REVIEW

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Porous Metal-Organic Framework-Polymer Composites Using High Internal Phase Emulsion Templates: A Review

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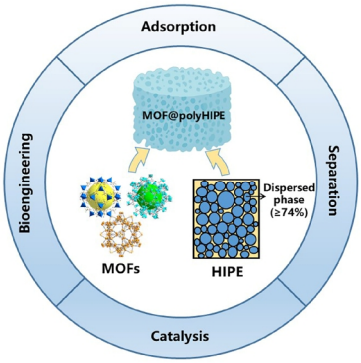
ABSTRACT As promising engineering materials for green and sustainable processes, porous metal-organic framework (MOF)-polymer composites show great potential in applications, including adsorption, separation, catalysis, and bioengineering. Owing to the mild and scalable operation, porous polymeric materials derived from high internal phase emulsion templates (polyHIPE) have received great interests in recent decades. In this contribution, research progress of the preparation of porous MOF@polyHIPE composites and their applications are reviewed, highlighting how can MOF particles be shaped by HIPE templates, in particular the polymerizable ones. Four different emulsion templates stabilized by MOFs and the applications of corresponding MOF@polyHIPE are included. Hopefully, both the state-of-art and future directions present herein can give rise to the development of high-performance porous MOF@polyHIPEs.

Keywords: high internal phase emulsion (HIPE), metal-organic frameworks (MOFs), adsorption and separation, heterogeneous catalysis, bioengineering



High internal phase emulsion (HIPE), also known as super concentrated emulsion or gel emulsion, refers to emulsion with the volume fraction of dispersed phase above 74.05%.[1,2] HIPEs widely exist in many fields such as cosmetics, pharmaceuticals, and food.[3] In recent decades, they are used as templates in the preparation of low density polymer foams or monoliths with the advantages of high specific surface area, high porosity and low density.[2,4,5]

Choice of stabilizer is the key to produce HIPE templates. Emulsion stabilizers mainly include organic surfactants, amphiphilic particles and gels.[5] Low molecular surfactants are the most conventional stabilizer for HIPE preparation. Unlike surfactants reducing the interfacial tension of two liquid phases, particles can irreversibly adsorb at the liquid-liquid interface, preventing droplet coalescence and ensuring the dynamic stability of emulsion.[6,7] Emulsions stabilized by micrometer- or nanometer-scale solid particles, termed Pickering emulsion, were first proposed by Ramsdem[8] and Pickering.[9] In earlier works, it has been thought to be extremely difficult to stabilize HIPEs using commonly used particles because phase inversion occurs when internal phase volume fraction is above 0.7.[10-12] Nonetheless, several groups have succeeded in creating Pickering HIPEs, either by the surface modification of particles[13-18] or by the use of synthetic particles that have appropriate surface properties.[19-22] Unlike previous researches, Kim et al. reported a versatile strategy to produce Pickering HIPE by exploiting a depletion interaction between an emulsion droplet and a particle with the help of water-soluble polymers as a depletant.[23] By using this strategy, diverse particles can be applied to stabilize an interface.

Among the diverse particle emulsifiers, MOFs have attracted considerable attention owing to their unique features and potential applications.[24] MOFs are self-assembled by metal ions or metal clusters and organic ligands through coordination bonds, which have regular and tunable porous structures, a huge specific surface area and wide applications in gas storage,[25] catalysis,[26] sensors,[27] and drug delivery.[28] However, the bulk powder or crystal form of MOFs severely restrict their processability and usage. Immobilization of MOFs to achieve a macroscopic shape of MOFs (i.e., shaped MOFs), such as a monolith or other structural materials, is a key driver to enhance their application and handling. The resulting structured MOF-based materials are capable of hierarchical porosity for high mass diffusion, and thus promote their potentials.[29,30] In fact, shape-engineering of MOFs has been a long-standing challenge. Among the strategies reported so far, the combination of MOFs with easily processable organic polymers provides a convenient strategy to address the challenge. MOFs-stabilized Pickering HIPE templating represents a promising strategy for the immobilization of MOFs. In addition, if the continuous phase of the HIPE template contains polymerizable monomers, highly porous MOF@polymer monoliths can be prepared, referring to as MOF@polyHIPEs, which combine the features of MOFs and polyHIPE into novel hybrid materials going beyond the interest of classical organic/inorganic hybrids development.

This contribution highlights the recent progress of MOF-stabilized HIPEs and the corresponding porous MOF@polyHIPE composites. Figure 1 shows the scope of this review. Four different emulsion templates stabilized by MOF particles that can be utilized for the fabrication of porous MOF-based polyHIPEs are included. In addition, their applications involving adsorption, separation, catalysis, and bioengineering are briefly discussed from the green and sustainable points of view. As an ending remark, a comprehensive table summarizing MOF@polyHIPE composites is given. This minireview aims to stimuli more works on developing high-performance MOFs-based hybrid materials for the appli-

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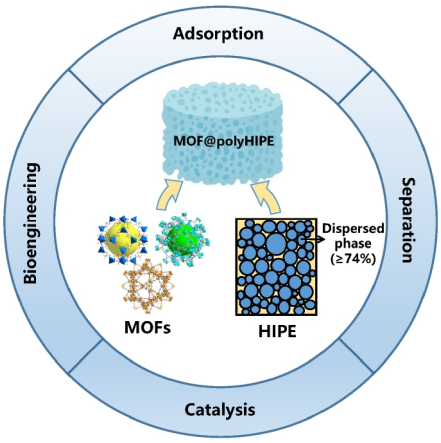

