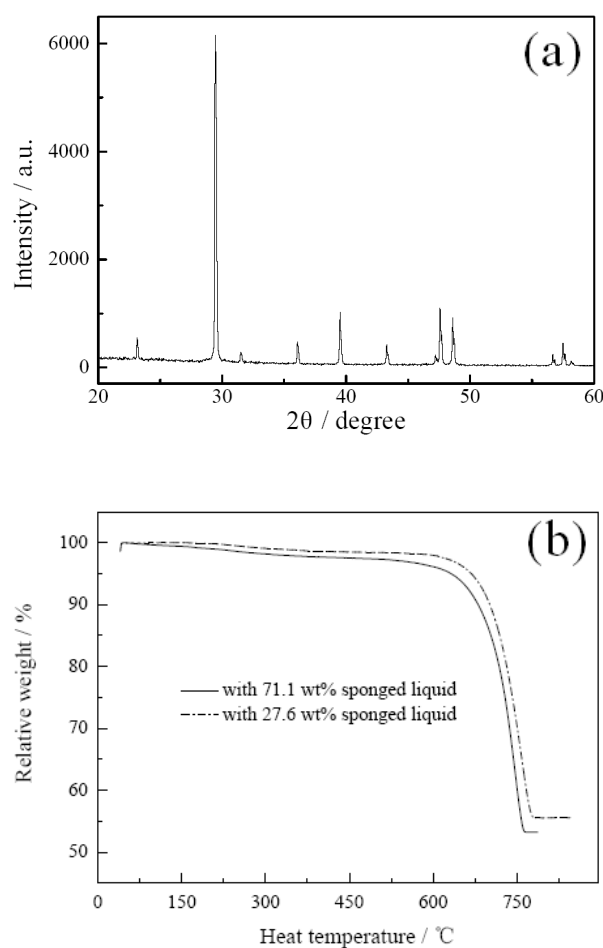


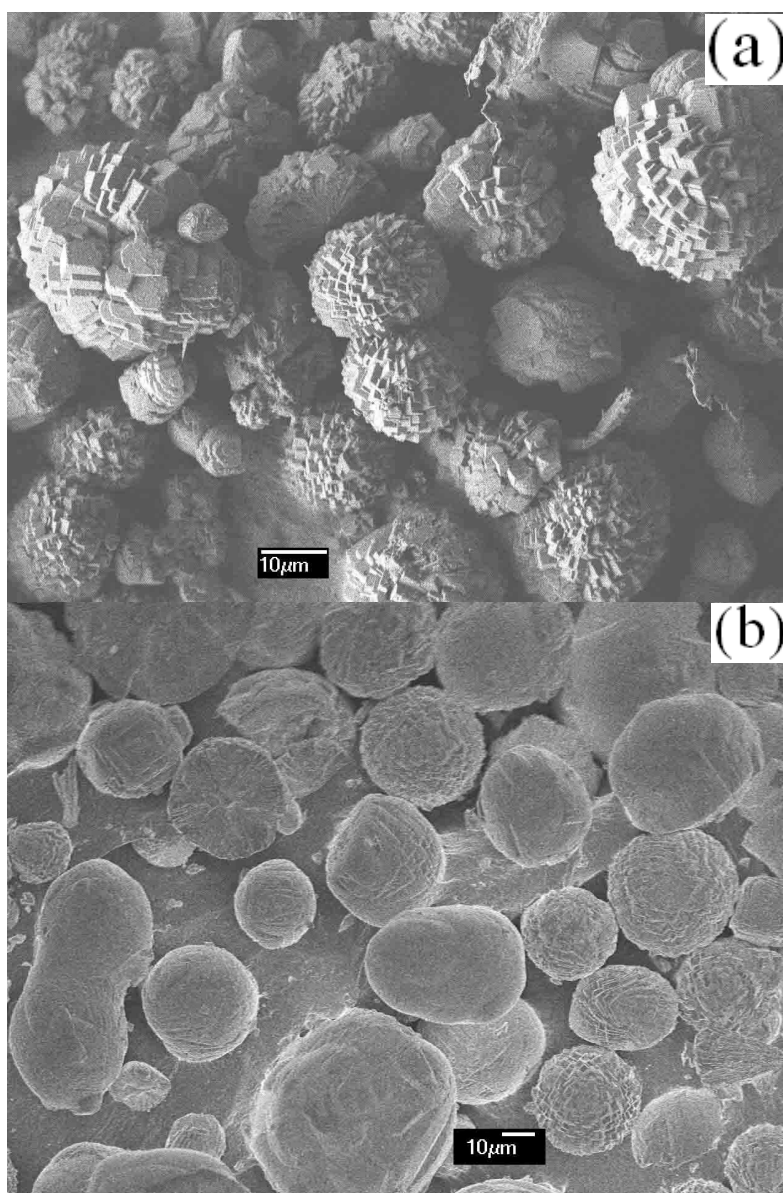
# Supporting Information

## Structure-Function Relationship of Calcium Alginate Hydrogels: A Novel Crystal-Forming