In-Situ Probing of ZIF-8 Colloid Self-Assembly into Photonic Mesocrystals

Sophie Ray [a,b], Hamish Yeung[a], Andy Smith[b], Phil Chater[b], Satoshi Tominaka[c]

[a] School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K
[b] Diamond Light Source, Harwell Science and Innovation Campus, Fermi Ave, Didcot, OK11 0DE, U.K
[c] Center for Basic Research on Materials, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan.

sxr954@student.bham.ac.uk

Controlling the self-assembly of colloidal particles into superstructures with long-range order is important for the design of photonic crystals (PhCs) [1] . In the last decade, metal-organic framework (MOF)-based PhCs have been of interest because their tuneable structure, porosity, and surface area in turn tune the photonic band gap [2,3] . However, control over the morphology and size of the MOF colloidal nanoparticles is essential to the successful fabrication of PhCs. Furthermore, understanding their self-assembly behaviour is key to enabling greater control over PhC formation. This research focused on ZIF-8 synthesis and looked to understand how several synthesis parameters, including zinc node:2-methylimidazole molar ratio, could control morphology and size of ZIF-8 colloidal nanoparticles. It was found that decreasing the zinc to 2-methylimidazole molar ratio resulted in morphological change from truncated rhombic dodecahedra to truncated cubes, as well as a decrease in nanoparticle diameter (Fig.1 (a) to (b)). Optimised ZIF-8 colloids were subsequently self-assembled into monocrystalline superstructures with photonic properties, and as such, exhibited a range of structural colours, that red shifted as the particle size increased (Fig.1 (c) to (f)). Small angle X-ray scattering (SAXS) was then used to resolve the packing structure of these mesocrystals (Fig.1 (g)). Combined with nuclear magnetic resonance (NMR) and dynamic light scattering (DLS) studies, these studies provided insight into why particles of certain sizes prefer packing, differences between crystallised colloids and those remaining in the supernatant, and the formation of mesocrystals via self-assembled colloidal clusters. Additionally, humidity-controlled *in-situ* grazing incidence small angle X-ray scattering (GISAXS) revealed the role of interfacial water in establishing photonic behaviour, where shifts in reflectance peaks indicated a contraction of the lattice parameter of the superstructure upon drying. To our knowledge, this work is the first *in-situ* study of the self-assembly process of ZIF-8 colloidal systems. These results provide a deeper understanding of MOF colloid assembly and potentially provide pathways to more efficient self-assembly of MOF colloids in the future and enabling the fabrication of new photonic structures experimentally.

Keywords:
Metal-Organic Frameworks, Photonic Crystals, Small Angle X-ray Scattering, Self-Assembly

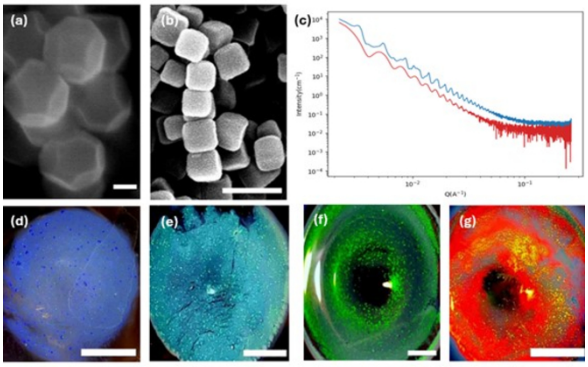

Figure 1. (a-b) SEM images of ZIF-8 synthesised with different morphologies, (c) SAXS data showing the nanoparticles in the mesostructure (blue) compared to in the supernatant (red), (d-g) optical images of the different coloured photonic crystals. Scalebars (a-b) 500 nm, (d-g) 1 cm.

References:

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