Figure 1. Scope of this review featuring MOF@polyHIPEs hybrid porous materials with potential applications in adsorption, separation, catalysis, and bioengineering.

cations in green chemical processes, which further contribute to global carbon neutrality.

n PICKERING HIPES AND MOF@POLYHIPE

MOF particles are highly suitable for assembling at liquid-liquid interfaces to form Pickering emulsions due to their hybrid composition, mid-range zeta potential and facile surface functionalization.[31-33] Owing to the metal ions or clusters that are hydrophilic and organic ligands which are hydrophobic, MOFs have been known as amphiphilic and surface-active materials, and some specific MOFs (e.g., HKUST-1, UiO-66) can stabilize both oil-in-water and water-in-oil emulsions, where phase inversion is governed by the oil volume fraction. According to the type of emulsion, MOFs-stabilized HIPEs can be roughly divided into four categories: oil-in-water (O/W), water-in-oil (W/O), supercritical CO_2-in-water (C/W) and ionic liquid-in-water (IL/W) Pickering HIPEs.

Oil-in-Water Pickering HIPEs. Oil-in-water emulsion is the most commonly used emulsion template for preparing MOF@polyHIPE composites. So far, MOF particles, such as $Cu_3(BTC)_2$ (BTC, 1,3,5-benzenetricarboxylic acid) or HKUST-1, $Mn_3(BTC)_2$, Ni(BDC) (BDC, 1,4-benzenedicarboxylic acid), UiO-66, MIL-96 (Al), and ZIF-8 (ZIF, zeolitic imidazolate frameworks), have been used to stabilize O/W emulsions.

In 2016, the Zhang group[34] for the first time prepared MOF-stabilized O/W HIPEs by mechanically stirring the mixture of water, oil and MOF at room temperature, with no additional additives or high-energy input involved. It was found that MOF nanocrystals, including 0D nanoparticles $Cu_3(BTC)_2$, 1D nanowires $Mn_3(BTC)_2$ and 2D nanosheets Ni(BDC), can produce stable O/W HIPEs. They explored the underlying mechanism for the HIPE formation, and demonstrated that all the three MOFs have negative and mid-range zeta potentials, allowing suitable amphiphilicity and weak repulsions between MOF nanocrystals. Therefore, the MOF nanocrystals can be anchored at oil-water interface to emulsify the two immiscible phases. The MOF nanocrystals assembled at oil-water interface play a key role in HIPE stabilization. Based on MOF-stabilized HIPE, the authors proposed a versatile strategy

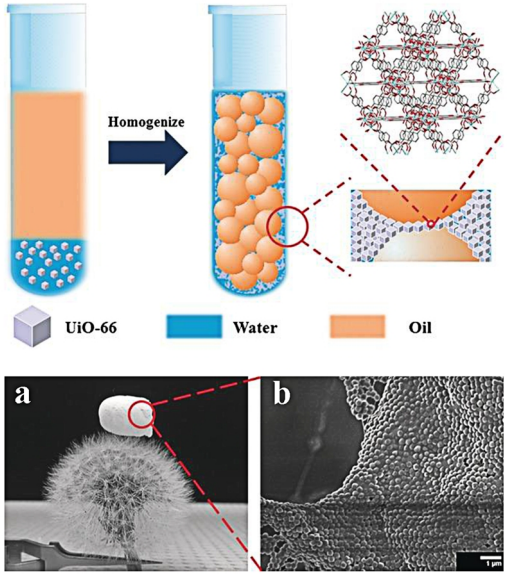

Figure 2. Top half: preparation of Pickering HIPEs stabilized by MOF particles. Bottom half: (a) Optical image of MOF/PVA porous monolith with a density of 15 mg·cm^{-3} on a dandelion flower, (b) Scanning electron microscopy (SEM) image of the MOF/PVA porous monolith.[35] Copyright 2016, WILEY-VCH.

for the preparation of metal-organic aerogels (MOAs) with unique features. The resulting MOAs preserve the skeleton replica of HIPE and are expected to be applied in the fields of adsorption, catalysis and so on.

In the same year, Zhu[35] et al. prepared O/W Pickering HIPEs with internal phase up to 90% solely stabilized by MOF particles UiO-66, as shown in the top half of Figure 2, and systematically studied the effects of internal phase type and volume, as well as MOF particle concentration on stability of the resulting Pickering HIPEs. The authors demonstrated that UiO-66 particles absorbed at the interface provide sufficient barrier against coalescence of the oil droplets. On the other hand, excessive particles in the continuous phase closely pack together, which results in a dramatic increase in viscosity and thus inhibits creaming and phase inversion. Furthermore, taking Pickering HIPEs as templates, they successfully prepared two MOF-based hierarchical porous monoliths via adding small amount of polyvinyl alcohol (PVA) as binder or copolymerization of acrylamide (AM) and bis(acrylamide) in the continuous phase followed by freeze-drying. The former monolith has an open-cell structure. By fine-tuning internal oil phase volume, UiO-66/PVA monolith with a density as low as 12 mg·cm^{-3} can be obtained. As illustrated in the bottom half of Figure 2, ultralight UiO-66/PVA monolith can stably stay on a dandelion flower. In contrast, the later UiO-66/polyacrylamide (PAM) monolith exhibits a closed-cell structure, because its thicker cell wall avoids the break caused by either volume shrinkage during polymerization or the mechanical force in the freeze drying. As an extension, the same group fabricated porous UiO-66/PAM monoliths with open-cell structure by adding a small amount of PVA as co-stabilizer.[36] Actually, to obtain interconnected MOF@polyHIPE porous monolith, co-stabilizer is commonly added for the