Engineering

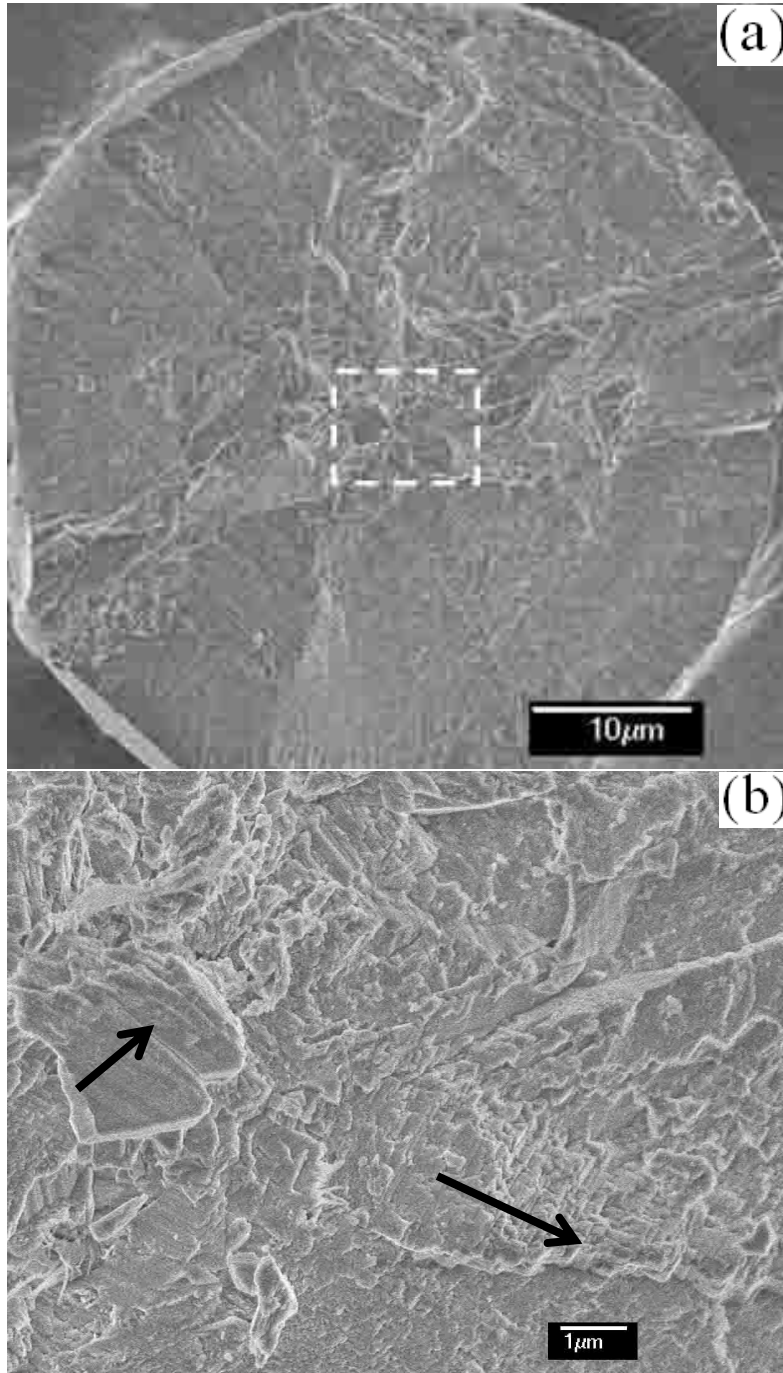
*Xinping Li,<sup>†</sup> Qiang Shen,<sup>\*,†</sup> Yunlan Su,<sup>‡</sup> Fang Tian,<sup>†</sup> Ying Zhao,<sup>‡</sup> and Dujin Wang<sup>‡</sup>*



