Supplementary Material (ESI) for CrystEngComm

Supporting Information

Polymorphic and Morphological Selection of $CaCO_3$ by Magnesium-Assisted Mineralization in Gelatin: Magnesium-Rich Spheres Consisting of Centrally Aligned Calcite Nanorods and Their Good Mechanical Properties

*Junwu Xiao, and Shihe Yang**

Department of Chemistry, William Mong Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (China)

E-mail: chsyang@ust.hk

Calculating the percentages of aragonite and magnesium calcites: The percentages of aragonite (A) and magnesium calcite (MC) in the samples of G_3Mg_{50} and G_5Mg_{50} are determined by the Reference Intensity Rations (RIR) method, and calculated by the following equations:

$$W_A = \frac{I_A}{I_A + \frac{I_{MC}}{K_A^{MC}}} \qquad W_{MC} = \frac{I_{MC}}{I_{MC} + \frac{I_A}{K_{MC}^{A}}} = 1 - W_A$$

$$K_A^{MC} = \frac{K_{Al_2O_3}^{MC}}{K_{Al_2O_3}^{A}} = 2.00 \qquad K_{MC}^{A} = \frac{K_{Al_2O_3}^{A}}{K_{Al_2O_3}^{MC}} = 0.50$$

W_A and W_{MC} are the percentages of aragonite and magnesium calcite phases in the samples, respectively. I_A *and* I_{MC} are the intensity of (111) of aragonite and (104) of magnesium calcite phases in the XRD pattern, respectively. K_{Al2O3}^{A} and K_{Al2O3}^{MC} are the K values of aragonite and magnesium calcite phases relative to Al_2O_3 crystals, respectively.

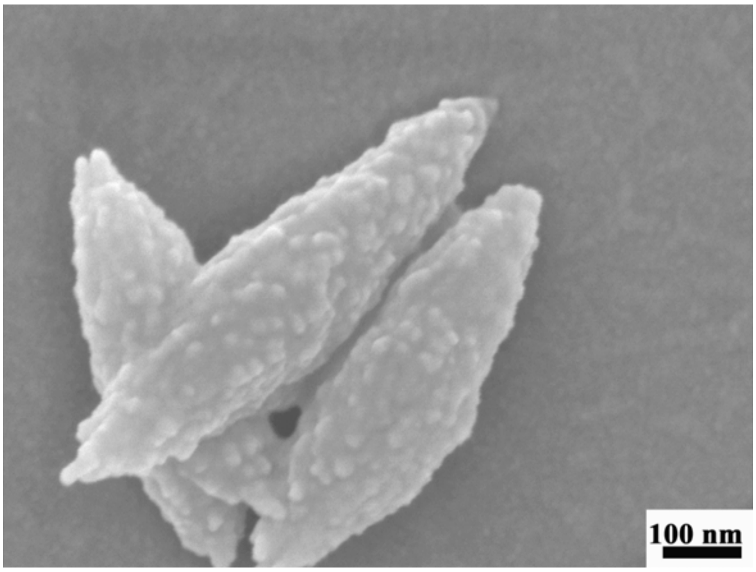

Fig. SI-1. The high magnification SEM image of $CaCO_3 \cdot H_2O$ in the sample of G_1Mg_{50}. Together with Fig. 2B, it shows that the $CaCO_3 \cdot H_2O$ particles in the sample of G_1Mg_{50} are in spindle shape.

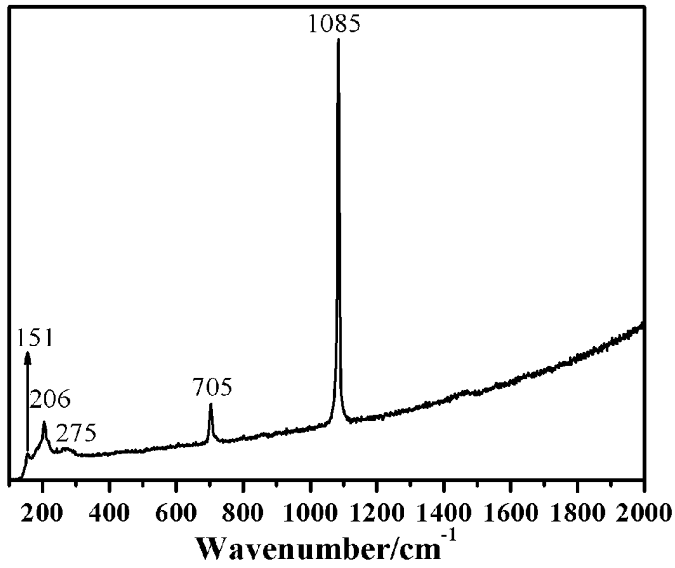

Fig. SI-2. Raman spectrum of hemispherical shaped microparticles of G_3Mg_{50} (Lattice mode of aragonite: 151, 206 and 275 cm^{-1}; ν_4 in-plane bending of aragonite: 705 cm^{-1}; ν_1 symmetric stretching of aragonite: 1085 cm^{-1}).[1] The Raman spectrum reveals that the hemispherical shaped microparticles are in aragonite phase.