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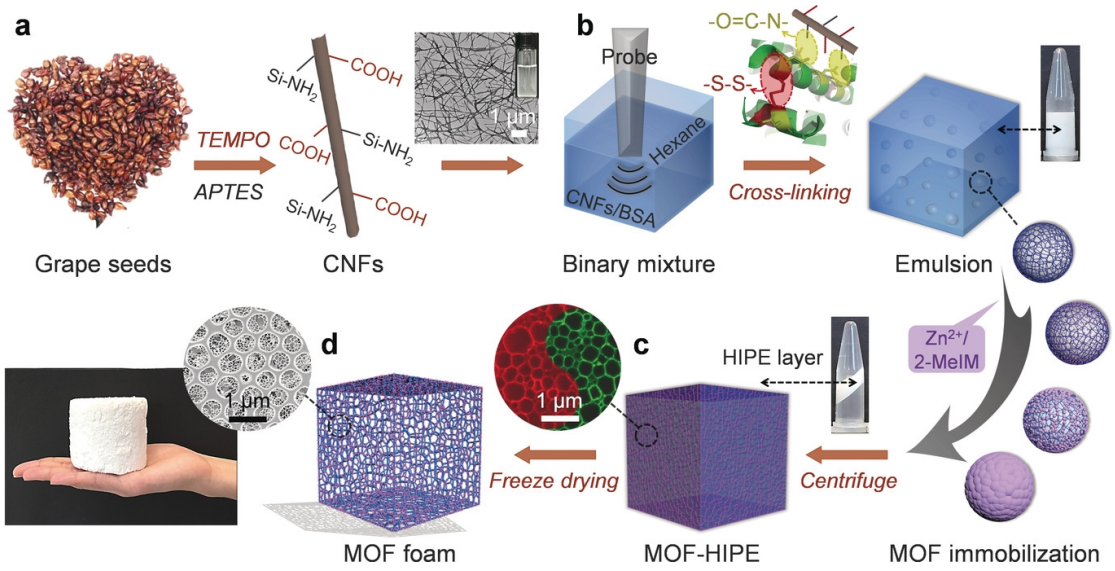

Figure 3. Schematic illustration of the preparation of ZIF-8 monolithic foam. (a) 2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO)-exfoliation of CNFs from grape seed with further 3-aminopropyltriethoxysilane (APTES) modification. (b) Fabrication of shell-cross-linked microspheres. (c) Preparation of a gel-like HIPE layer. (d) Fabrication of the hierarchical porous ZIF-8 foam by freeze-drying[41]. Copyright 2020, WILEY-VCH.

Pickering HIPE template preparation. For example, Lorignon et al.[37] prepared PAM-MOFs composite monoliths based on a MIL-96(Al) particles stabilized paraffin-in-water Pickering emulsion template. The existence of PVA in the continuous phase of emulsion promotes the formation of pore throats, and thus improves interconnectivity of the monoliths.

ZIF-8 is a tetrahedrally-connected framework constructed from zinc(II) ions and 2-methylimidazole that displays high thermal and chemical stability,[38,39] and has previously been employed to provide Pickering-stabilization to form emulsion droplets.[40] More recently, Chen et al.[41] have proposed an elegant strategy for preparing a spiderweb-like ZIF-8 multifunctional monolithic foam via HIPE templating. As detailed in Figure 3, the synthesis of MOF monolithic foam follows the steps: (a)-(b) the formation of shell-cross-linked microspheres by ultrasonication using functionalized cellulose nanofibers (CNFs) and bovine serum albumin (BSA) as the shell materials; (b)-(c) the in-situ growth of ZIF-8 MOF nanoparticles on the microspheres with the addition of the precursor solutions including zinc nitrate and 2-methylimidazole (2-MeIM); and (c)-(d) concentrating the MOF-microsphere composites to form stable HIPEs by centrifugation, which are then freeze-dried to produce the porous foam structure. The resulting monolithic foam composes of ordered pores with plentiful MOF particles evenly distributed, enabling excellent catalytic and adsorption capacity even at high MOF loading.

Water-in-Oil Pickering HIPEs. Using ZIF-8 as a model MOF, Jin et al.[42] proposed a strategy for preparing robust hierarchically porous MOF-polyHIPE composites through an interfacial nanoassembly/emulsion polymerization method using MOF stabilized Pickering HIPE as template. Specifically, the W/O HIPEs were prepared by using MOF nanoparticles containing water as the dispersed phase and a mixture of polymerizable monomers (St, styrene and DVB, divinylbenzene) as the continuous phase. After polymerization in shaped moulds and washing, bulk ZIF-8/polystyrene (PS) monolithic composites with various shapes can be obtained, as shown in Figure 4a. The pore size, shape and mechanical properties of the resulting materials can be adjusted by changing the composition and dosage of MOF particles. The composites prepared by this method have excellent stability and mechanical properties, which can be extended to different MOF@polyHIPE systems, such as UiO-66 and Cr-MIL-101 (Figure 4b).