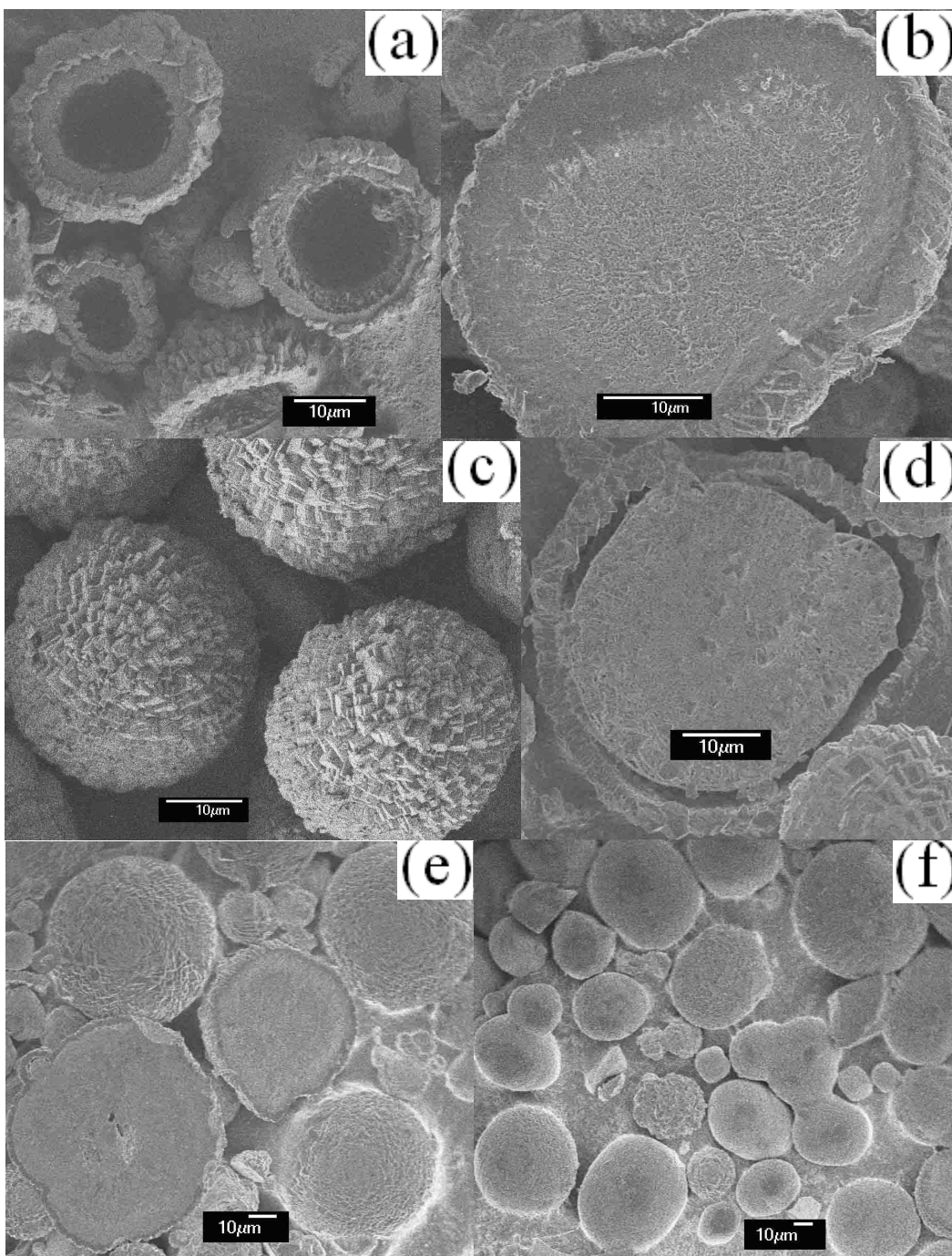
**Figure S1.** The powder XRD profile (a) and the TGA curves (b) of  $\text{CaCO}_3$  sampled from the calcium alginate hydrogels. In panel (a) the representative XRD pattern coincides well with that of the randomly oriented calcite powder (JCPDS 47-1743). In panel (b), the mass losses of  $\text{CaCO}_3$  products were 2.9 and 1.7 wt% for the reaction per-gels with 71.1 and 27.6 wt% sponged liquid, respectively.



