Supplementary Information

Bio-Inspired Formation of Functional Calcite/ Metal Oxide Nanoparticle Composites

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Analysis of TGA Data

Thermogravimetric analysis (TGA) of the calcite/nanoparticle-gel samples estimated the amounts of nanoparticles entrapped within the calcite crystals as ~ 4 wt% for ZnO and ~ 2 wt% for Fe_3O_4. TGA spectra obtained under nitrogen gas flow showed that the calcite/nanoparticle-gel composites underwent gradual weight loss up to 600 °C equal to 4-5 wt % for the calcite-ZnO-gel and 8-9 wt % for the calcite/Fe_3O_4-gel, due to dehydration (1-2 wt%) and degradation of the Xyg polymer (Figure S3). Further heating above 600 °C led to decomposition of the $CaCO_3$, and higher amounts of residue were obtained than expected based on the decomposition of pure $CaCO_3$. These excess values over those expected for $CaCO_3$ decomposition alone amounted to ~13 wt % for the calcite/ZnO-gel and ~ 3 wt % for calcite/Fe_3O_4-gel, and can be attributed to entrapped metal oxide nanoparticles and incomplete decomposition of the Xyg polymer. The lower residual for the iron oxide system can be attributed to the fact that the magnetite nanoparticles convert to FeO under heating, which then facilitates decomposition of the biopolymer, even under nitrogen. Therefore, heating to decomposition under nitrogen of the calcite/nanoparticle-gel crystals is accompanied by greater weight loss than would be expected for calcite alone, equal to (5 + 13 = 18 wt%) for the ZnO system and (9 + 3 = 12 wt%) for the Fe_3O_4 system. Given that TGA analysis of the nanoparticle-functionalised Xyg biopolymers under oxygen flow revealed that they comprised ~20 wt% inorganic nanoparticles (Figure S4), the amounts of nanoparticles entrapped within the calcite crystals were estimated as (20% × 18 wt% = ~ 4 wt%) for ZnO and (20% × 12 wt% = ~2 wt%) for Fe_3O_4. These results compare with calcite crystals grown in Xyg-gel (*ie*. in the absence of inorganic nanoparticles) which under TGA in oxygen shows a weight loss of only 3-4 wt% loss before 600 ^{o}C and stoichiometric decomposition of $CaCO_3$ at 600 ^{o}C (Figure S3).

Figure S1: (A) Raman spectra of calcite/Fe_3O_4-gel and calcite/ZnO-gel composite crystals showing peaks at 1091 or 1090 cm^{-1} (ν_1) which correspond to the internal CO_3^{2-} symmetric stretch, a peak at 719 or 717 cm^{-1} (ν_4) which corresponds to the CO_3^{2-} symmetric bending mode and lattice mode peaks at 161,289 cm^{-1} and 160,287 cm^{-1} respectively. (B) Powder XRD spectra of calcite/Fe_3O_4-gel and calcite/ZnO-gel composite crystals, where only the strongest (104) peak of calcite was observed due to the limited amounts of samples available.