Wang and co-workers prepared W/O HIPEs with internal phase volume as high as 85.3 vol% through a two-step emulsification strategy by using ZIF-8 MOF particles and macromolecular surfactant Pluronic L-121 as emulsifier.[43] The addition of the secondary emulsifier Pluronic L-121 provides plenty of smaller internal phase droplets, and leads to a decrease in the size of ZIF-8-stabilized large droplets, both of which greatly increase the viscosity of emulsion and enable the conversion of dilute O/W emulsion into HIPEs. This strategy can be applied to commonly use solvents such as toluene, cyclohexane, dichloromethane, and monomers such as styrene and methyl methacrylate. Taking the ZIF-8/L-121 stabilized HIPE as template, ZIF-8-based hierarchically

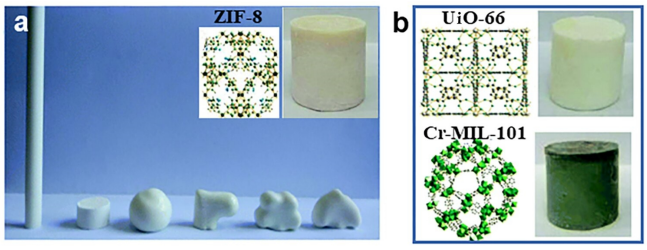

Figure 4. Hierarchically porous MOF/PS composites prepared by the interfacial assembly/polymerization fabrication procedure: (a) various shapes of hierarchically porous ZIF-8/PS; (b) UiO-66/PS and Cr-MIL-101/PS composite monoliths obtained.[42] Copyright 2018, Royal Society of Chemistry.

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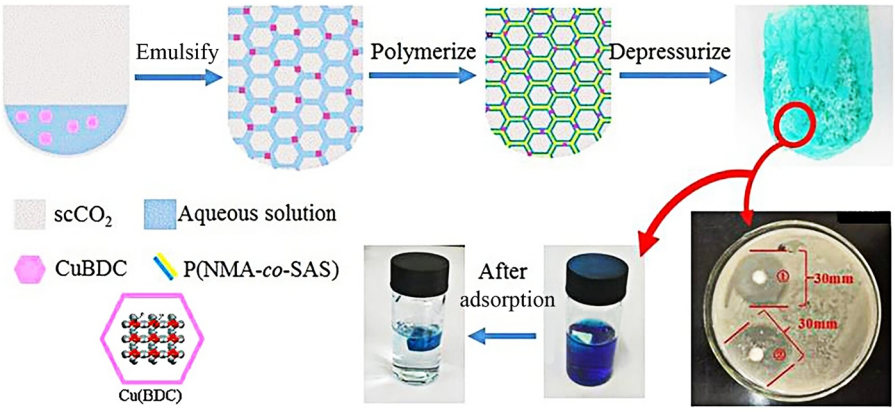

Figure 5. Cu-BDC@P(NMA-co-SAS)-HIPE with potential applications in adsorption and antibacterial material obtained by C/W emulsion templating with Cu-BDC as stabilizer.[49] Copyright 2020 Elsevier.

porous monoliths (ZIF-8@polyHIPE) were fabricated. Remarkably, micron sized ZIF-8 particles selected in their work are able to penetrate the cellular wall of polyHIPE, making about 80% of MOFs accessible to the guest molecules, which thus effectively solves the problem of MOF embedding. In addition, the obtained porous ZIF-8@polyHIPEs exhibit enhanced mechanical and mass transfer properties, showing great application prospects in adsorption, separation and industrial catalysis.

In addition to most commonly used MOFs mentioned above, researchers have also developed many other MOF polymeric composites using W/O Pickering HIPE templates, such as MIL-100(Fe)@polydicyclopentadiene (PDCPD)-polyHIPE [44] and wettability tunable $CONH_2$-MIL-101(Cr)@polyHIPE for fast solid-phase extraction.[45]

Supercritical CO_2-in-Water Pickering HIPEs. Supercritical carbon dioxide ($scCO_2$) has moderate critical temperature and pressure (31.1 ℃ and 7.38 MPa), and has high solubility in several liquids, making it a green solvent with excellent properties.[46] Due to its advantages of non-toxic, pollution-free, cost effective and easy recovery, $scCO_2$ has been used to replace the traditional organic solvent to prepare novel C/W HIPEs.[47] MOFs, including Cu-BDC,[48,49] UiO-66,[50] HKUST-1,[51] and Ca-BDC,[52] having amphiphilic (CO_2-philic and hydrophilic) property, can be adsorbed at the interface of $scCO_2$-water phase and promote the stabilization of C/W Pickering HIPEs.

Yang and co-workers prepared porous monolithic composite based on C/W Pickering HIPE template using Cu-BDC as emulsifier.[48] The synthesized Cu-BDC@poly(N-methylol acrylamide) (PNMA)-polyHIPE has been proved to have strong compressive properties and the porosity of monomer is up to 81.6%, which can be adjusted by changing the composition of emulsion. By adding a co-monomer sodium allyl sulfonate (SAS) ion into C/W HIPE, they further prepared macroporous Cu-BDC@P(NMA-co-SAS)-polyHIPE composites, as shown in Figure 5.[49] The incorporation of sulfonated monomer SAS improves the expansion rate, antibacterial properties, and adsorption properties of the material, making it possible to have a potential application in adsorption and antibacterial material (Figure 5).

