Review

Preparation of porous adsorbent via Pickering emulsion template for water treatment: A review

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A B S T R A C T
Porous materials as emerging potential adsorbents have received much more attention because they are capable of capturing various pollutants with fast adsorption rate, high adsorption capacity, good selectivity and excellent reusability. In order to prepare porous materials with decent porous structure, Pickering emulsion template method has been proved to be one of the most effective technologies to create pore structure. This paper reviewed comprehensively the latest research progress on the preparation of porous materials from various Pickering emulsions and their applications in the decontamination of pollutants (e.g., heavy metal ions, organic pollutants) and in the oil/water separation. It was expected that the summaries and discussions in this review will provide insights into the design and fabrication of new efficient porous adsorbents, and also give us a better understanding of the subject.

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Introduction

Over the past decades, many techniques have been employed to decontaminate the pollutants from wastewater. Examples include filtration, chemical precipitation, neutralization, chelating ion-exchange and adsorption (Wang et al., 2015; Wang et al., 2018a; Cheng et al., 2016; Tian et al., 2016a; Zhang et al., 2018; Dong et al., 2019; Jiang et al., 2019; Xue et al., 2019). Among these techniques, adsorption is the most impactful and promising method for large-scale applications (Tian et al., 2016b; Jiang et al., 2017a; Natarajan et al., 2018). Not only does the adsorption technique have the advantage of high clean-up efficiency, ease of operation and low-cost, the useful substances can also be recycled selectively from water by endowing the adsorbents with special recognition ability (Lv et al., 2019).

Although adsorption technique is advantageous for water purification, there are still some problems needing to be solved. For examples, the capturing capability of adsorbents for different pollutants needs to be improved further, and the adsorption rate also needs to be enhanced. Much effort has been engaged to develop new adsorbents with high adsorption capacity and fast adsorption rate. It has been demonstrated that porous adsorbents (e.g., porous monolithic or powder adsorbents) with more adsorption sites and porous texture, are proved to be very efficient to remove various pollutants (Wang et al., 2013; Filina et al., 2019; Hao et al., 2019). The substantial exposed adsorption sites inside the porous adsorbent and high porosity greatly enhanced the mass transfer capability and rate of adsorbents (Yang et al., 2014; Nan et al., 2018). In addition, the structure, texture and shape of porous adsorbents can also be designed and tuned according to the types of pollutants by employing different preparation technology.

So far, many methods have been reported for the preparation of porous materials. Common examples include hydrothermal synthesis (Kozyatnyk et al., 2019), freeze-drying (Anoshkin et al., 2018), solvent porogenic (Jiang and Kim, 2013) or sacrificial hard template (Estevez et al., 2017). The hard template method depends on the availability of hard template materials structured on the required length scale, and can be removed from the porous structure after synthesis (Lai et al., 2019). These approaches can be used to form porosity within the matrix effectively. However, it is not easy to tune the pore structure. Compared with other approaches, soft template methods, including block copolymer template and colloidal template, have been recognized to be more effective to synthesize ordered and disordered porous matrices (Wright et al., 2017).

As one of the soft template technologies, emulsion template method is recognized to be a versatile one for the preparation of cellular polymers with a well-defined porosity. The vast majority of cases concern high internal phase emulsions (HIPEs) having a dispersed phase volume greater than 74% (Chen et al., 2017a; Yang et al., 2017; Zhang et al., 2017; Zhang and Silverstein, 2018; Gui et al., 2019; Huang et al., 2019). Above this critical value, droplets of the emulsion are in close contact with each other and separated by a very thin film. Upon polymerization and removal of the dispersed phase, the thin membranes between the droplets are perforated, leading to form low density open-cell macroporous polymer matrices (Tan et al., 2018).