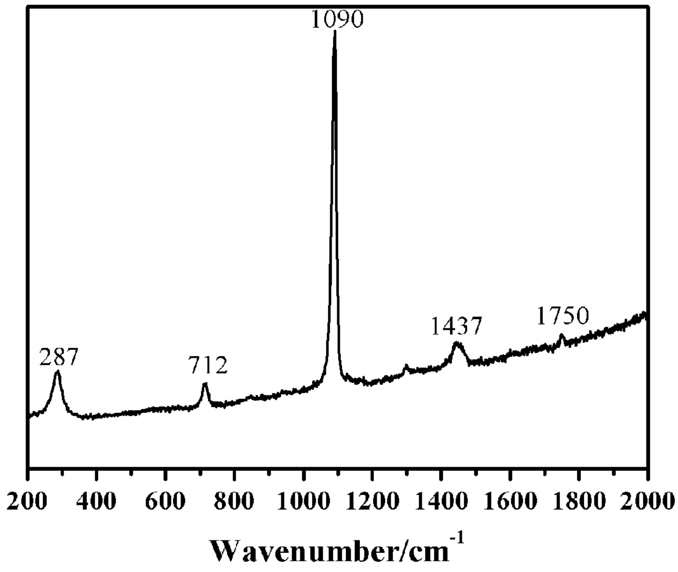

Fig. SI-3. Raman spectrum of microspheres of G_5Mg_{50} (Lattice mode of magnesium calcite: 287 cm^{-1}; ν_4 in-plane bending of magnesium calcite: 712 cm^{-1}; ν_1 symmetric stretching of magnesium calcite: 1090 cm^{-1}; ν_3 asymmetric stretching of magnesium calcite: 1437 cm^{-1}; overtone (ν_2 out of plane bending×2) of magnesium calcite: 1750 cm^{-1}).[1] The Raman spectrum reveals that the microspheres of G_5Mg_{50} are in magnesium calcite phase.

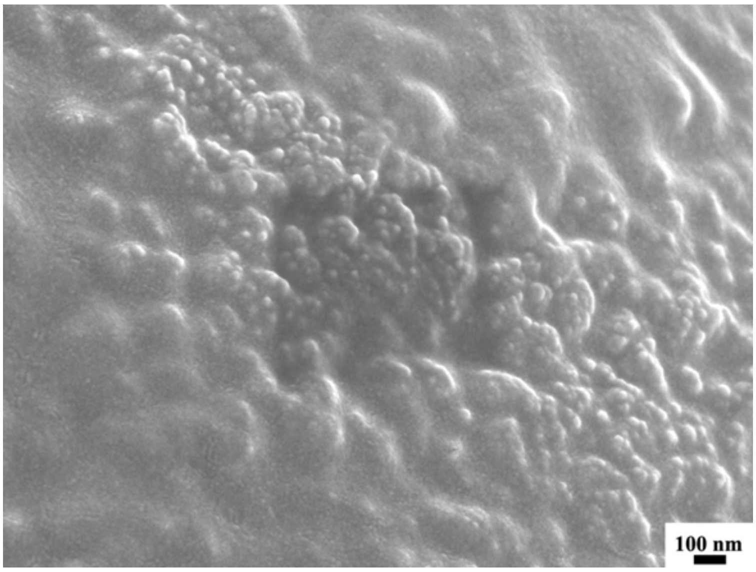

Fig. SI-4. SEM image showing the surface of hemispherical shaped aragonite microparticles of G_3Mg_{50}. Together with Fig. 2C and D, it shows that aragonite hemispheres are assembled by random aggregation of ~30 nm nanoparticles.