Although MOFs can emulsify C/W HIPEs, the emulsions usually become unsteady in the presence of hydrophilic monomers,

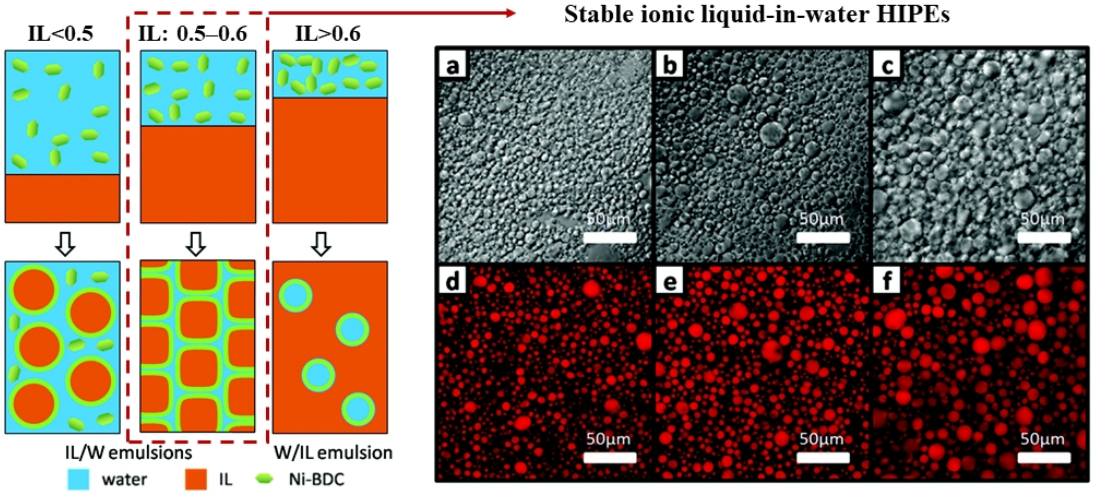

Figure 6. Proposed formation mechanism of the IL-in-water HIPEs stabilized by Ni-BDC and CLSM images of HIPEs stabilized by Ni-BDC (0.05 g mL^{-1}) at IL volume fractions of 0.5 (a and d), 0.55 (b and e), 0.6 (c and f).[55] Copyright 2016, Royal Society of Chemistry.

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which can be solved by adding co-stabilizers such as PVA. Therefore, benefiting from PVA as co-stabilizers, Cao et al. synthesized a hydrophilic porous composite HKUST-1@PAM-polyHIPE,[51] and a bio-compatible porous composite MOF/P(AM-co-HEMA)-polyHIPE (HEMA, 2-hydroxyethyl methylacrylate)[52] from C/W HIPE templates.

Ionic Liquid-in-Water Emulsions. Ionic liquid (IL) refers to the salt that is liquid at or near room temperature and completely composes of cation and anion, also known as low-temperature molten salt.[53] ILs have attracted more and more attention because of their incomparable advantages over traditional solvents and their application as green solvents in the synthesis of organic and polymer substances.[54]

Li and co-workers[55] firstly studied the stabilizing effect of MOFs on IL/W emulsion and the mechanism of MOF-stabilized HIPEs. The experimental results show that Ni-BDC has strong hydrophilicity to emulsify water and ionic liquid under certain conditions. As demonstrated in the left of Figure 6, when the volume fraction of ionic liquid is less than 0.5, a part of MOF particle crystals can be adsorbed on the interface of water and IL to form IL-in-water emulsion. However, the stability of emulsion is poor due to the gravitational sedimentation of IL droplets. When the volume fraction of ionic liquid increases to 0.5-0.6, most MOF nanocrystals are adsorbed at the interface between water and IL, leading to a high viscous and stable emulsion, namely IL/W HIPE. It has been found that as the volume fraction of IL is higher than 0.6, only an unstable water-in-IL emulsion can be formed. As shown in the right of Figure 6, images obtained by confocal laser scanning microscopy (CLSM) confirm that IL-in-water HIPEs can be formed with IL volume fractions of 0.5, 0.55, and 0.6. Given the stable IL/W HIPEs formed, macroporous Ni-BDC@PAM polymer composite was prepared. Strictly speaking, the stable IL/W emulsions shown here are medium internal phase emulsions as the IL volume factions are lower than 0.74.

n APPLICATIONS

Adsorption and Separation. According to the good adsorption properties for CO_2 and dyes, MOF@polyHIPE composites are often used as adsorbent in various adsorption and separation processes. Wang et al. successfully synthesized UiO-66@PAM-polyHIPE composites with closed- and open-cell structures, and measured the adsorption capacity towards CO_2.[36] Compared to the closed-cell monoliths, the open-cell structure improved the CO_2 adsorption behavior of the monoliths, having a higher adsorption capacity that increases from 5.72 to 6.67 mg g^{-1} and a faster adsorption rate which rises from about 30 to 10 mins to reach saturation. The same group also prepared ZIF-8@PS-polyHIPE composite for achieving an enhanced iodine adsorption capacity compared to ZIF-8 powder.[43]

Inspired by the seeded growth strategy proposed by Zhan et al.,[56] Majaz et al.[57] proposed a new synthetic route to prepare MOF@polyHIPE hybrid materials via secondary recrystallization of the pre-synthesized metal-oxide@polyHIPE nanocomposites. As illustrated at the left in Figure 7, the nanocomposite foams MO_x@PDCPD-polyHIPE were prepared using metal-oxide nanoparticles (MO_x-NPs)-stabilized W/O Pickering HIPE with Pluronic-121 as co-stabilizer. After that, the corresponding metal-based MOFs were recrystallized under the solvothermal conditions, leading to the formation of MOF@polyHIPE. Referring to the secondary recrystallization approach, two hybrid materials were synthesized, i.e., HKUST-1(Cu)@polyHIPE and MOF-5(Zn)@polyHIPE, which exhibit a high MOF phase loaded with pronounced micropore accessibility. After 20 cycles, the CO_2 adsorption capacity of the hybrid MOF@polyHIPE materials under 50% humidity does not change significantly, showing stable and durable adsorption capacity of CO_2 under humid conditions. In addition, Zhu et al.[58] synthesized an HKUST MOF@PGMA-polyHIPE (GMA, glycidyl methacrylate) based on in-situ generation strategy, followed by grafting polyethyleneimine (PEI). The resulting HKUST-type MOF/polyHIPE composites are abbreviated as PEI@PGDH, which combine the advantages of chemical CO_2 absorbent of PEI, hierarchical interconnection porous skeleton of PGMA, and