Usually, porous materials were prepared from the emulsion template stabilized with only surfactants (Zhao et al., 2018). The morphology of the resultant porous polymer materials (polyHIPEs), such as the surface roughness of pore and the average pore diameter, is tailored by altering the type and dose of surfactant, internal phase volume fraction, electrolyte, and crosslinker concentrations (Wong et al., 2013; Teo and Jana, 2017; Davis et al., 2018). One of major drawback of conventional polyHIPEs is poor mechanical property, despite it possesses many other unique properties such as low foam density and interconnected pore structure. In addition, large amounts of surfactants (5%-50%) have to be used to stabilize the HIPEs, so the use of hazardous surfactant as the risk to cause severe secondary environment pollution (Barbetta and Cameron, 2004).

To solve these problems, particle-stabilized HIPEs, also known as Pickering HIPEs, have been used as templates to prepare highly porous polymers termed poly-Pickering HIPEs (Chevalier and Bolzinger, 2013). Pickering emulsions are stabilized by amphiphilic particles that spontaneously migrate onto the oil–water interface, forming rigid shells around the internal phase droplets and preventing their coalescence (Pickering, 1907). As compared with the emulsion droplets that are kinetically stabilized with conventional small molecule surfactants, solid particle-stabilized emulsions have relatively higher interfacial energy of attachment and long-term stability, which enable them to serve as outstanding templates to produce various porous materials (Pan et al., 2016a; Chen et al., 2017b). The unique stability of particle-stabilized systems depends on three main factors: (1) high energy of desorption of a particle from the interface; (2) strong capillary forces between adjacent particle-stabilizing liquid films (as well as high capillary pressure in the solid-stabilized film); and (3) formation of a network-structure incorporating the interfacial layers of adsorbed particles and free particles in the continuous phase (Nushtaeva, 2016). The stabilizing particles can be classified into two categories according to the origin of particles and the properties of particles: synthesized particles and natural particles.

This review serves the purpose of finding numerous approaches to obtain porous materials using Pickering emulsion as template. The important applications of such porous materials for removal of various pollutants that are available in recent literatures are presented along with highlighting the key advancement of porous adsorption materials. We hope that the summaries and discussions in this review would provide insights of the design and fabrication of highly efficient porous adsorbents.
1. Preparation of porous materials via Pickering emulsion

1.1. Preparation of porous materials via Pickering emulsion stabilized with synthesized particles

The synthesized particles used to stabilize Pickering emulsion can be classified into two categories according to their characteristics: inorganic particles and polymer particles. Inorganic particles such as Fe$_3$O$_4$, SiO$_2$, TiO$_2$, and hydroxyapatite are used more widely (Li et al., 2014; Yang et al., 2017; Zhu et al., 2018b). Recently, new types of inorganic materials such as MOF nanoparticle have also attracted considerable attention in the study of Pickering emulsion (Zhu et al., 2019). Generally, these particles are synthesized in water or hydrophilic solvent system. Therefore, they should be modified to adjust the hydrophobic–hydrophilic nature of the particle surfaces due to their inherent hydrophilicity. The non-covalent interactions and the chemical grafting are both used to modify the bare particles. As for the non-covalent interactions, the micromolecules, surfactants or the surfactant-like molecules which have opposite charges against the particles surface (Zheng et al., 2013; Zafeiri et al., 2017; Lebdioua et al., 2018). Due to the simplicity and flexibility of the modification process, great attention has been paid by many researchers (Tshilumbu and Masalova, 2015; Yi et al., 2016). Besides, it is advantageous to forming the interconnected pore structures in the porous materials (Xu et al., 2016).

