

Figure S1 Representative SEM images for energy-dispersive spectroscopy analysis on the calcium carbonates products formed from mother solutions with varying  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  ratios at  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  of 2. The  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  ratios in the SEM images were (a) 1.39; (b) 3.89.

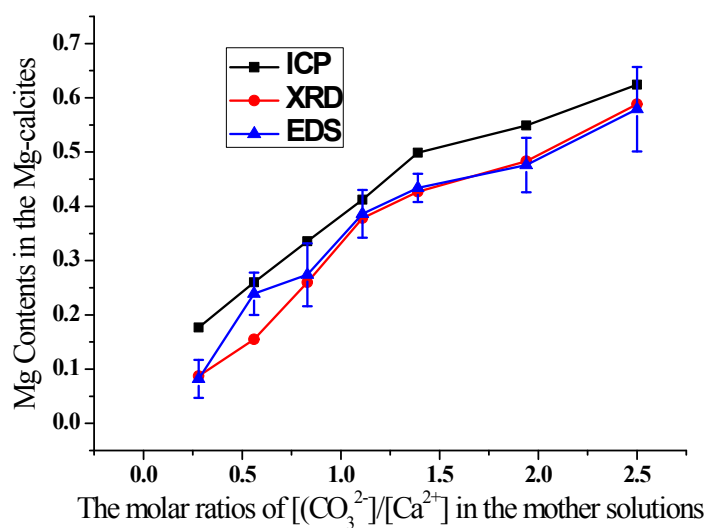


Figure S 2 Characterizations on the Mg contents for the Mg-calcites in pure phase obtained at  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  of 2 when the molar ratios of  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  were relatively low by using ICP, EDS and XRD characterizations. The error bars of the EDS data represent standard deviation.

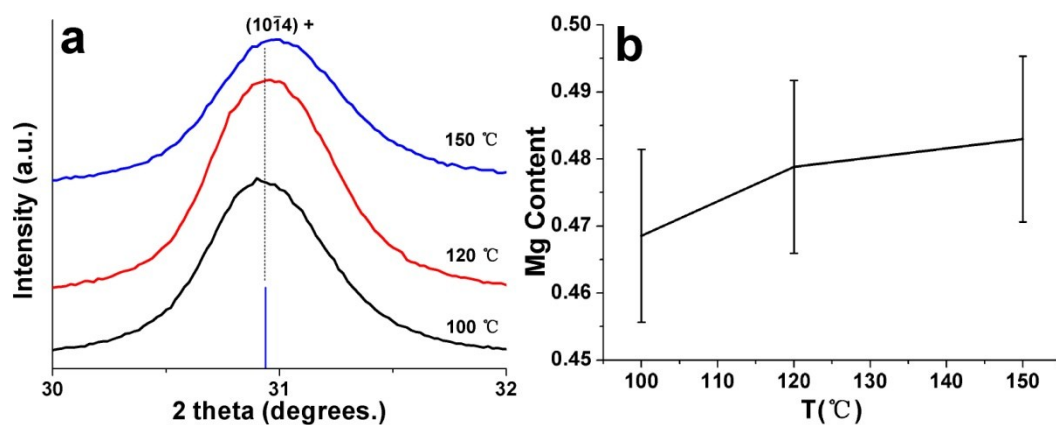


Figure S3. The high Mg-calcites in pure phase obtained after hydrothermal process under varying temperatures for 24 hours while keeping the molar ratio of  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  as 1.67 and the molar ratio of  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  as 4.

