Communication

Exceptional Function of Nanoporous Metal Organic Framework Particles in Emulsion Stabilisation

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A new concept of nanoroporous metal organic framework particles stabilising emulsions was investigated. The copper benzenetricarboxylate MOF particles adsorbed at oil/water interface play an exceptional function in stabilising both oil-
10 **in-water and water-in-oil emulsions.**

Pickering emulsion has many important applications in our daily lives, involving food, pharmaceutics, cosmetics, oil well drilling fluids and fuel conversion.[1] This interesting phenomenon is achieved by adsorption of small size solid particles at the
15 interface of immiscible liquid phases. To stabilise emulsion effectively, the solid particles are required to have hydrophilic and hydrophobic characteristics similar to surfactants, are able to be wetted by both oil and aqueous phases with an ideal contact angle ~ 90° at the interface.[2] Adsorption of the solid particles at
20 the interface is irreversible. Desorption requires much higher energy than the thermal energy at ambient temperature.[3] This differs solid particle stabilisers from surfactants used in emulsion stabilisation. A number of micro/nanoparticles such as silica, bacteria, proteins, gold nanoparticles, clay, metal oxides, carbon
25 black and latex colloids, have been used for stabilising emulsions.[1e,4] For these particles, to achieve the desired emulsions, surface modification is the prerequisite. We herein report a new approach to use nanoporous metal organic framework (MOF) particles to stabilise oil-water emulsions.
30 Different from the other solids, nanoporous MOFs are a new class of crystalline materials, consisting of organic ligands and inorganic metal cations, have a high surface area ~ 1000 - 7000 $m^2 g^{-1}$. Their diverse coordination and organic functionalities give MOFs the tonable shape and size of nanopores and unique
35 hydrophilic and hydrophobic features. The guest molecules adsorbed in the pores to some extent provide MOFs with an 'additional' functionality. These characteristics have MOFs found a wide potential applications, for example hydrogen storage, anticancer drug delivery, catalytic reaction and electrochemical
40 applications.[5] In making new microstructure objects through Pickering emulsion, MOFs will have distinct advantages over other solids currently in use. To our best knowledge, relevant study is rare at this time.

In this study, the nanoporous MOF nanoparticles were
45 prepared at ambient temperature using a simply stirring reaction method (see ESI), which could be scaled up more easily than a hydrothermal method. 1,3,5-benzenetricarboxylic acids (H3BTC) reacted with copper acetates in an ethanol/water medium,

yielding a turquoise blue coloured MOF slurry (Cu-BTC). The
50 obtained Cu-BTC particles have an effective diameter *ca* ~ 291 nm with a polydispersity of 0.113 and a zeta potential of - 0.3 mV. The X-ray diffraction pattern of Cu-BTC particles were in a good agreement with that of single crystals produced by the hydrothermal method (Fig. S1, ESI).
55 The nanoporous Cu-BTC MOFs (HKUST-1[6]) structure was illustrated in Fig. S2 (ESI). The square-shaped pores accounts for around 40% of the material porosity, which are accessible to many interesting molecules such as hydrogen, bioactive nitric oxide, pyridine, 4-(methylamino) pyridine.[5f,7] Furthermore, the
60 hybrid structure built by coordination of copper cations and benzentricarboxylate endows the Cu-BTC particles with a combined hydrophilic and lipophilic feature that is necessary for solid particles to stabilise the water-in-oil or the oil-in-water dispersion system. Next concern was centred on the feasibility of
65 MOF particles in stabilising emulsions without further surface modification.