Even though many bare particles can be directly used to stabilize Pickering emulsion and prepare Poly-HIPEs from Pickering HIPEs templates, polymerization of the dispersed phase always results in closed cell polymers with poor interconnectivity (Yu et al., 2015). When using micromolecules, surfactants or surfactant-like molecules to stabilize the emulsion, this issue will be effectively addressed. Specifically, it has obvious curative effects of the stable particles modified with surfactants. Relevant researches have proven that when particles and surfactants are synergistically used to stabilize the emulsion, the stability of emulsion will be improved significantly and the polyHIPEs have thus attained excellent homogeneity. Meanwhile, the use of surfactants leads to the formation of an interconnected pore structure (Zheng et al., 2013). The shapes, connectivity and homogeneity of pore structure can be varied by altering the ratio of surfactant/particle (Yin et al., 2016b) (Fig. 1).

Recently, surfactant as co-stabilizer for synergistic stabilization of Pickering emulsion has become a classical approach to form porous materials with interconnected pore structure (Ikem et al., 2010; Nallamilli and Basavaraj, 2017). Studies also proved that the increase of surfactant concentration in the mixture of surfactants and NPs would result in the formation of smaller emulsion droplets and a smaller pore structure (Khan and Kumaraswamy, 2018). For example, the porous materials prepared from hydrophobic silica nanoparticles H30 solely stabilized emulsion had a typical poly-poly-Pickering-HIPEs morphology. The large closed cell pores had a broad size distribution from tens of micrometers to hundreds of micrometers. At the same time, the pore size decreased with increasing the dosage the surfactant Span 85. A possible synergistic stabilization mechanism is demonstrated in Fig. 2. There are two main takeaways from Fig. 2. The first is the interaction between H30 and Span 85. The adsorption of surfactants on particles may change their wet ability and thus encouraging their attachment to oil–water interfaces. Moreover, some particles dispersed into continuous phase

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**Fig. 1** – SEM images of porous material prepared from the emulsion stabilized solely by particles or surfactants or particles and surfactants. Reproduced with permission from Yin et al. (2016a).
The particles modified by chemical grafting have all the emulsification process. Compared to the non-covalent interactions, the particles modified by chemical grafting have a more steady state. Polymers or small molecules are fixed on the surface of particles by covalent bonds, causing the particle to be less vulnerable to change of surrounding conditions. Recently, the modification strategy of chemical crosslinking has been more frequently used to modify the stabilized particle and studies on the silylation modifications have been the most extensive ones (Zhou et al., 2012; Zhang et al., 2015; Liang et al., 2018). The long alkyll chains of silicones are anchored onto the surface of the particle by the covalent bond of Si–O–Si, and the surface amphipathicity of the particles can be adjusted by changing the type of silane and the reaction conditions. Furthermore, functional groups such as vinyl group whose double bond can be introduced onto the surface of particles through silylation modification (Jiang et al., 2017b). These incorporated functional groups on the surface of particles can be used to extend the role of the stabilized particles beyond HIPEs stabilization. The incorporation of vinyl groups makes the particles to serve as cross-linking centers while the incorporation of initiator groups can produce particles that can serve as initiation centers.

The polymeric particles used as stabilizers of Pickering emulsion have attracted much more attention. These particles mainly include the poly(styrene-co-N-isopropylacrylamide) (PS-co-PNIPAM) core-shell particles (Li and Ngai, 2010; Tu et al., 2016) and polystyrene/silica (Zhu et al., 2016b). The stability of emulsion and the pore structure of as-prepared polyHIPEs are all affected significantly by the size, morphology, charge of the polymeric particles. Zhu et al. produced uniform copolymer particles with different structures by simply varying the concentration of cross-linker divinylbenzene (DVB) in the emulsion polymerization (Fig. 3) (Zhu et al., 2014). Particles obtained as stabilizer in the Pickering HIPEs and the corresponding porous materials have different morphology, as illustrated in Fig. 4.