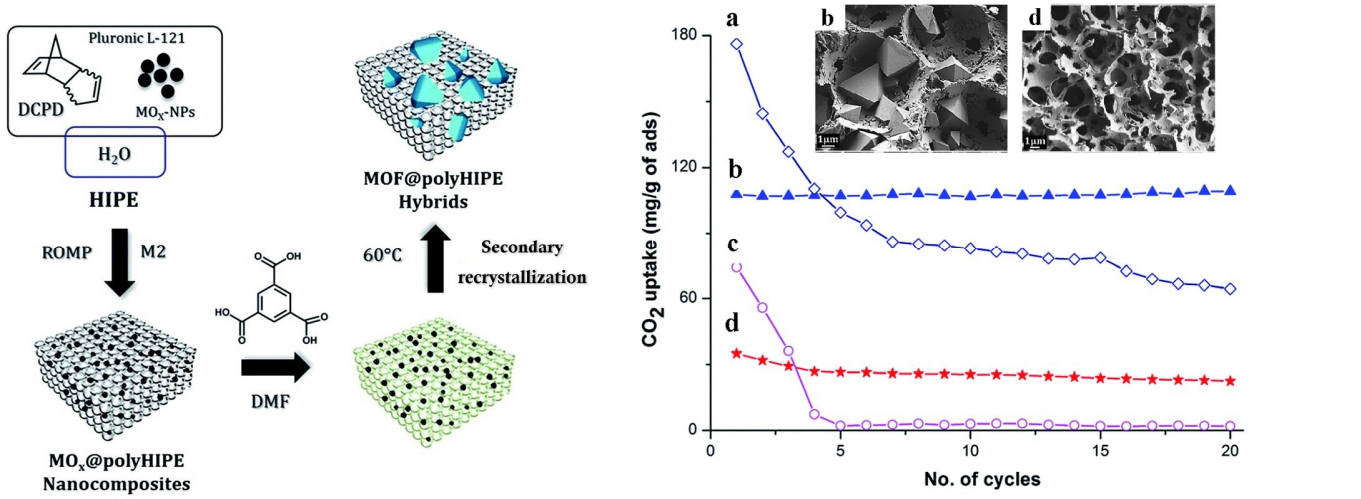

Figure 7. Left: schematic illustration of the MOF nanocrystals grown through the secondary recrystallization of MOx-NPs within the polyHIPEs. Right: CO_2 adsorption cycling test of (a) parent HKUST-1, (b) HKUST-1@polyHIPE hybrid, (c) parent MOF-5, and (d) MOF-5@polyHIPE hybrid.[57] Copyright 2017, Royal Society of Chemistry.

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high specific surface area of MOF, enabling high CO_2 adsorption rate, capacity, and selectivity. At 50 °C, 1 g of PEI_{70}@PGD-H (70 denotes the mass percentage of feeding PEI based on PGD-H) can adsorb 4.3 and 3.0 mmol of CO_2 at 1 and 0.15 atm, respectively, with a high CO_2/N_2 separation factor of 76.

Besides, Dong et al.[50] prepared interconnected macroporous UIO-66@PAM HIPE composites which have potential applications in oil-water separation and methylene blue (MB) adsorption. Yang et al.[59] synthesized MC-g-PMAANa/Cu-BTC (MC, methyl cellulose and MMANa, sodium methacrylate) composite based on the C/W HIPE template and applied it to dye adsorption. Liu et al.[60] prepared hydrophilic hydrogel adsorbents (H-UiO-66-NH_2-IHIPEs) derived from a biphasic synergistic HIPE for specific enrichment of luteolin with high selectivity and recyclability.

It should be mentioned that there are some MOF@polyHIPE composites prepared by an alternative method, which incorporates MOF particles after the formation of polyHIPE. For example, Janiak et al.[61] successfully synthesized MIL-101(Cr)@PHEMA-polyHIPE composite and measured the adsorption capacity towards the vapor of methanol and water. Compared with pure polyHIPE, MIL-101(Cr)@PHEMA-polyHIPE composite performs better adsorption capacity. In the subsequent study,[62] the same group embedded different MOF particles, i.e., MIL-100(Fe), MIL-100(Cr) and MIL-101(Cr) into the pre-synthetic PNIPAM-polyHIPE (NIPAM, N-isopropyl acrylamide) and found that MIL-101(Cr)@PNIPAM-polyHIPE composite shows good adsorption capacity for water vapor and can be used in heat transformation process.

Catalysis. MOF/polymer composites based on HIPE templates have been used as catalysts for different catalytic reactions. In this regard, Jin et al. realized a highly efficient Knoevenagel condensation reaction of malononitrile with benzaldehyde catalyzed by ZIF-8/PS-polyHIPE compared with bulk ZIF-8 nano- and microparticles.[42] Kovacic et al. demonstrated that the as-prepared MIL-100(Fe)@PDCPD-polyHIPE hybrid membranes show an appealing catalytic activity in Friedel-Crafts alkylation (e.g., benzyl bromide coupling reaction with *p*-xylene) in a batch mode as well as in a flow-through mode.[44]

In addition, Niu et al.[63] prepared a porous ZIF-8@PAM-polyHIPE composite through the combination of ZnO/PVA co-stabilized C/W HIPE template and in-situ growth of ZIF-8, which is a high-efficient photocatalyst in water pollution treatment. Kalinovskyy et al.[64] prepared a porous polymeric sponge containing MOF-808 using a W/O HIPE template, which is able to immobilize and catalytically degrade chemical warfare reagents. These works may promote the development of other functional materials for the catalytic degradation of organic pollutants.