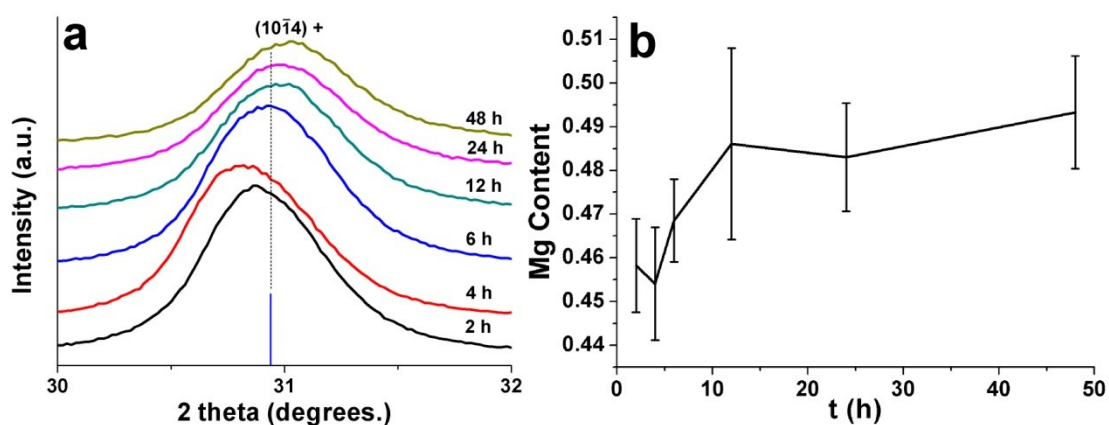


Figure S4. The high Mg-calcites in pure phase obtained after hydrothermal process at 150 °C for varying times while keeping the molar ratio of  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  as 1.67 and the molar ratio of  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  as 4.

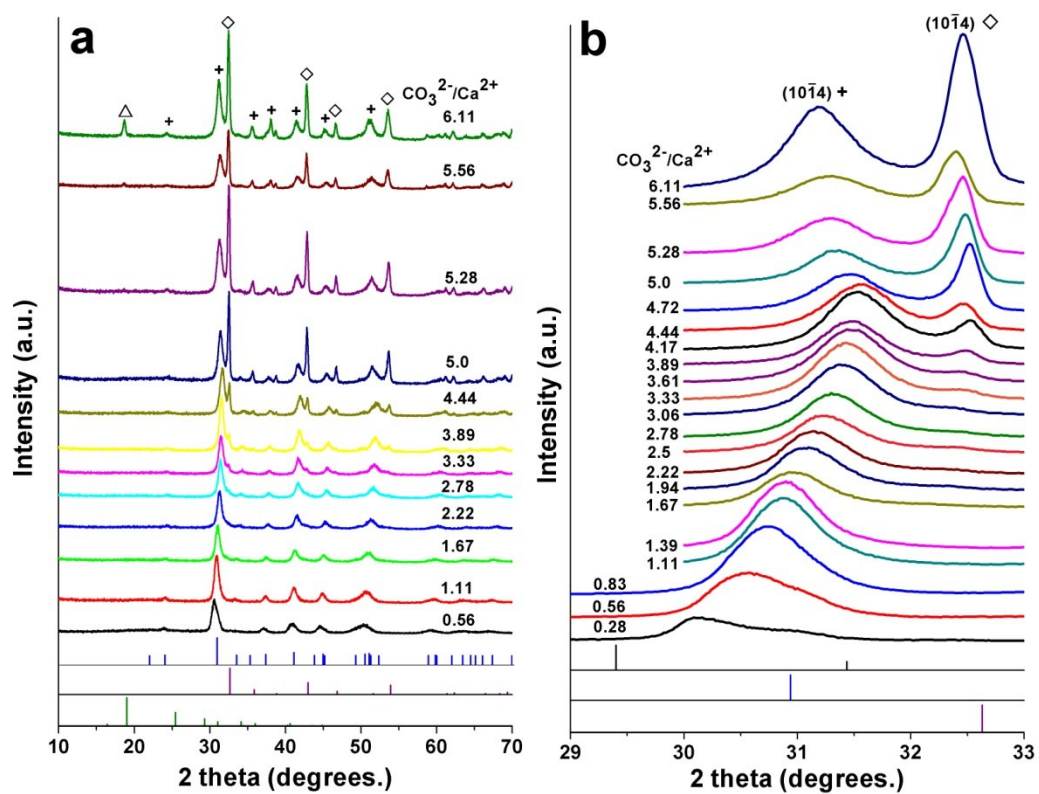


Figure S5. XRD patterns for the calcium carbonate products prepared from mother solutions with varying  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  ratios at  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  of 4. Meaning of symbols (+: Mg-calcite,  $\diamond$ : Ca-magnesite,  $\Delta$ : brucite,  $\circ$ : aragonite). Reference patterns: dolomite, Blue, JCPDS 75-1759; magnesite, purple, JCPDS 88-1802; magnesium hydroxide, green, JCPDS 74-2220, calcite, black, .

