Electronic Supplementary Material (ESI) for Chemical Communications

Supplemental information

Exceptional Function of Nanoporous Metal Organic Framework Particles in Emulsion Stabilisation

Bo Xiao, Qingchun Yuan and Richard A. Williams

1. Preparation of MOFs nanoparticles

A stirring reaction method of mixing organic ligand source and metal source has been used for preparation of MOF nanoparticles. In a typical preparation, 0.42 g (2mmol) of 1,3,5-benzenetricarboxylic acid (H_3BTC) was dissolved in a 5 ml ethanol solution, 0.60 g (3mmol) of copper acetate monohydrate dissolved in 5 ml distilled water. Two aliquot solutions were then mixed in a beaker, followed by stirring at room temperature for ~15 minutes to form gel-like dark turquoise suspension. The particles were then separated by centrifugation of the suspension and washed using ethanol/water (1:1 v/v) solutions to remove residual 1,3,5-benzenetricarboxylic acids and copper acetates. In the last the gel-like product was sealed in a vial for subsequent Pickering emulsion experiments, coded as Cu-BTC. As a comparison, larger crystals were synthesized using a hydrothermal method, in which 6 mmol $Cu(NO_3)_2 \cdot 3H_2O$ and 4mmol H_3BTC mixed in a 12ml ethanol/water (1:1 v/v) solution in a PTFE liner autoclave that was then heated at 110^{o}C for 24hours.