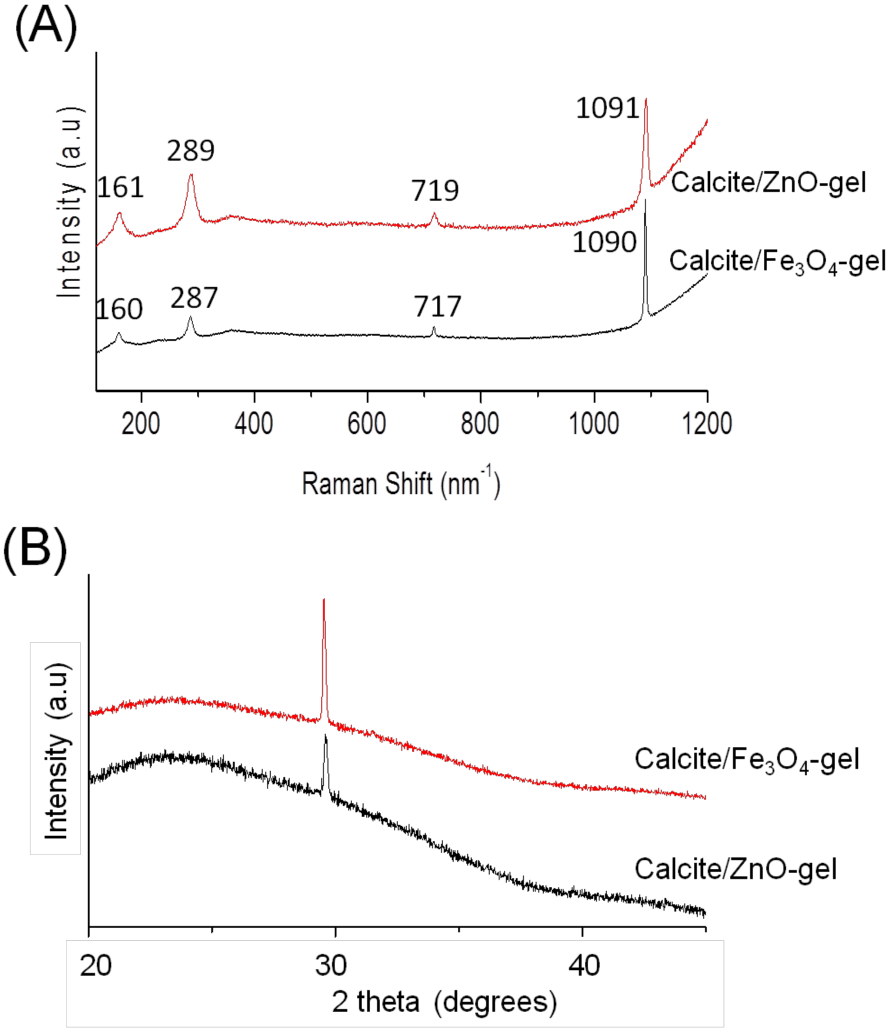
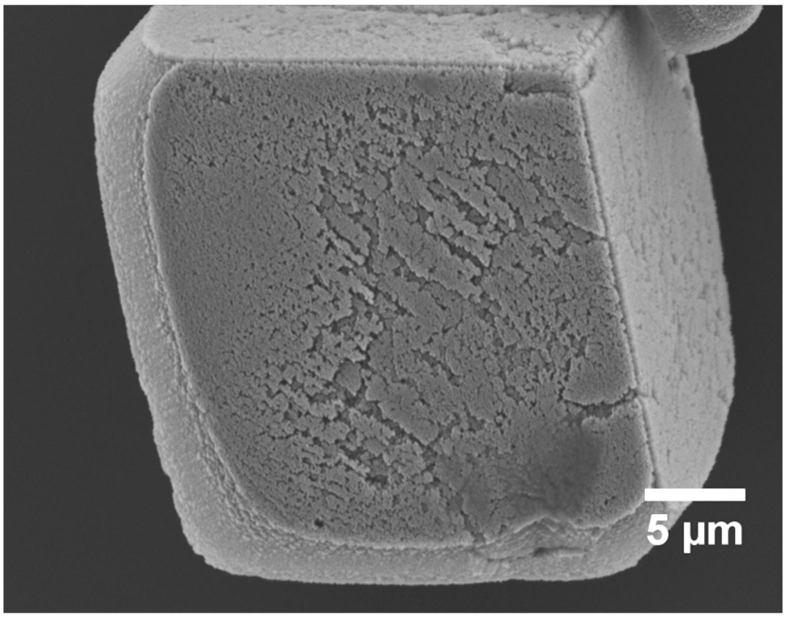
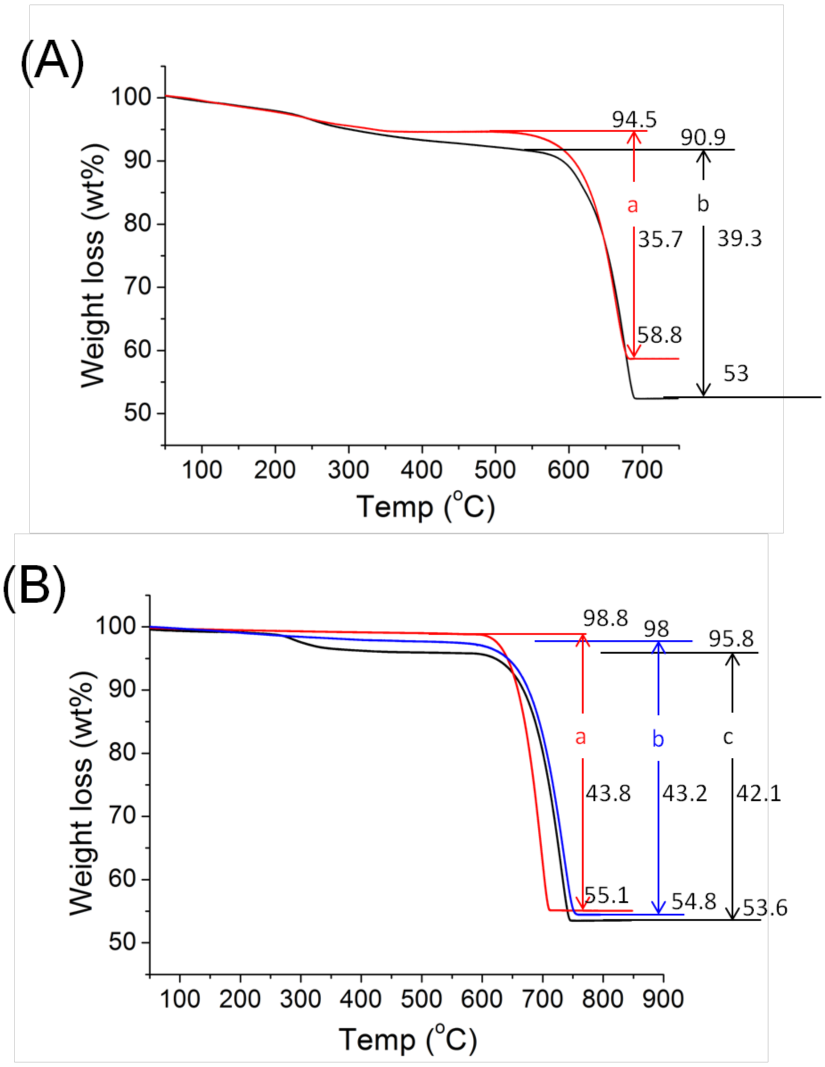