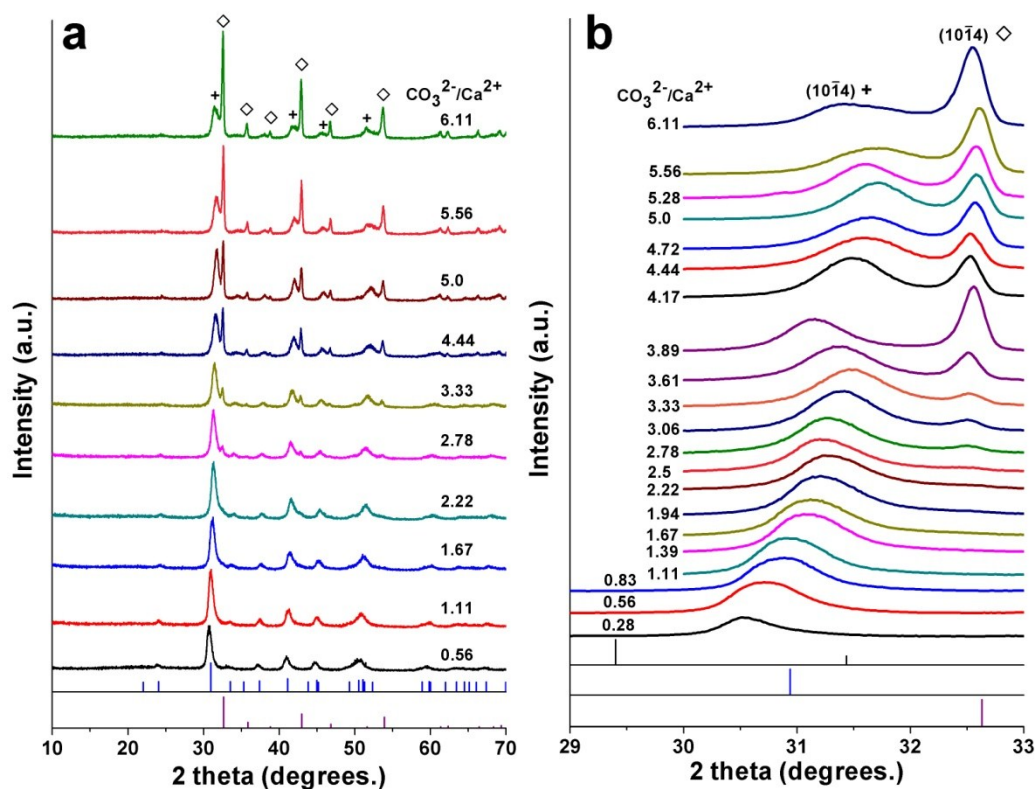


Figure S6. XRD patterns for the calcium carbonate products prepared from mother solutions with varying  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  ratios at  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  of 6. Meaning of symbols (+: Mg-calcite,  $\diamond$ : Ca-magnesite,  $\Delta$ : brucite,  $\circ$ : aragonite). Reference patterns: dolomite, Blue, JCPDS 75-1759; magnesite, purple, JCPDS 88-1802; calcite, black.

Table S1 Representative pH values for the supernatant solutions after the hydrothermal process for the reaction systems at different  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$  and  $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$  molar ratios.

$[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$ $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$	3.61	3.89	5.56	6.11
2	9.42	9.83	9.99	10.1
4	7.10	7.24	9.14	9.69
6	6.70	6.71	7.32	7.54