Artificial Biominerals and Beyond: Bio-Inspired Approaches to Creating Crystals with Composite Structures

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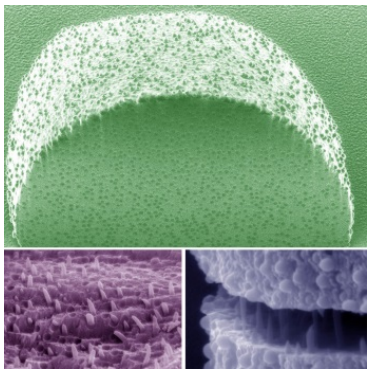
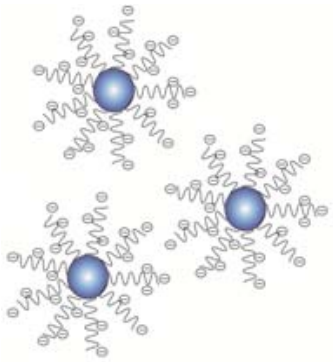
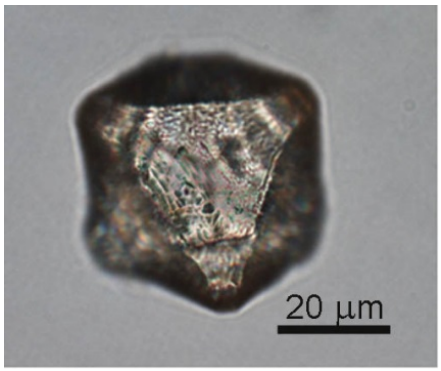
The production of crystalline materials with structures and properties resembling those of biominerals is a challenging synthetic goal that is relevant to a wide range of technologies, including the formation of nanomaterials, ceramics and biomaterials. A characteristic feature of biominerals is that they are invariably composite materials in which organic macromolecules are associated with the inorganic phase. Indeed, even incorporation levels of just a few weight percent leads to a significant enhancement of the mechanical properties.

This talk will describe how this biogenic strategy can be used to generate synthetic crystals with novel composite structures and properties and to determine the "design rules" which govern the occlusion of additives within crystals. Occlusion-species ranging from micron-scale particles, to organic and inorganic nanoparticles, to small molecules were incorporated within calcite single crystals using a simple one-pot method. Very high levels of occlusion of particles were achieved, according to the particle surface chemistry and growth conditions.[1] The incorporation of 20 nm anionic diblock copolymer micelles resulted in composite crystals with structures and mechanical properties comparable to those of biominerals.[2] The micelles also act as "pseudo-proteins", and their influence on the short and long range structures of the crystal host, and through this the mechanical properties, was determined. This system also provides a unique opportunity to study additive/crystal interactions in real-time using atomic force microscopy (AFM). Considering then additives an order of magnitude smaller in size, amino acids could also be occluded within calcite, providing significant insight into the origin of the superior mechanical properties of many biominerals.

Finally, our strategy was extended to generate nanocomposites in which inorganic nanoparticles are uniformly distributed throughout a crystal matrix with true nano-scale mixing.[3,4] Highly effective incorporation of gold and magnetite nanoparticles was achieved within host calcite crystals by controlling the nanoparticle surface chemistry using a physically-adsorbed double hydrophilic diblock copolymer. This methodology can potentially be applied to a huge number of nanoparticle/ host crystal systems, where its experimental simplicity makes it an attractive and general method for generating composite materials.







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[2] Kim Y-Y, Ganesan K., Yang P., Kulak A.N., Borukhin S., Pechook S., Ribeiro L., Kröger R., Eichhorn S.J., Armes S.P., Pokroy B., Meldrum F.C. *Nature Mater*. 2011, **10**, 890.
[3] Kulak A. N., Yang P., Kim Y-Y, Armes, S. P. and Meldrum F. C. *Chem. Commun*. 2014, **50,** 67.
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