Unlike the rigid particles (e.g., Fe3O4, SiO2), the deformability of the polymeric particles is considered to be a crucial criterion affecting the stability of Pickering emulsion (Picard et al., 2017). The other study results proved that the emulsion prepared in the swollen state of the microgels, yet covered with highly flattened microgels, exhibiting strong adhesive bonds between drops due to bridging of opposite interfaces by microgels (Destribats et al., 2012). As a result, these emulsions were flocculated, and its flow rate was thus limited. When emulsification was carried out in the shrunk state and followed by rapid swelling of the interfacial microgel from a temperature quench, the microgels were trapped at the oil–water interface in a dense and rigid configuration due to the forced interpenetration of their lateral polymer chains. Monitoring emulsification energy is an easy means to control their deformation state at the interface, thus controlling their packing density and the macroscopic properties of the emulsions. Emulsions produced with high energies are stabilized by flattened microgels and their drops are flocculated by bridging. Emulsions produced with low energies are stabilized by compressed microgels and no bridging can be observed (Fig. 5).

Core cross-linked star (CCS) polymers which advocate their roles as intermediates between linear polymers and polymeric nanoparticles, can also act as effective interfacial stabilizers for emulsions (Ren et al., 2016; Wang et al., 2018b). The core tends to stay at the interface with low interfacial...
tension and long arms dispersed and intertwined with each other in the continuous phase (Zhang and Hadjichristidis, 2018). The core of the CCS polymer cannot tightly attached on the interface with high-density like particles due to the arms obstruction (Fig. 6). The linear arms act as the surfactants during polymerization of the continuous phase, resulting in formation of small pore throats on the wall.

1.2. Preparation of porous materials via Pickering emulsion stabilized with natural particles

Recently, natural polymer particles have shown great potential in stabilizing HIPEs. Some polysaccharide such as chitin nanocrystal particles, cellulose nanocrystals (CNCs), chitosan and gelatin have been used as solid emulsifiers for fabricating

![Diagram of polymer particle formation](image1)

**Fig. 3** – Formation of an anomalous polymer particle through one-pot surfactant-free emulsion polymerization. Reproduced with permission from Zhu et al. (2014).

![SEM images of poly-Pickering-HIPEs](image2)

**Fig. 4** – SEM images of the poly-Pickering-HIPEs. PPH1: particles P1 with core–shell structure as stabilizer; PPH2: particles P2 with single-cavity structure as stabilizer; PPH3: particles P3 having single cavity with multiprotrusions in edge structure as stabilizer; and PPH4: particles P4 with multiprotrusions structure as stabilizer. Reproduced with permission from Zhu et al. (2014).
O/W Pickering emulsions (Wongkongkatep et al., 2012; Perrin et al., 2014; Alison et al., 2016; Wang and Heuzey, 2016; Du et al., 2017; Tian et al., 2017; Huang et al., 2018a). The easy availability, biodegradability and nontoxic characteristics of natural particles enable them to be potential substitute of conventional emulsifiers to fabricate eco-friendly Pickering emulsion and then get the porous materials. Tan et al. (2017) reported a novel macroporous hydrophilic 3D scaffold prepared from gelatin nanoparticle-stabilized HIPE templates with acrylamide (AM) as the monomer in the continuous phase. Tuning the concentrations of gelatin nanoparticle or content of AM led to different porous structures with void diameters varying between 30 and 78 μm. This helps to draw the conclusion that the formation of open-cell PolyHIPEs depends on a suitable mass ratio of gelatin nanoparticles to monomers (Fig. 7).

However, the high hydrophilicity and poor emulsification performance of CNCs limited their applications in this field. Therefore, introducing salts or molecular surfactants, or modifying surface of cellulose has usually been employed in the emulsification process to improve amphiphilicity (Hu et al., 2015). Besides, the chemical modifications, e.g., oxidation and grafting with surface-active polymers, are also effective ways to improve the performance of CNCs during the

Fig. 5 – Schematic representation of the adsorbed microgels and the polymer density profile at the interface for (a) large and (b) small microgels. In a similar way the effect of the cross-linking density may be schematically drawn (c and d) as well as the effect of process parameters like stirring temperature or energy (e and f). Reproduced with permission from Destribats et al. (2014).