Figure S2. SEM image of a calcite crystal grown in a Xyg gel, showing rough surfaces and slightly truncated edges.



Supplementary Information

Figure S3. (A) Thermogravimetric analysis (TGA) data of (**a)** Calcite/ZnO-gel and (**b**) Calcite/Fe_3O_4-gel composites. (B) Thermogravimetric analysis (TGA) data of (**a**) pure calcite (red), (**b**) calcite grown in presence of freely-dispersed ZnO nanoparticles (blue) and (**c**) calcite grown within Xyg gel (black). All 3 samples showed stoichiometric decomposition of $CaCO_3$ to CO_2 and CaO (100 $CaCO_3$ $\rightarrow$56 CaO + 44 CO_2).



Supplementary Information

Figure S4. Thermogravimetric analysis data of Xyg biopolymer and Xyg functionalized with Fe_3O_4 and ZnO nanoparticles. Xyg biopolymer fully decomposed before 430 ^{o}C such that the ~ 20 wt % residue remaining at 500 ^{o}C could be attributed to Fe_3O_4 or ZnO nanoparticles.

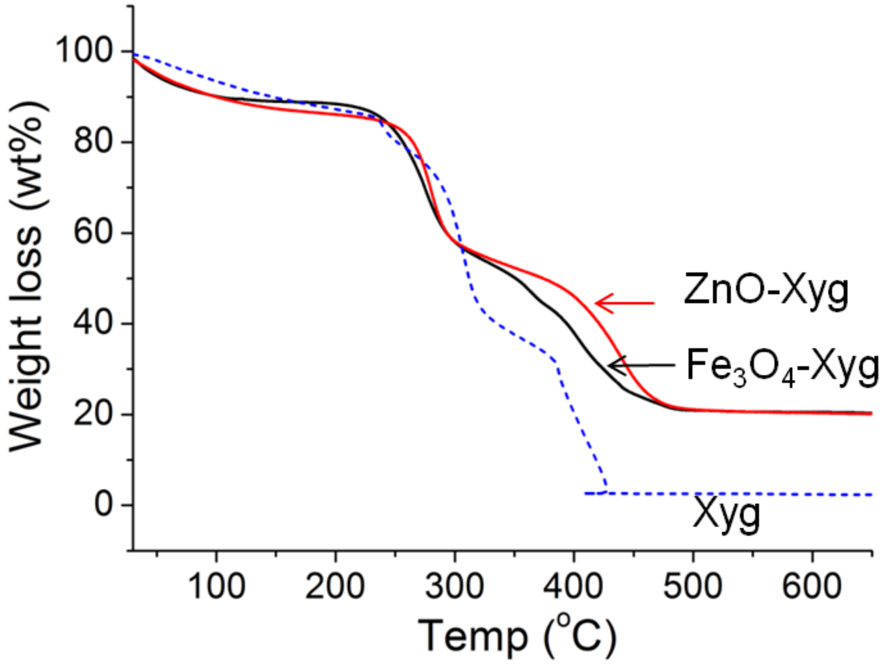
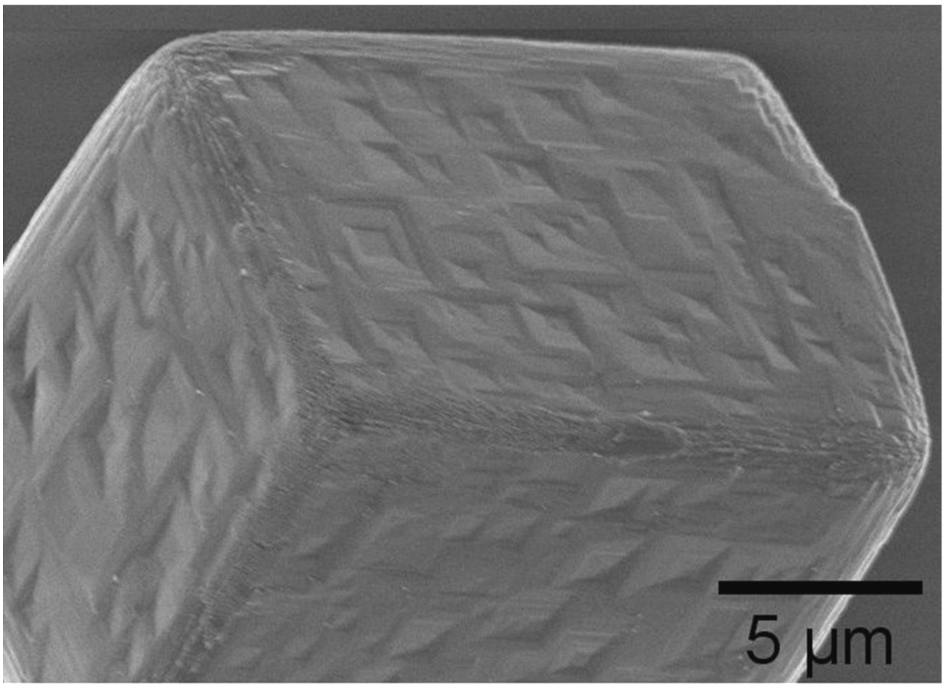


Figure S5. A SEM image of a pure calcite crystal etched with 0.05 M EDTA solution.



Supplementary Information

Figure S6. A SEM image of a fractured, pure calcite crystal.

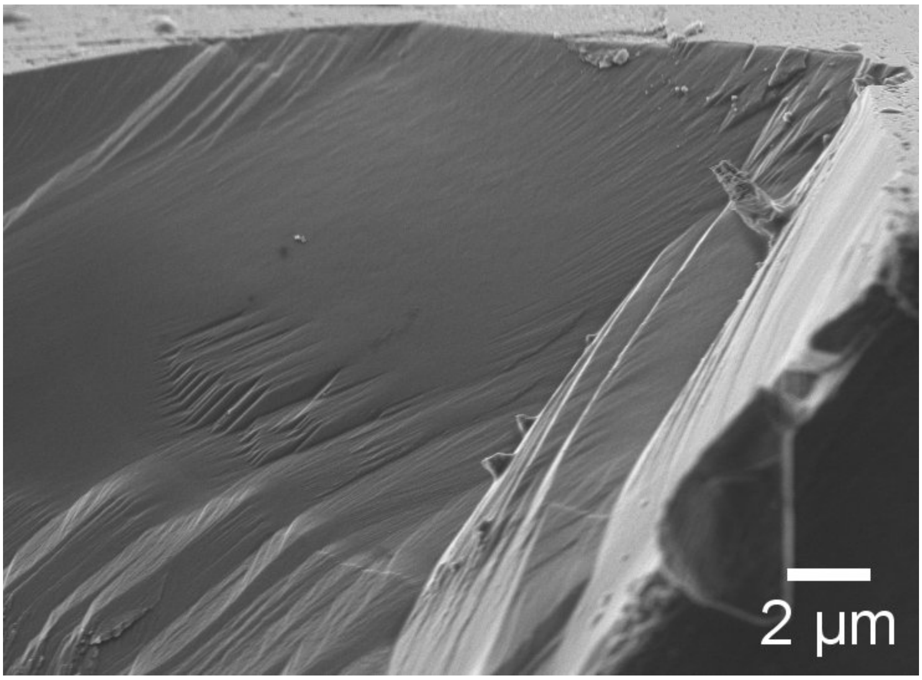


Figure S7. Cross-sections through fractured calcite crystals precipitated in the presence of 100 µg/ml (A) enzyme-treated magnetite nanoparticles and (B) enzyme-treated zinc oxide nanoparticles. Images of intact crystals are shown in the insets.