Recently, Yan's group[65] have reported an acid-base bifunctional macroporous polymeric catalyst (UiO-66@P(AM-co-SS)-polyHIPE) (SS, sodium 4-vinylbenzenesulfonate) for the conversion of cellulose to hydroxymethylfurfural (5-HMF). As illustrated in Figure 8, the polymer catalyst was prepared by using the functional MOFs (UiO-66-SO_3H and UiO-66-NH_2)/Tween 85 co-stabilized Pickering HIPEs as templates. The obtained MOF@polyHIPE composite has a great catalytic ability for the conversion of cellulose into 5-HMF process as well, attributing to the synergistic effect between the large pore size and acid-base active sites. The highest 5-HMF yield achieves 40.5%, and the catalyst has great recyclability. Alternatively, Zhao et al. [66] grafted UiO-66-NH_2 onto the sulfonated PGMA-polyHIPE precursor and synthesized a new catalyst for transforming cellulose to 5-HMF, which was proved to have good catalytic ability as well, and can be recycled for four times while maintaining the catalytic activity.

Bioengineering. In addition to the above-mentioned fields, recent studies demonstrate that MOF@polyHIPE composites can be also competent in bioengineering fields such as antibacterial and protein recognition. The Cao group fabricated different porous MOF@polyHIPE composites based on Cu-BDC,[48,49] HKUST-1,[51] Ca-BDC,[52] and MIL-100(Fe)[67] stabilized Pickering C/W HIPEs for potential bioengineering applications. Both as-fabricated Cu-BDC@PNMA-polyHIPE and Cu-BDC@poly(NMA-co-SAS)-polyHIPE composites can be used as efficient antibacterial materials, with a larger diameter of the bacteriostatic zone towards *Escherichia coli* compared to pure Cu-BDC MOF material.[48,49] The resulting HKUST-1-based PAM-polyHIPE composite possesses a good adsorption capacity towards BSA, giving that 7 wt% HKUST-1 reaches a capacity of 350.4 mg g^{-1} in 1.0 g L^{-1} BSA solution and has potential applications in protein

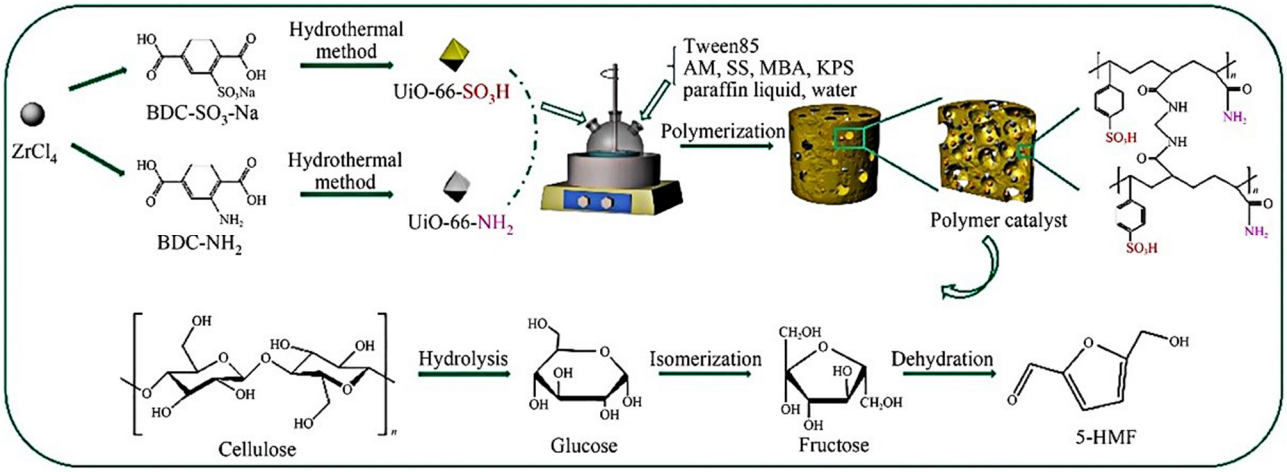

Figure 8. Schematic illustration for the preparation of a dual acid-base bifunctional macroporous polymer catalyst[65]. Copyright 2022 Elsevier.