Fig. 6 – (A) Synthetic route for the AIE-active core crosslinked multi-miktoarm star copolymers; (B) Illustration of water-in-oil emulsion formation; (C) Images of water (pH buffer)-in-oil (toluene) emulsions stabilized by (PE)_{19.4}-(PMAA)_{14.5}-P(TPE-2St). Reproduced with permission from Zhang et al. (2018).
emulsification process (Habibi, 2014; Chen et al., 2018; Tang et al., 2018; Song et al., 2019). Sousa et al. (2017) developed novel nanocomposite foams with distinguished thermal stability and mechanical strength by a water-in-oil Pickering emulsion template stabilized by acetylated bacterial cellulose. Tang et al. (2018) grafted successfully hydrophobic polystyrene onto the reducing end of cellulose nanocrystals through a selective-end group modification protocol. The modified nanoparticles displayed favorable surface properties and were capable of stabilizing toluene or hexadecane-in-water emulsions (Fig. 8).

The biomacromolecules such as protein can also be used to stabilize Pickering emulsion (Zeng et al., 2017), and the relevant researches are increasingly receiving attention in this field. However, proteins also need to be treated for enhanced protein aggregation due to their inherent nature. The most popular method to treat proteins is thermal treatment (Liu and Tang, 2013, 2016; Liu et al., 2017; Qin et al., 2018; Xu et al., 2018; Zhou et al., 2019). Due to the electro negativity of the protein, the emulsification process and interfacial properties are highly dependent on the pH and specific ionic strength (Xiao et al., 2016; Zhu et al., 2018a). Combined with covalent cross-linking methods, certain protein species can form a special class of soft colloidal entities referred to as protein microgels during the Pickering emulsion process.

In the past decades, clay particles have attracted much attention for applications in stabilizing the Pickering emulsion, since clay-based materials provide a group of solid particles with colloidal size, large reserves and low cost. However, strong hydrophilicity causes the clay particles to remain in the aqueous phase, which makes the difficult to stabilize at the interface. Hence, surface modification is necessary to obtain amphipathic clay particles. One popular method is combining clay particles with surfactants (Reger et al., 2011; Brunier et al., 2016). The studies in recent years focused on polymer–clay nanocomposites and exchange of cations in clay galleries with long-chain aliphatic quaternary ammonium compounds or phosphonium compounds (Machado et al., 2019). Another approach to form hydrophobic clay particles is using trialkoxysilanes as the silicon source (Minet et al., 2004). This approach utilizes chloro- or alkoxy-silanes and leads to a reaction that presumably involves edge SiOH groups (Fig. 9).

2. Applications of porous material in decontamination of wastewater

The porous materials prepared from Pickering emulsion have been widely used in the decontamination of pollutants for removal of heavy metal ions, organic contaminants (i.e., dyes, surfactant, and pesticide) and for oil spilling. The roles of pores in the adsorbent are to increase the adsorption capacity, adsorption rate and improve the adsorptive selectivity. Therefore, we reviewed the research progress on application of porous material in decontamination of wastewater.

Fig. 7 – Synthesis of open-cell porous 3D scaffolds through gelatin nanoparticle-stabilized HIPE templates. Path A: The as-prepared HIPEs are placed in a 60°C water bath to start polymerization immediately after emulsification; Path B: The as-prepared HIPEs are placed at room temperature for 24 hr to go through the limited coarsening procedure before polymerization. Reproduced with permission from Tan et al. (2017).
2.1. Removal of heavy metal ions

