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Facile synthesis of Cu-BDC/Poly(N-methylol acrylamide) HIPE monoliths *via* CO_2-in-water Emulsion stabilized by metal-organic framework

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HIGHLIGHTS

- Composite HIPE Monoliths obtained via C/W HIPE Emulsions.
- The volatile organic solvent is avoided.
- Exhibited a high compressive stress of 2.2 MPa and 91.5% strain.
- Exhibited antibacterial activity against *Escherichia coli.*
- A coordination polymer uniformly dispersed in PolyHIPE.

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ABSTRACT

Macroporous poly(*N*-methylol acrylamide)–high internal phase emulsion [poly(NMA)HIPE] composite monoliths were prepared by carbon dioxide-in-water (CO_2/W) emulsions using metal-organic framework (MOF) Cu-BDC (BDC = 1,4-dicarboxybenzene) as stabilizer. The composite monoliths were characterized using XRD, SEM, EDS-mapping, FT-IR, TG, and mercury injection methods. Increasing the internal phase fraction would lead to the decrease of monolith density and the increase of void size, and it is favorable for the formation of macroporous interconnected structure with low density and porosities up to 81.6%. The mechanical properties of the Cu-BDC/poly(NMA)HIPE and Cu-BDC removal were also evaluated. The composite polyHIPEs exhibited high antibacterial activity against *Escherichia coli*. The presented approach facilitated the clean manufacture of open-celled MOF based scaffolds in a one-pot process with porosity of up to 82%.

1. Introduction

Porous monoliths with well-defined pore structure have attracted considerable attention due to their multifarious applications, such as scaffolds for tissue engineering, vehicles for drug delivery, and self-healing materials. Emulsion-templating technology is often used during fabrication of the monoliths and the porous inorganic-organic composites [1,2].

Traditionally, a high internal phase emulsion (HIPE) of more than 74% v/v internal phase is usually adopted and to lock the structure of the continuous phase after polymerization [3,4]. The high internal phase of supercritical carbon dioxide-in-water (CO_2/W) emulsion method facilitates the post-processing operation and avoids material contamination due to the residual organic solvents [5]. In general, the formation of stable CO_2/W emulsions depends on hydrophilic head-composed surfactants connected with a CO_2-philic tail, which consists of fluorinated, polysiloxane chain, or polyvinyl esters [5–7]. A low density, monolithic macroporous polyHIPE retain a typical open-pore structure with larger voids, which interconnected by the smaller windows [8].

The organic units in metal-organic framework (MOF) [9,10] are usually polycarboxylates, which coordinated to metal ions, yielding architecturally robust crystalline MOF structures. MOFs have amphiphilic properties that can assemble at the CO_2 and water interface or the liquid-liquid interface [11,14], and are a great potential to be used as templates for synthesis, such as porous nanocomposite materials [12–15], nanoporous carbons (NPC) as electrode materials [16], nanoporous carbons as catalyst [17], homochiral polymer thin film [18], and poly-pickering-foams [12]. The hybrid structure built by coordination of copper cations and benzenetricarboxylate endows the Cu-

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BDC particles with a combined hydrophilic and lipophilic feature that is needed for solid particles to stabilize the water-in-oil or the oil-in-water dispersion system (Pickering emulsion) [14,25].

In the periodic table of elements, most of the elements in the transition metal region have a certain inhibitory or killing effect on the microorganism, and the three ideal elements are silver [19], copper [20,21], and zinc [22]. Among the chemical antibacterial materials, the third-generation of bacteriostat is an MOF antibacterial material, which has a structured and highly specific surface area [23,24]. Furthermore, to attain the long-term antibacterial influence on cells, stable and continual release of metal ions is required. To our knowledge, antimicrobial studies about MOF@polyHIPE and the presented method have less reported in the literature.

In this contribution, Cu-MOF(Cu-BDC) is used as a key stabilizer for the stabilization of CO_2/W HIPE emulsion. The mechanical properties and antibacterial activity of Cu-BDC/Poly(N-Methylol acrylamide [NMA])HIPEs, obtained from different internal phase fraction of CO_2/W emulsion, were investigated.

2. Experimental

2.1. Materials

N-Methylol acrylamide(NMA), polyvinyl alcohol (PVA) (Low molecular weight Mw < 27000 g/mol) were purchased from aladdin (China) and used as received. *N,N′*-methylenebisacrylamide (MBAM, 96%, Acros), potassium persulfate ($K_2S_2O_8$, Merck Chemicals).

CO_2 was supplied by Wurumqi Gas Factory (purity > 99.9%). Triethylamine was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). And other used reagents were supplied by Tianjin Chemical Reagent Co. Ltd. (analytical reagent grade, Tianjin, China). High-pressure reactor with a design pressure of 40 MPa. (100 mL, Dalian fourth Instrument Factory, China). Deionized water was used during the whole of experimental.