The aqueous dispersion of the Cu-BTC nanoparticles was used as the aqueous phase for the subsequent preparation of oil-water emulsions. In this study, the emulsions type was defined by a
70 lower volume ratio of the disperse phase to the continuous phase in favour of the formation of disperse droplets. Both types of emulsions (oil-in-water and water-in-oil) were successfully prepared using a rotor-stator high speed homogenization method (Fig. 1a and e). In the water-in-oil emulsion (Fig. 1a), the
75 aqueous droplets were heavier than the oil and therefore creamed down to the bottom of the container. After a few hours, a translucent and colourless oil layer was formed at the top. In contrast, the oil droplets in the oil-in-water emulsion (Fig. 1e) were lighter than the aqueous phase and thus creamed up as the
80 blue layer. Underneath was a clear aqueous phase without the precipitated particles at the bottom. It suggests all of the Cu-BTC nanoparticles being virtually adsorbed at the oil-water interface. These emulsions were stable in a sealed container without the droplet appearance changing.
85 To study the droplet appearance and the interactions of the droplet-droplet and the droplets to the continuous phase, optical microscopic method was adopted to examine a single layer of the droplets. Obviously, the droplets in both types of emulsions clearly identified themselves from the continuous phase. The
90 aqueous droplets dispersed in the oil gradually lost their inner volume, caused by the evaporation of aqueous phase, led the surface to become wrinkled with a clearly visible skin/shell as
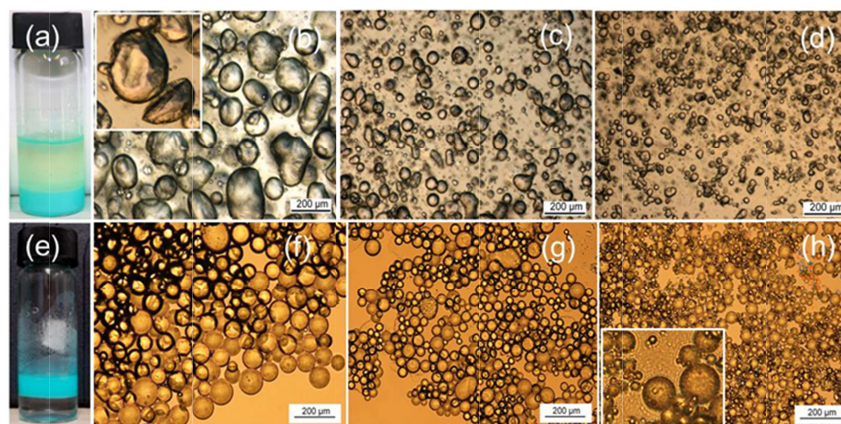
Fig. 1. Cu-BTC particles stabilise both water-in-oil and oil-in-water emulsions. Above: (a) water-in–oil emulsion (1.0 ml aqueous suspension in 3.0 ml oil), with MOF particle concentrations: (b) 0.8 wt%; (c) 1.6 wt% and (d) 3.2wt%. Below: (e) oil-in-water emulsions; (f) 1.0 ml oil and 0.8 wt% MOFs; (g) 1.0 ml oil and 1.8 wt% MOFs; (h) 0.5 ml oil and 1.8 wt% MOFs, in 2.0 ml aqueous phase.

shown in the inset of Fig. 1b. These results confirmed that the MOF particles have been adsorbed at the oil-water interface to form a physical barrier preventing droplets from coalescence. Compared with water droplets, the oil droplets kept their spherical shape for a longer time, implying that the Cu-BTC particles were favourable to stabilise oil-in-water emulsions. Coalescence under the action of capillary force was observed with the continuous phase disappearing.

A few factors influence the droplet size, two of which are the particle population in the emulsion system and the kinetics of solid particle adsorption at the oil-water interface. Reducing droplet size will increase the interfacial area. High particle population is therefore required in place to facilitate particles to be spontaneously adsorbed onto the fresh droplet surface to stabilise the droplets. Both the water-in-oil and the oil-in water systems (Fig. 1) followed this general rule. With particle concentration increasing from 0.8 to 3.2 wt% (in Fig. 1b, c and d), the size of water-in-oil droplets decreased from ~ 150 to ~ 10 µm. At a rotor-stator homogenization condition, a very strong turbulent shear force was applied for two minutes, which gave the droplet sufficient time to break and coalesce repeatedly until the droplet size and the particle adsorption reached to quasi-equilibrium.

