

Supporting Information for

Biomimetic mineralization of metal-organic frameworks around polysaccharides

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Materials

Dextran of various molecular weights, pullulan of various molecular weights, fluorescein labelled dextran, and 2-methylimidazole (HmIm) were purchased from Sigma Aldrich (Australia). Zinc acetate dihydrate was obtained from Alfa Aesar (Australia). All other reactants were purchased from Sigma-Aldrich and used without further purification.

Methods

Biomimetic crystallization of ZIF-8 using polysaccharides. HmIm (263 mg) and various quantities of polysaccharide (e.g. 0.5, 1, 5, 20 mg mL⁻¹) were combined and dissolved in deionised water (20 mL) in a glass beaker. In a separate glass beaker, zinc acetate dihydrate (176 mg) was dissolved in deionised water (20 mL). The two solutions were then combined, and the solution slowly turned cloudy after mixing. The reaction mixture was left at room temperature for various time-points before collection via centrifugation, followed by three ethanol washing steps. The particles were finally re-suspended in ethanol.

Biomimetic crystallization of MOFs on cellulose fibers. The MOF precursor solution was prepared by mixing equal volumes of aqueous solutions of HmIm (160 mM) and zinc acetate dihydrate (40 mM). The cellulose fibers obtained from cotton wool or tissue paper were fully immersed into the MOF precursor solution and left immersed for 16 h, followed by immersion in deionised water to wash off the excess MOF precursors. Finally the fibers were dried in a stream of N₂.

Characterisation techniques

Synchrotron SAXS data were collected at the SAXS/WAXS beamline at the Australian Synchrotron. Diffraction patterns were collected using a Pilatus 1M detector. Optical micrographs (DIC and fluorescence) were obtained using an Olympus BX60M microscope.

Scanning electron microscope (SEM) images of samples were taken on a Zeiss MERLIN SEM at an accelerating voltage of 5.0 kV. Confocal microscopy images were acquired via a Nikon A1R confocal laser scanning microscope. FTIR was performed using an alpha Bruker spectrometer using ATR mode (128 scans, 2 cm^{-1} resolution).

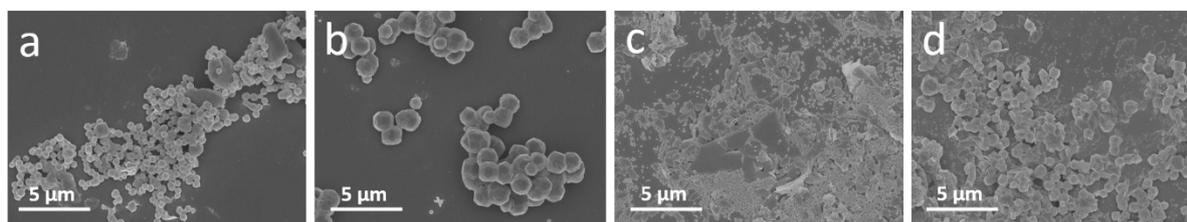


Fig. S1. SEM images showing ZIF-8 particles synthesized in the presence of (a) 0.5, (b) 1, (c) 5, and (d) 20 mg mL^{-1} dextran.

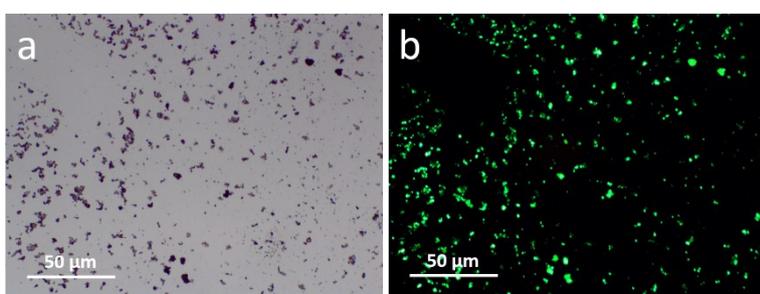


Fig. S2. (a) DIC and (b) CLSM images of ZIF-8 particles crystallized around FITC-dextran.