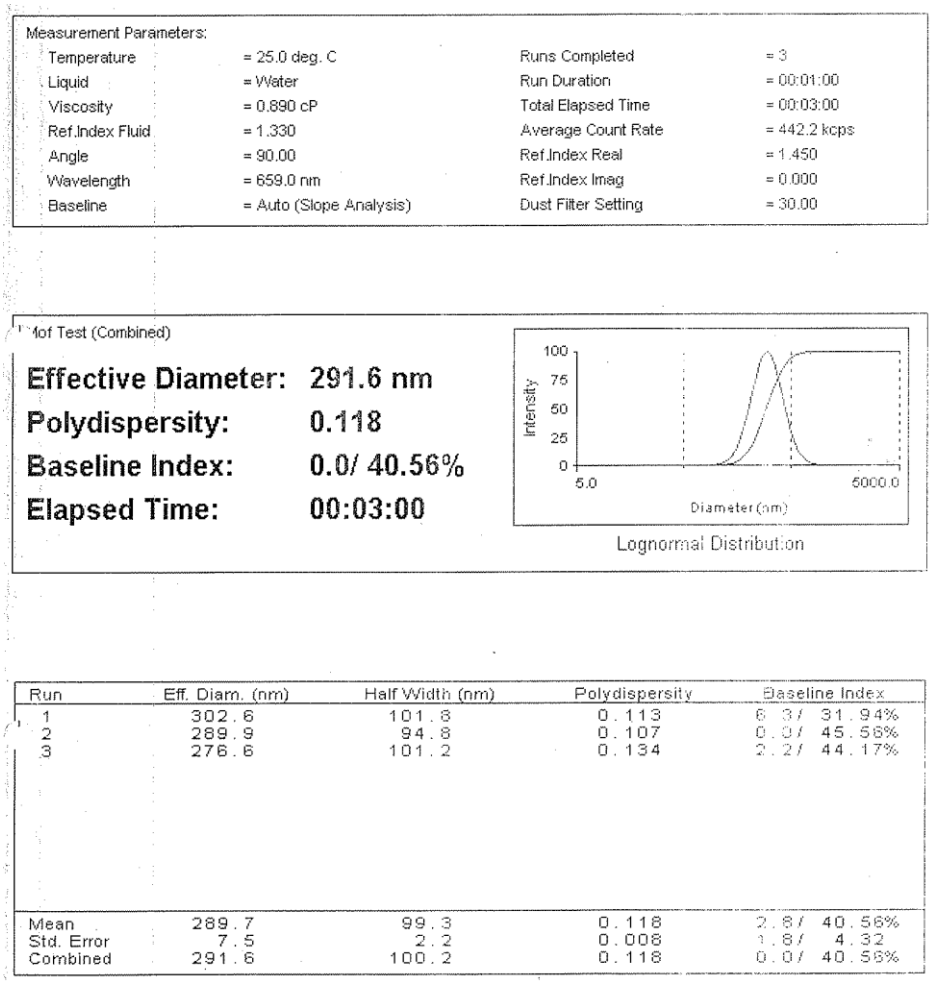
2. Emulsification

Both rotor-stator high speed and membrane emulsification methods were used in the preparation of the MOFs stabilised emulsions. A mini homogenizer (PolyTron PT2100, Kinematica AG) was used for the rotor-stator emulsification. Either a volume of 3.0 ml aqueous suspension or a weight of 3.2 g oil was used as continuous phase for oil-in-water and water-in-oil systems, respectively. The continuous phase was mixed with a known volume of the disperse phase (1.0 to 3.0 ml), and then homogenised at 22,000 rpm for 2 minutes. The resulting emulsions were examined using optical microscopy for the droplet appearance, size and size stability.

The membrane emulsification was carried out using a rotating rig. A cylindrical stainless steel membrane tube was used. It has an outer diameter of 8 mm, a wall thickness of 0.5 mm with an effective area of pores at 5 mm in length along the tube, pore size 80x80 μm, vertical distance 1.0 mm. The membrane is mounted on a stirrer motor (IKA Eurostar digital agitator) and carefully positioned in the middle of a stationary cylindrical container, which has an inner diameter of 30 mm. The amount of continuous aqueous phase used was 30 ml, which ensures that the pore area of the membrane is fully immersed. The disperse phase was added into the hollow cylindrical shaft connected with the membrane when the membrane was rotated at a rotational speed of 1000 rpm. The emulsification lasted 10-30 minutes. All the emulsification experiments were performed at room temperatures of ~19^{o}C.

3. Characterisation

Zeta potential A Brookhaven ZetaPlus was used to measure the size and Zeta potential of the nanoparticles. The data were processed using ZeatPlus Particle Sizing Software Ver.3.72. The effective diameter of the obtained MOF particles is *ca* ~291nm with half width ~100 nm.



Measurement Parameters:

Temperature	= 25.0 deg. C	Runs Completed	= 3
Liquid	= Water	Run Duration	= 00:01:00
Viscosity	= 0.890 cP	Total Elapsed Time	= 00:03:00
Ref.Index Fluid	= 1.330	Average Count Rate	= 442.2 kcps
Angle	= 90.00	Ref.Index Real	= 1.450
Wavelength	= 659.0 nm	Ref.Index Imag	= 0.000
Baseline	= Auto (Slope Analysis)	Dust Filter Setting	= 30.00

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	302.6	101.8	0.113	6.3/ 31.94%
2	289.9	94.8	0.107	0.0/ 45.56%
3	276.6	101.2	0.134	2.2/ 44.17%
Mean	289.7	99.3	0.118	2.8/ 40.56%
Std. Error	7.5	2.2	0.008	1.8/ 4.32
Combined	291.6	100.2	0.118	0.0/ 40.56%

Microscopy Optical microscopes (Nikon Eclipse ME600 and SMZ800 stereomicroscope) were used to examine the emulsion droplet appearance and stability. Images were recorded using a digital camera and processed using commercial software packages. Prior to optical microscopy analysis, each sample was carefully spread as a thin layer on a standard glass slide.

Interfacial tension measurement A Krüss DSA 100M was used to measure surface and interfacial tension by pending drop method. Blunt stainless steel needles with an inner diameter of 0.17 mm were used to generate and holding the pending droplet. The system was characterised by measuring the surface tension of MiniQ water before the measurement. Droplet image videos are recorded and analysed using the commercial software. The reported data has been mathematically smoothed.