Similar phenomena were observed in the oil-in-water system (Fig. 1f-h). However, the droplets in Fig. 1h showed a high polydispersity. The emulsion system contained 0.5 ml of the oil and 2.0 ml of the aqueous phase with 1.8 wt% Cu-BTC particles, which had the highest ratio of the particle population to the disperse phase volume, ~ 7.2 (particle concentration × suspension volume)/1.0 ml. Comparison of the results in Fig. 1g and 1h showed that at a given particle concentration a lower oil ratio (Fig. 1h) tended to produce a large population of smaller droplets. They coexisted with the big droplets similar to that in Fig. 1g. This reflected the cooperative effect of the droplet breakage under the strong turbulent conditions and the particle dynamic adsorption at the freshly formed oil droplet surfaces, followed a mechanism that the droplet breakage accompanied with particle stabilisation occurred in a series of stages. Only at a condition that there were sufficient free particles present in the system at each stage, stable uniform droplets could be formed.

Although the ratios of the particle population to the disperse phase volume in Fig. 1c and d (at 1.6/1.0 ml and 3.2/1.0 ml,

respectively) are close to that in Fig. 1g and h, the oil-in-water droplets are apparently larger than the water-in-oil droplets. This resulted from the higher viscosity of the oil phase and the diffusion of the particles from continuous phase to the interface.

In addition to particle diffusion, particle wetting kinetics also plays an important role for efficient homogenization, especially when the microfluidic/membrane emulsification method was used to produce droplets with precisely controlled size.[8] Different from rotor-stator homogenisation, the membrane method undertakes a different droplet formation mechanism. The droplets were formed through the membrane pores in a drop-by-drop manner, as shown by a high speed camera image (Fig. 2a). In this process, if the stabiliser is effectively adsorbed onto the oil-water interface spontaneously, the formed droplets will proportionally respond to the pore size and uniformity. As a result, the droplet size and distribution could be maintained in the final product.

In the membrane emulsification, approximate 10 ml of the oil was dispersed into 30 ml of the aqueous phase that contains 1.8 wt% of the Cu-BTC nanoparticles. In this case, the number of particles was in excess. The prepared sample was then separated into three layers after standing for a while (Fig. 2b), that is, a top oil droplet layer stabilised by the Cu-BTC particles, a middle clear aqueous phase and a bottom blue layer with the precipitated free Cu-BTC nanoparticles. The size of the formed oil-in-water droplets were in a region of ~ 200 - 300 µm in diameter (Fig. 2c), which was in proportion to the membrane pore size of 80×80 µm. This result was consistent with previous study of which affinitive surfactants were used as stabilisers.[9] Fig. 2d showed a remained blue particle film after the aqueous phase was evaporated and the oil droplets were broken. The same blue colour as observed in the fresh Cu-BTC particles implied the particles were stable in the studied systems. This was also verified by the x-ray diffraction. Neglecting the apertures shown in Fig. 2d, the particle film had a good continuity, played exceptional function in stabilising the droplets in the continuous phase. The impact of particle adsorption at interface on the dynamic interfacial tension was investigated by pending an aqueous droplet in the oil (in Fig. 3). With the adsorption of particles, the interfacial tension gradually reduced from ~ 12 - 14 to ~ 6 - 7 mN/m and levelled at this value afterwards. The equilibrium time was governed by the wetting kinetics of the MOF particles.
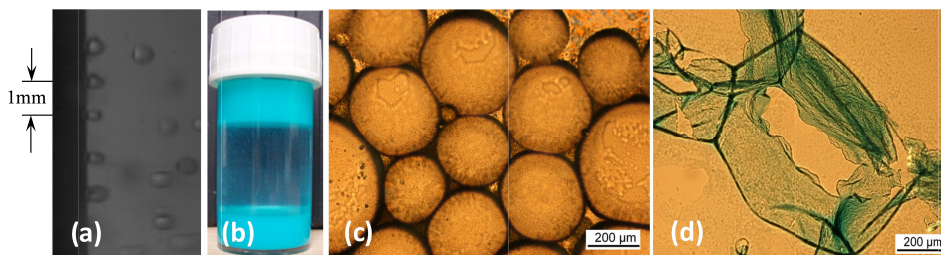
Fig. 2. Oil-in-water emulsions were produced by a rotating membrane emulsification method. (a) droplet formation process on the surface of a membrane at 300 rpm, recorded by a high speed camera at 3000 frame per second; (b) an emulsion sample with top layer: oil droplets; middle layer: aqueous phase and bottom layer: excess particles; (c) the formed oil droplets in uniform size of 200-300 µm; (d) a particle film formed on a droplet surface.
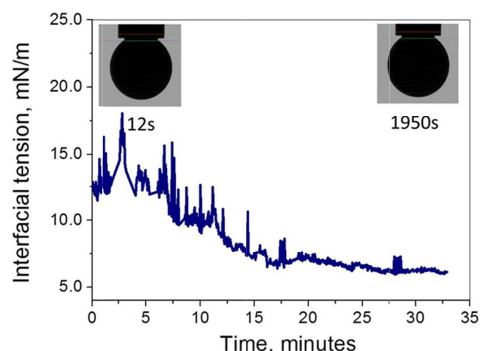
Fig. 3. Interfacial tension profile of an aqueous droplet in the oil phase measured by pending drop method.