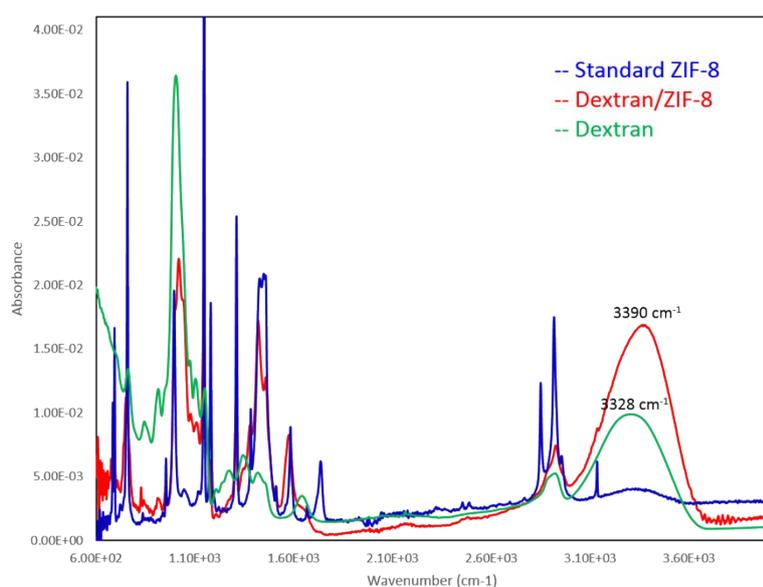


Fig. S3. FT-IR patterns of ZIF-8 mineralized around dextran (Dextran/ZIF-8, red), free dextran (Dextran, green), and a standard of pure ZIF-8 particles (Standard ZIF-8, blue). The IR band of the dextran hydroxyl groups was significantly shifted to higher wavenumbers upon encapsulation.

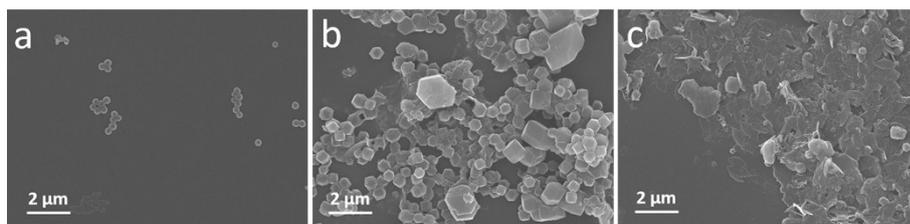


Fig. S4. SEM images showing ZIF-8 particles synthesized in the presence of (a) 1, (b) 5, and (c) 20 mg mL⁻¹ pullulan.

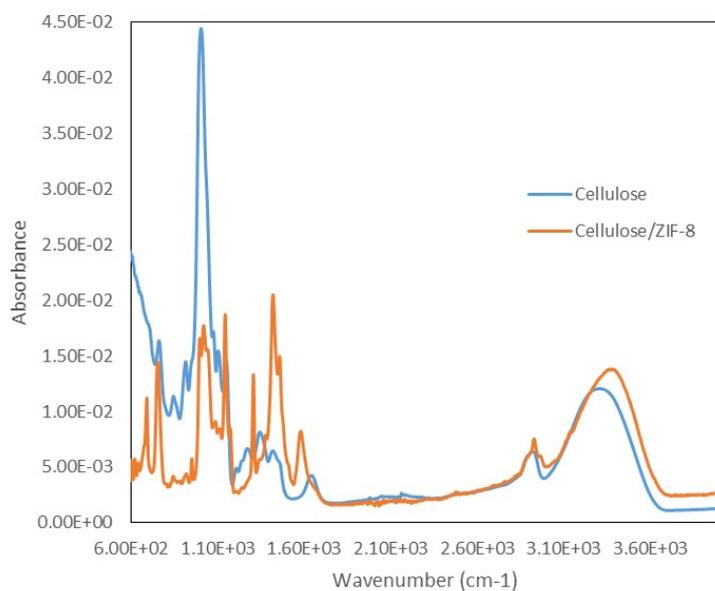


Fig. S5. FT-IR patterns of ZIF-8 mineralized around cellulosic cotton fibers (cellulose/ZIF-8, orange). The IR band of the dextran hydroxyl groups was significantly shifted to higher wavenumbers upon encapsulation.

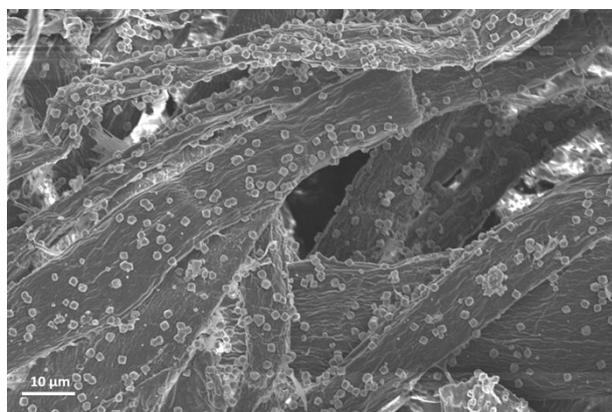


Fig. S6. SEM images of ZIF-8 particles on tissue fibers.