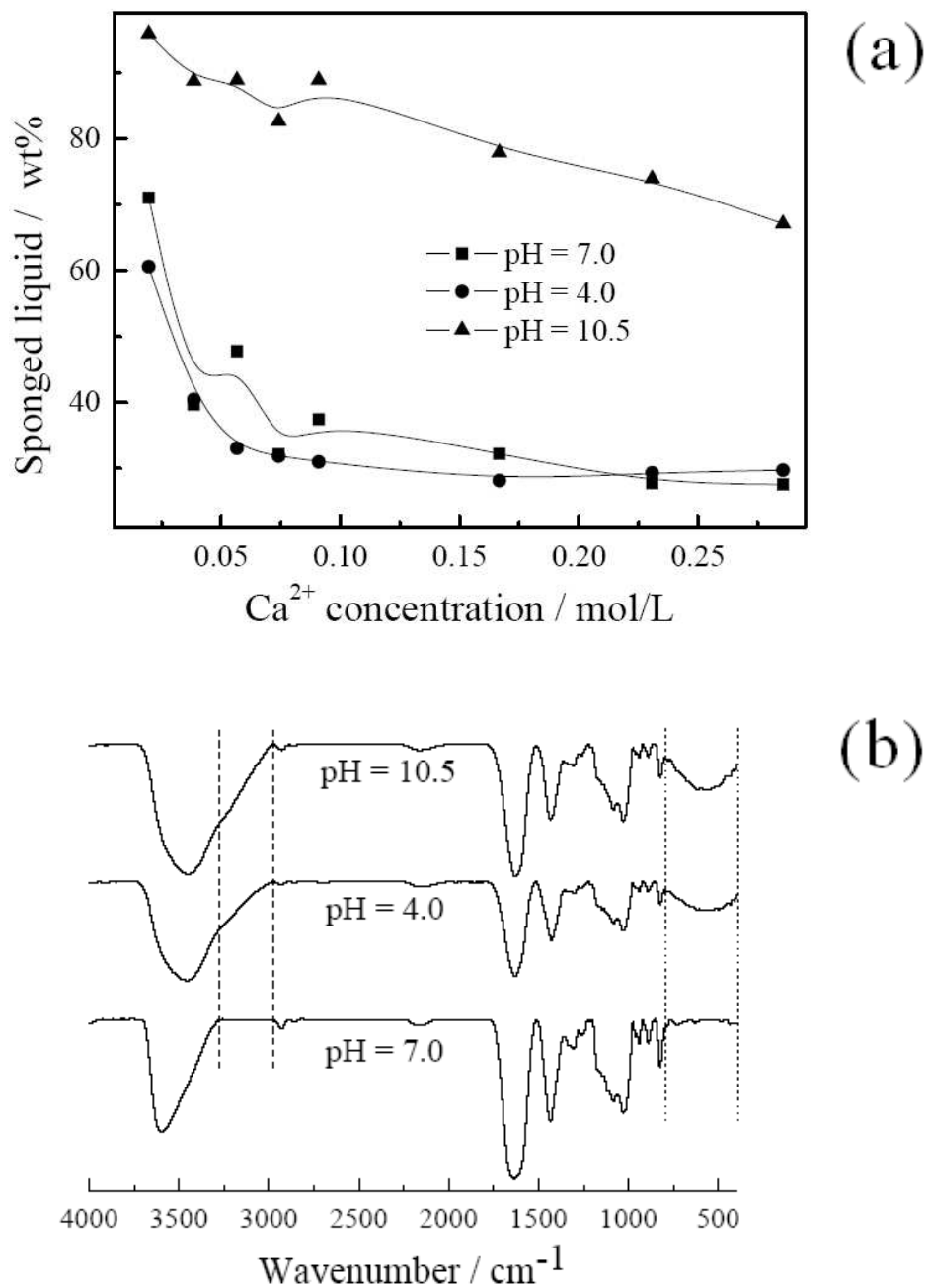
**Figure S2.** SEM images of calcite superstructures obtained from the calcium alginate hydrogels sponged up 39.7 (a) and 37.5 wt% liquid (b), respectively.