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Table 1. Summary of MOF@polyHIPE Composites Collected in This Work

HIPE type	MOF particles	stabilizer	structure	porous monolith	application	ref.
O/W	UiO-66	MOFs	closed-cell	MOF@PAM-polyHIPE	-	35
O/W	UiO-66	MOFs/PVA	open-cell	MOF@PAM-polyHIPE	CO_2 adsorption	36
O/W	MIL-96(Al)	MOFs/PVA	open-cell	MOF@PAM-polyHIPE	-	37
O/W	UiO-66-NH_2	MOFs/Span 80	open-cell	MOF@molecularly im-printed polymer-polyHIPE	luteolin adsorption	60
O/W	MIL-101(Cr)	Kolliphor P188	open-cell	MOF@PHEMA-polyHIPE	methanol vapor and water vapor adsorption	61
O/W	MIL-100(Cr/Fe), MIL-101(Cr)	Triton™-X-405	open-cell	MOF@PNIPAM-polyHIPE	water vapor adsorption	62
O/W	UiO-66-SO_3H and UiO-66-NH_2	MOFs/Tween 85	open-cell	UiO-66@P(AM-co-SS)-polyHIPE	catalysis for the conversion of cellulose into 5-HMF	65
W/O	ZIF-8	MOFs	open-cell	MOF@PS-polyHIPE	catalysis for Knoevenagel condensation reaction	42
W/O	ZIF-8	MOFs/pluronic L-121	open-cell	MOF@PS-polyHIPE	iodine adsorption	43
W/O	MIL-100(Fe)	MOFs/pluronic L-121	open-cell	MOF@PDCPD-polyHIPE	catalysis for in Friedel-crafts alkylation	44
W/O	$CONH_2$-MIL-101(Cr)	MOFs/Span 80	open-cell	MOF@PDVB-polyHIPE	heterocyclic amines extraction	45
W/O	MOF-5, HKUST-1	MOFs/pluronic L-121	open-cell	MOF@PDCPD-polyHIPE	CO_2 adsorption	57
W/O	HKUST	CuO/synperonic PEL 121	open-cell	PEI-grafted MOF@PGMA-polyHIPE	CO_2 adsorption	58
W/O	UiO-66-NH_2	halloysite nanotubes-NH_2/hypermer 2296	open-cell	MOF@PGMA-polyHIPE	catalysis for the conversion of cellulose into 5-HMF	66
W/O	MOF-808	MOFs/span 80	open-cell	MOF@PS-polyHIPE	catalysis for nerve agent degradation	64
C/W	Cu-BDC	MOFs/PVA	open-cell	MOF@PNMA-polyHIPE	antibacterial material	48
C/W	Cu-BDC	MOFs/PVA	open-cell	MOF@P(NMA-co-SAS)-polyHIPE	dye adsorption and antibacterial material	49
C/W	UiO-66	MOAs/PVA	open-cell	MOF@PAM-polyHIPE	oil-water separation and dye adsorption	50
C/W	HKUST-1	MOFs/PVA	open-cell	MOF@PAM-polyHIPE	bovine serum albumin adsorption	51
C/W	Ca-BDC	MOFs/PVA	open-cell	MOF@P(AM-co-HEMA)-polyHIPE	β-amylases immobilization	52
C/W	Cu-BTC	ethyl cellulose/PVA	open-cell	MOF@P(MC-g-MAANa)-polyHIPE	dye adsorption	59
C/W	ZIF-8	ZnO/PVA	open-cell	MOF@PAM-polyHIPE	photocatalysis for MB degradation	63
C/W	MIL-100(Fe)	MOFs/PVA	open-cell	MOF@P(AM-co-NIPAM)-polyHIPE	protein adsorption and β-amylases immobilization	67
IL/W	Ni-BDC	MOFs	closed-cell	MOF@PAM-polyHIPE	-	55

analysis.[51] Recently, Ca-BDC[52] and MIL-100(Fe) have been used to stabilize $ScCO_2$-in-water HIPEs and biocompatible porous hybrid monoliths were prepared for the immobilization of β-amylase by the same group.[52,67] The addition of MIL-100(Fe) particles improves thethermal stability and specific surface area of the composite, enabling the highest protein adsorption rate of 55% and the immobilization efficiency of 89%. Moreover, MIL-100(Fe) @P(AM-co-NIPAM)-polyHIPE immobilized enzyme shows a higher biocatalytic activity in the acidic medium than the free enzyme.

n CONCLUSIONS AND OUTLOOK

In summary, HIPEs serve as good templates for preparing porous MOF/polymer composites, combining the advantages of HIPE templates (e.g., large specific surface area, high porosity, light weight) and MOF materials (e.g., diverse microstructures and functionalities). Moreover, the structures and properties of the composite can be easily manipulated by changing the type of MOF and the composition of emulsion. At present, the emulsion templates used include oil-in-water, water-in-oil, $ScCO_2$-in-water, and ionic liquid-in-water Pickering HIPEs. In general, MOF and polymeric co-emulsifier are used simultaneously to prepare stable HIPEs, thus leading to mechanically robust porous composites.

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For the sustainable point of view, water-in-oil and $ScCO_2$-in-water HIPE templates are attractive due to the use of eco-friendly dispersed phase solvent. As alternative methods, in-situ growth of MOF@polyHIPE based their corresponding metal oxide particle precursor-stabilized HIPE templates is attractive, providing a high MOF accessibility, while post-incorporation of MOF particles into polyHIPE scaffolds by either immersing or chemically binding also works but the loading of MOF may be not that high. So far, the as-prepared MOF@polyHIPE composites have been used in adsorption and separation, heterogenous catalysis, and bioengineering. By comparison, the first two applications are more efficient and successful, while the last one is still in infancy. As a conclusive remark, Table 1 summarizes MOF@polyHIPE composites reviewed, highlighting diverse HIPE types and MOFs used, as well as their applications.

Given the progress that has been made in the development of MOF@polyHIPE, various MOF particles have been designed and synthesized for targeted applications. Future researches can concentrate on i) further improving the stability and recyclability of MOF/polymer composite already in use, ii) processing MOF particles into different ordered shapes and morphologies while having high accessibility, which are usually required in commercial applications, iii) developing different kinds of MOFs to stabilize HIPE for preparing new porous polymer materials, and iv) exploring their potential applications in more fields.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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