Supporting Information

Polymorphic and Morphological Selection of CaCO₃ 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 G₃Mg₅₀ and G₅Mg₅₀ are determined by the Reference Intensity Rations (RIR) method, and calculated by the following equations:

\[
W_A = \frac{I_A}{I_A + \frac{I_{MC}}{K_{MC}^A}} \quad W_{MC} = \frac{I_{MC}}{I_{MC} + \frac{I_A}{K_{MC}^A}} = 1 - W_A
\]

\[
K_{MC}^A = \frac{K_{MC}^{Al_2O_3}}{K_{Al_2O_3}^A} = 2.00 \quad K_{MC}^A = \frac{K_{Al_2O_3}^A}{K_{Al_2O_3}^{MC}} = 0.50
\]

\(W_A\) 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. \(K_{Al_2O_3}^A\) and \(K_{Al_2O_3}^{MC}\) are the K values of aragonite and magnesium calcite phases relative to Al₂O₃ crystals, respectively.
**Fig. SI-1.** The high magnification SEM image of CaCO$_3$·H$_2$O in the sample of G$_1$Mg$_{50}$. Together with Fig. 2B, it shows that the CaCO$_3$·H$_2$O particles in the sample of G$_1$Mg$_{50}$ are in spindle shape.
Fig. SI-2. Raman spectrum of hemispherical shaped microparticles of G₃Mg₅₀ (Lattice mode of aragonite: 151, 206 and 275 cm⁻¹; \(\nu_4\) in-plane bending of aragonite: 705 cm⁻¹; \(\nu_1\) 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 G₅Mg₅₀ (Lattice mode of magnesium calcite: 287 cm⁻¹; ν₄ in-plane bending of magnesium calcite: 712 cm⁻¹; ν₁ symmetric stretching of magnesium calcite: 1090 cm⁻¹; ν₃ asymmetric stretching of magnesium calcite: 1437 cm⁻¹; overtone (ν₂ out of plane bending × 2) of magnesium calcite: 1750 cm⁻¹).[1] The Raman spectrum reveals that the microspheres of G₅Mg₅₀ are in magnesium calcite phase.
Fig. SI-4. SEM image showing the surface of hemispherical shaped aragonite microparticles of G₃Mg₅₀. 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 G₅Mg₅₀. Together with Fig. 2E and F, it shows that G₅Mg₅₀ 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$_5$Mg$_{20}$. Together with Fig. 3A and B, it reveals that G$_5$Mg$_{20}$ 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 $< 200 \, ^oC$. Second, gelatin matrix was decomposed in the temperature range between 200 and 350 $^oC$, and the organic residues were continually burned between 350 and 600 $^oC$. Third, the CaCO$_3$ crystals began to decompose at $> 600 \, ^oC$. As for calculating the percentages of the different components in the samples, the percentages of inorganic component are calculated from the transition around 600 $^oC$. The percentages of water are calculated before the first transition. The rests are the percentages of gelatin matrix.