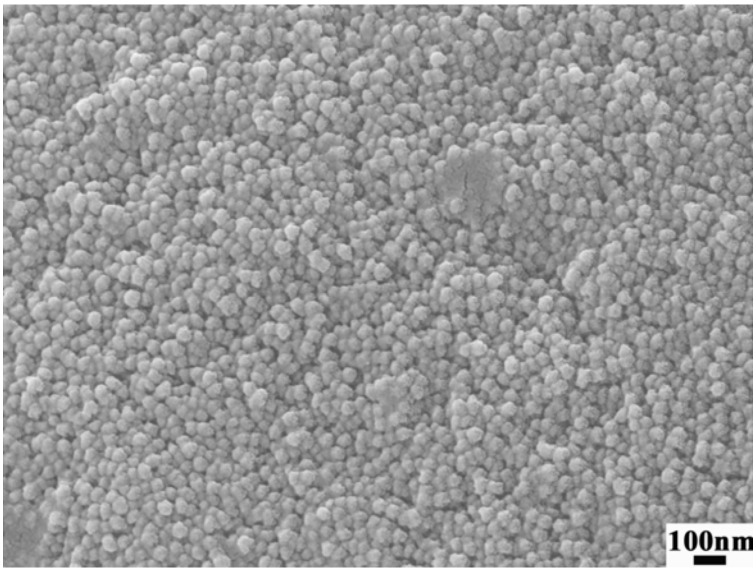

Fig. SI-5. SEM image of the surface of high magnesium calcite microspheres (HMCMs) in the sample of G_5Mg_{50}. Together with Fig. 2E and F, it shows that G_5Mg_{50} HMCMs are composed of the centrally aligned nanorods.

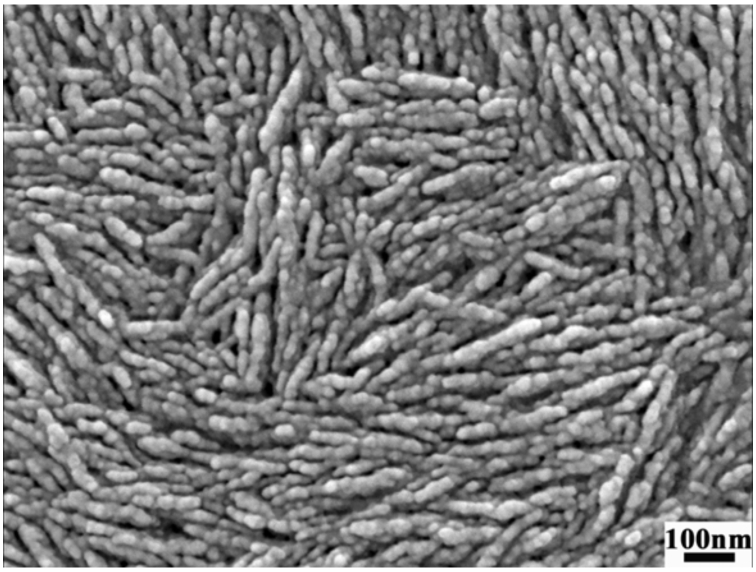

Fig. SI-6. SEM image showing the surface of low magnesium calcite microspheres (LMCMs) in the sample of G_5Mg_{20}. Together with Fig. 3A and B, it reveals that G_5Mg_{20} LMCMs are assembled from worm-like nanoparticles ~15 nm in diameter and ~100 nm in length in a way similar to wing wool into a ball.

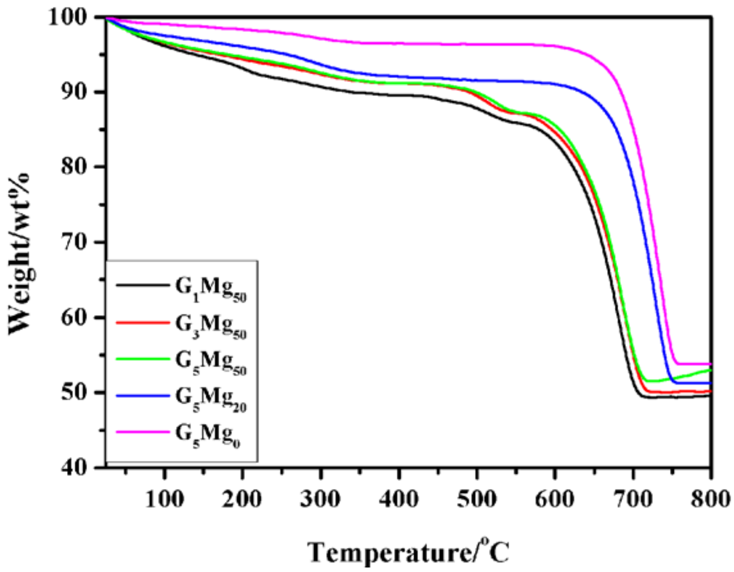

Fig. SI-7. TGA curves of G_1Mg_{50}, G_3Mg_{50}, G_5Mg_{50}, G_5Mg_{20} and G_5Mg_0. Several features can be recognized from the TGA curves. First, free and bound water molecules were fully lost at < 200 °C. Second, gelatin matrix was decomposed in the temperature range between 200 and 350 °C, and the organic residues were continually burned between 350 and 600 °C. Third, the $CaCO_3$ crystals began to decompose at > 600 °C. As for calculating the percentages of the different components in the samples, the percentages of inorganic component are calculated from the transition around 600 °C. The percentages of water are calculated before the first transition. The rests are the percentages of gelatin matrix.

[1] C. Gabrielli, R. Jaouhari, S. Joiret and G. Maurin, *J. Raman Spectrosc.*, 2000, **31**, 497-501.