSF concentration; however, the peaks on XRD patterns of PbCO_3 crystals are evidently influenced by changing the RSF concentration (Fig. S12b). Three peaks which are assigned to (020), (021) and (112) faces of cerussite gradually disappear with the increase of RSF concentration, indicating that RSF chains can impact or regulate the polymorph of PbCO_3 crystals.

References

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