In summary, the nanoporous Cu-BTC MOF nanoparticles have exhibited an exceptional function as a sole stabiliser to stabilise both water-in-oil and oil-in-water emulsions without further surface modification. The MOF nanoparticles were adsorbed at the oil-water interface to form a continuous thin film preventing the droplets from coalescence. Dynamic adsorption of particles at droplet surface determines the droplet size and distribution. Both water-in-oil and oil-in-water emulsions formed in this study have excellent stabilities. This unique property is attributed to the hybrid chemical nature of the MOF frameworks, leading MOFs to be advantageous over other surface active particles for applications in the controlled drug delivery, catalysis and microreaction. Nanoporous MOF particle stabilising emulsions provides a new approach to construct multifunctional microstructures, is worthy of further exploration.

Notes and references

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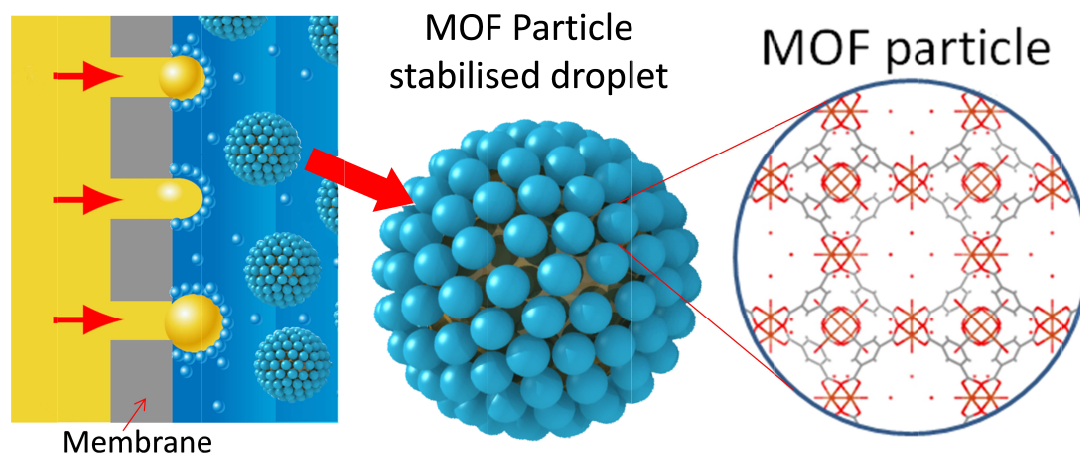
Communication

TOC

MOF Particle stabilised droplet

MOF particle

Membrane

5

Nanoporous metal organic framework (MOF) solid particles effectively stabilise both oil-in-water and water-in-oil emulsions