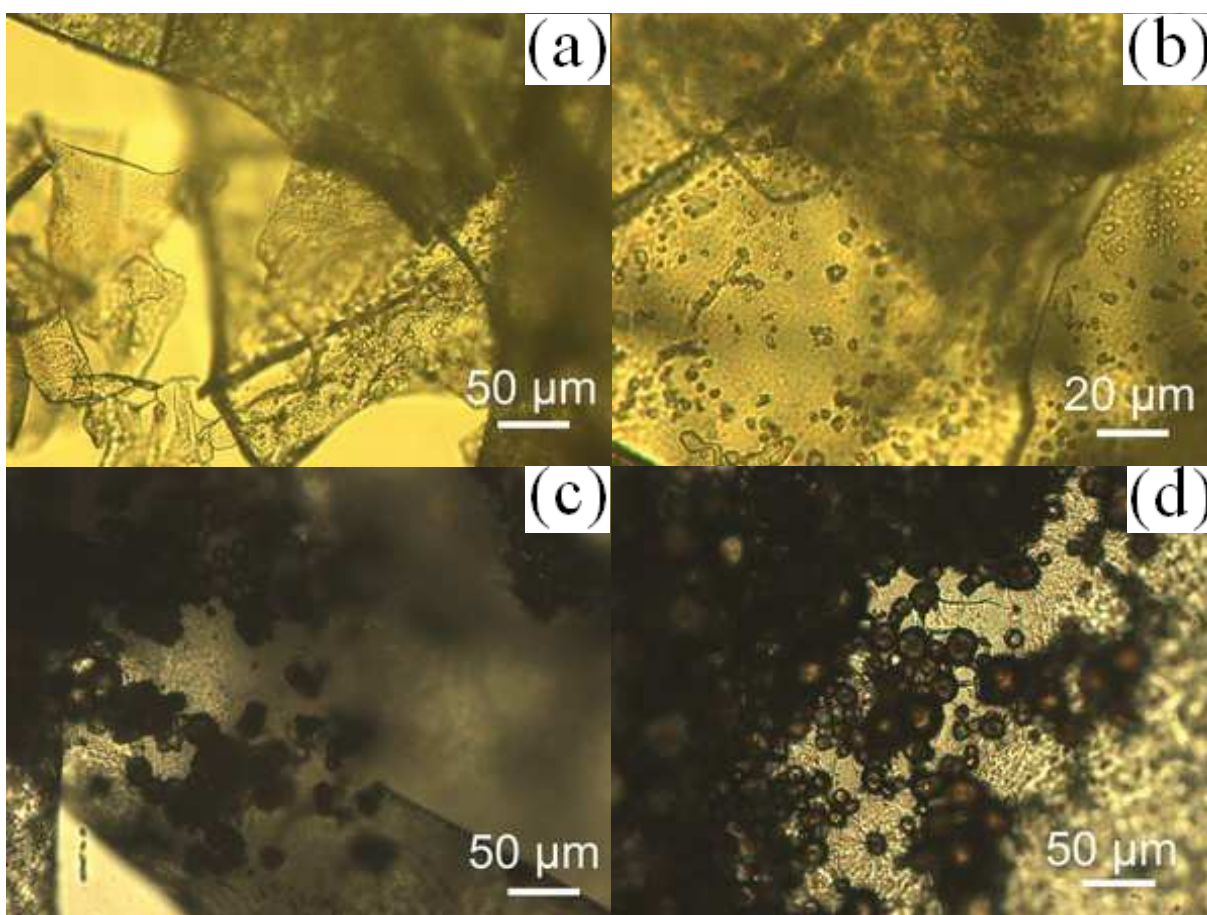
**Figure S3.** SEM images of the cross-sections of a cobblestone-like calcite superstructure. The selected part in panel (a) was magnified and shown in panel (b), and the arrows indicate the c-axes for the oriented aggregation of calcite building blocks.



**Figure S4.** SEM images of calcite superstructures obtained from various hydrogel systems of calcium alginate. These hydrogels were prepared by mixing 5.0 mL sodium alginate solution (1.0 wt%) + aspartic acid (10.0 mmol/L) with 0.1 (a), 0.2 (b), 0.3 (c), 0.4 (d), 0.5 (e), and 2.0 mL (f)  $\text{CaCl}_2$  solution (1.0 mol/L), respectively.



**Figure S5.** (a) The sponged percentage of liquid in calcium alginate hydrogels plotted against the concentration of calcium ions at various pH values. (b) FT IR spectra of the lyophilized pre-gels of calcium alginate at various pH values, the wavenumber regions labeled by the dash or dot lines display the different spectral characteristics of calcium alginate hydrogels formed at different conditions.



**Figure S6.** Transmission optical photographs of lyophilized samples of calcium alginate pre-gels obtained at the reaction times of 0 (a, b) and 12 h (c, d), respectively. Panels (a), and (b) present the lamellar arrangement of cross-linking alginate molecules without the coating of calcite particles, while panels (c) and (d) show the location and distribution of  $\text{CaCO}_3$  on alginate gelatinous lamellae and beads.