

## Prof Fiona Meldrum

f.meldrum@leeds.ac.uk

phone: 0113 343 6414

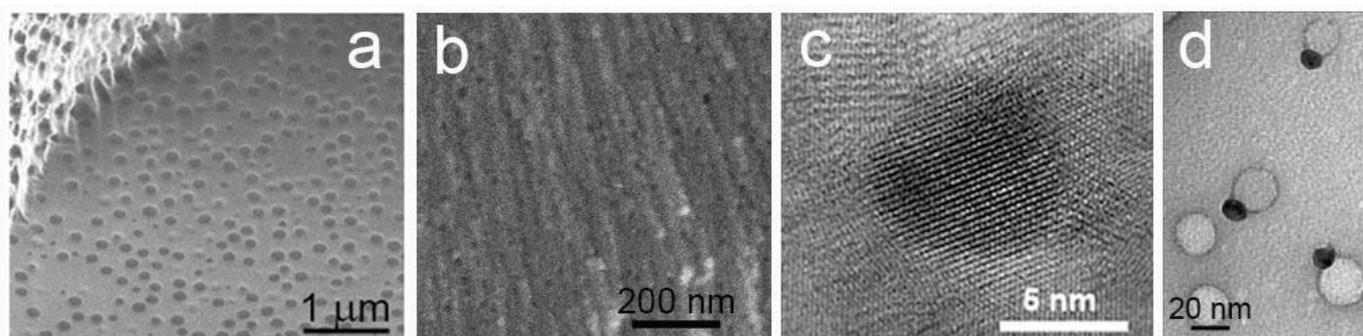
This proposal is representative of the projects currently on offer in our group. For more details of active research projects, please visit the Research and Publications sections of our webpage at: <http://www1.chem.leeds.ac.uk/FCM/>

### Bio-Inspired Approaches to Functional Nanocomposites

This project will develop a novel, experimentally straightforward and highly scalable assembly-based strategy for the generation of functional inorganic nanocomposites. Nanocomposites are an exciting new class of materials, where the ability to engineer compositions, structures and properties at the nanoscale and mesoscale promises the possibility of creating new functionalities. Taking inspiration from the remarkable composite materials that are biominerals,<sup>1</sup> we have pioneered a novel “occlusion strategy” to create a new class of materials – single crystals containing embedded nanoparticles – using polymer-functional nanoparticles as simple crystal growth additives. Control over the surface functionality of the nanoparticles enables us to programme their encapsulation and distribution within the host crystal lattice and therefore tune the physical properties of the nanocomposites. To date we have created composite single crystals comprising calcite ( $\text{CaCO}_3$ ) crystals containing polymer particles<sup>2-4</sup> and polymer-coated  $\text{Fe}_3\text{O}_4$  (magnetic)<sup>5</sup> and Au (coloured) nanoparticles. Recent results have shown that it can be extended to other host crystals to create  $\text{ZnO}/\text{Fe}_3\text{O}_4$  nanocomposites.<sup>6</sup>

We will now develop our fabrication strategy to identify commercially-available organic additives that can be used to drive efficient nanoparticle occlusion. These will be used to incorporate a range of nanoparticles, varying from functional inorganic nanoparticles to emulsion particles, within a variety of host crystals. Particular goals of the project will be to target nanocomposites with photocatalytic properties and nanocomposites for controlled release. Photocatalysts will be created by the occlusion of metal nanoparticles within functional single crystals, while controlled release systems will be generated by encapsulating structures such as gel particles, emulsions and vesicles. The structures and compositions of the composite crystals will be characterised using techniques such as electron microscopy and thermogravimetric analysis, and the mechanism of occlusion using liquid cell AFM. Finally, the physical properties of the composite crystals will be determined, enabling us to link structure with properties.

This project will give experience in crystal growth techniques, photocatalysis and controlled-release studies, and a wide range of analytical methods including scanning and transmission electron microscopy, X-ray diffraction, Raman microscopy, atomic force microscopy and IR spectroscopy.



(a) poly(styrene) particles within calcite, (b) CdSe NPs (dark spots) within  $\text{Cu}_2\text{O}$  and (c) copolymer-coated  $\text{Fe}_3\text{O}_4$  NP within a calcite single crystal showing continuity of the lattice and (d) Ag/copolymer micelle Janus particles

### References

- (1) Kim, Carloni, Demarchi, ... Harding, Estroff, Baker, Meldrum, “*Tuning hardness in calcite by incorporation of amino acids*” *Nature Mater.* **2016**, 15, 903. (2) Kim, Ganesan, Yang, Kulak, Borukhin, Kröger, Eichhorn, Armes, Pokroy, Meldrum “*Artificial Biominerals – Incorporation of Copolymer Micelles in Calcite Single Crystals*” *Nature Mater.* **2011**, 10, 890. (3) Cho, Kim, Yang, Cai....Meldrum, De Yoreo “*Direct observation of mineral-organic composite formation reveals occlusion mechanism*”, *Nature Commun.* **2016**, 7, 10187. (4) Kim, Semsarilar, Carloni ... Armes, Meldrum “*Structure and Properties of Nanocomposites Formed by the Occlusion of Block Copolymer Worms and Vesicles Within Calcite Crystals*” *Adv. Func. Mater.* (2016), **26**, 1382. (5) Kulak, Semsarilar, Kim, ...Armes, Meldrum “*One-Pot Synthesis of an Inorganic Heterostructure: Uniform Occlusion of Magnetite Nanoparticles within Calcite Single Crystals*”, *Chem. Sci.* **2014**, 5, 738. (6) Kulak, Grimes, Kim, Semsarilar, Cespedes, Armes, Meldrum “*Polymer-Directed Assembly of Single Crystal ZnO/ Magnetite Nanoparticle Nanocomposites under Standard and Hydrothermal Conditions*” *Chem. Mater.* **2016**, 28, 7528.