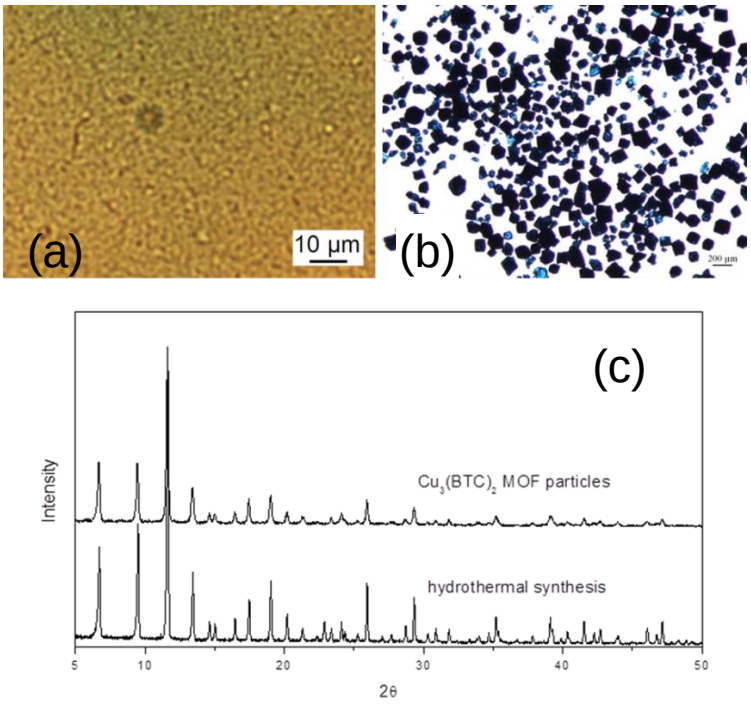


Figure S1. (a) Microscopic images of Cu-BTC nanoparticles synthesized by stirring reaction method; (b) larger size crystals obtained by autoclave hydrothermal method; (c) comparison of XRD patterns of products (a) and (b).

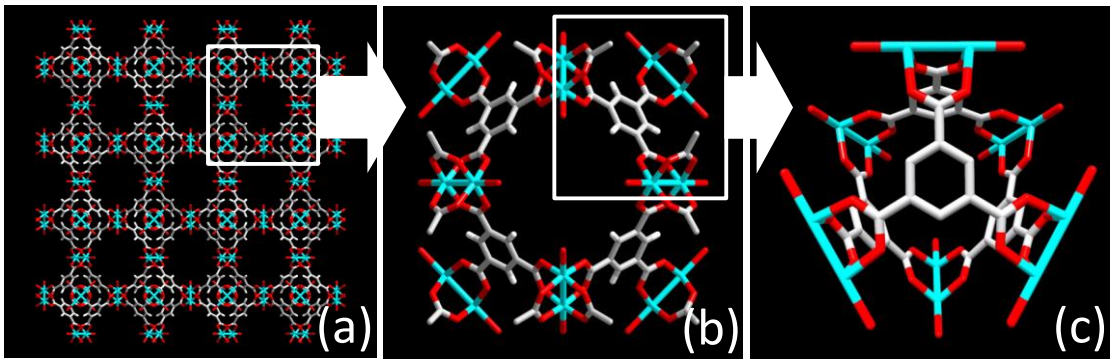


Figure S2. Cu-BTC particles have the same framework structure as that of HKUST-1. Each copper-carboxylate cluster (paddle wheel) is connected by four benzenetricarboxylates. Four benzenetri-carboxylate panes are placed at four alternated faces of the eight triangular faces with Cu2 dimmers at the six vertices, forming an octahedral secondary building unit (SBU). By means of assembling SBUs through sharing vertices (direct edge sharing of the Cu–Cu bond), large square-shaped pores (9 × 9 Å) are produced which intersect each other.