2.2. Synthesis of Cu-BDC MOF

The MOFs were synthesized in ethanol(Fig. 1). Cu-BDC crystals were prepared by mixing $Cu(OAc)_2{\cdot}H_2O$ (3.99 g), H_2BDC (3.32 g)), and ethanol (50 mL). All the reagents were dissolved by stirring for 100 min, and triethylamine (5 mL) was dropped into the rapidly stirred mixture. After stirring for 6 h at 25 °C, the reaction was terminated [25]. The solid was separated by centrifugation at a speed of 5000 r·min^{-1}, followed by washing with ethanol several times. Cu-BDC was obtained after drying at 60 °C by using a vacuum for 12 h.

2.3. Polymerization of CO_2/W HIPE emulsions

Adding small amount of polyvinyl alcohol (PVA) which served as the binder in the continuous aqueous phase, and the Cu-MOF was dispersed in the above solution by stirring for 15 min. The above-mentioned aqueous dispersion was placed in a high-pressure reactor (100 mL) and a mixture of NMA, MBA and the $K_2S_2O_8$ initiator was added to provide an aqueous/CO_2 ratio. The reactor was charged-

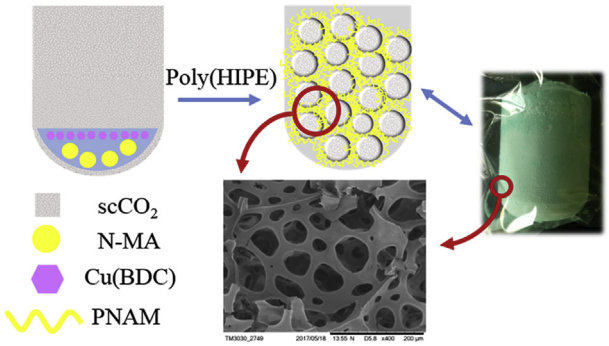

Fig. 2. Preparation of Pickering HIPEs stabilized by MOF particles.

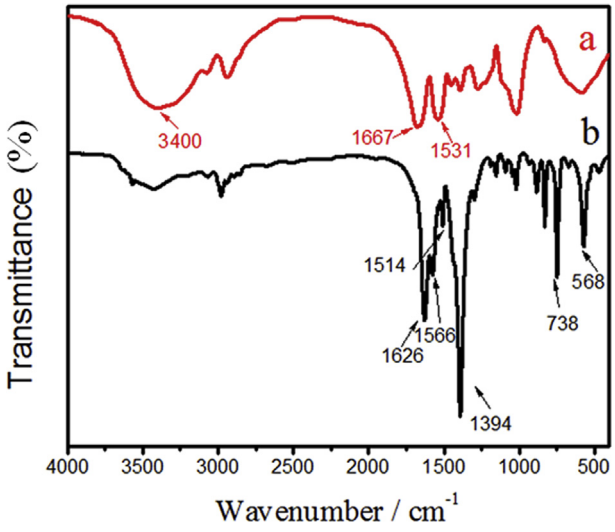

Fig. 3. The FTIR spectra of Cu-BDC/Poly(NMA)HIPE (a); Cu-BDC (b).

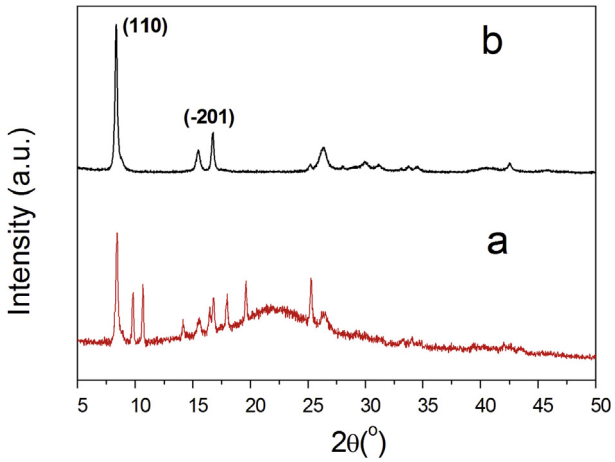

Fig. 4. The XRD pattern of Cu-BDC/Poly(NMA)HIPE (a); Cu-BDC (b).

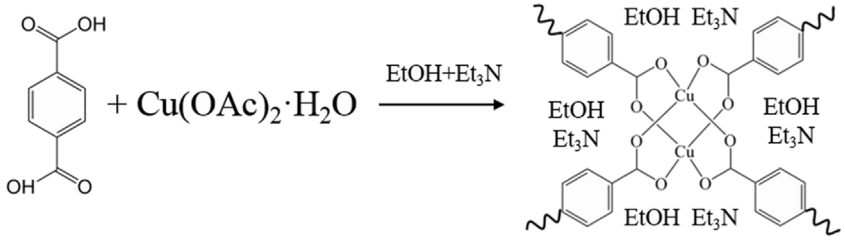

Fig. 1. Schematic illustration for the preparation of Cu-BDC.