Porous materials prepared from Pickering emulsion and used for removal of heavy metal have to be hydrophilic. PolyHIPEs with a hydrophilic surface are able to be produced through several different methods: post-synthesis modification of hydrophobic polyHIPEs (Cameron, 2005; Cohen and Silverstein, 2012), synthesis of polyHIPEs via oil-in-water (O/W) template (Park and Ruckenstein, 1989; Krajnc et al., 2005) and synthesis of bi-continuous polyHIPEs where a hydrophilic co-monomer is polymerized in the dispersion phase of W/O HIPEs (Ruckenstein and Park, 1990; Kováč et al., 2011). Among them, the most popular method to prepare porous adsorbent of heavy metal is considered to be the one based on hydrophobic polyHIPEs. Merta et al. (2013) prepared novel magnetic macroporous polymer monoliths by polymerization of the styrene/divinylbenzene (ST/DVB) high internal phase emulsions (HIPEs) which are stabilized by humic acid-modified oxide magnetic nanoparticles (Fe3O4@HA). The maximum adsorption capacity of the magnetic monoliths for Hg (II) was determined to be 4100.06 mg/g (20.44 mmol/g) at pH 4. Pribyl et al. (2017) reported a monolithic polyHIPEs foam column that was surface-grafted with a brush of polymer containing ion-exchange functionality for the separation of Pu. It was found that the loading curves of the foam material are steeper than a similarly scaled resin-based column and the elution profiles of the foams were narrower than that of the resin, thus generating more concentrated eluate relative to the amount of Pu loaded onto the foam columns (Fig. 10).

Fig. 8 – Procedure used to selectively modify the reducing end of CNC with polystyrene (via reductive amination). Photographs of (A) pristine CNC and (B) CNC-PS from room temperature (a: 0.3 wt%, b: 0.5 wt%, c: 1.0 wt%) suspensions as well as mixture after emulsifications (toluene water ratio 1:2, d: 0.3 wt%, e: 0.5 wt%, f: 1.0 wt%); and (C) optical micrographs of emulsions stabilized by CNC-PS from room temperature at different concentrations (toluene water ratio 1:2, 1:0.3 wt%, 2:0.5 wt%, and 3:1.0 wt%). Reproduced with permission from Tang et al. (2018).
these adsorbent is unsatisfactory. More effective adsorbent can be prepared directly by O/W Pickering emulsion. In the past few years, our group devoted to synthesize the porous adsorbents based on O/W emulsions. We employed silane-modified Fe₃O₄, silicone-modified magnetic attapulgite to stabilize HIPEs, and used the emulsions to prepare a series of magnetic porous monolithic and spherical adsorbents. The O/W Pickering emulsion has high stability and the pore structure of porous magnetic adsorbent is controlled by altering the amounts of magnetic particles, co-surfactant and volume fraction of dispersed phase. The obtained porous adsorbents can reach its adsorption equilibrium within a short duration (Zhu et al., 2016a, 2016b, 2016c, 2017a, 2017b) (Fig. 11). These series of magnetic porous adsorbent possess excellent adsorption capacities which are higher than most of reported adsorbents for the heavy metal ions Cu²⁺, Cd²⁺, Pb²⁺ and the alkali metal ions Rb⁺ and Cs⁺ (Lu et al., 2019a; Lv et al., 2019; Wang et al., 2019; Lu et al., 2019b).

In order to build better architecture and morphology and improve adsorption capacity of the template, multi-hollow structures in the polymer microspheres are usually required. A more commonly employed approach to achieve this requirement is to fabricate Pickering double emulsions. It is complex soft colloidal systems in which droplets of the dispersed phase themselves contain even smaller droplets. The first

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Fig. 9 – Schematic representation of the silane-functionalization of MMT platelets and the subsequent stabilized Pickering emulsion. Reproduced with permission from Yu et al. (2013).

Fig. 10 – Synthetic route to prepare HIPE foams with surface-grafted chains of poly(4-vinyl pyridine) (P4VP) and monolithic column prepared for testing (inset). Reproduced with permission from Pribyl et al. (2017).
Fig. 11 – Synthetic route of the interconnected magnetic porous spheres for enrichment of Rb⁺ and Cs⁺ (a) and the modification process of Fe₂O₄ with TEOS and APTMS (b). Reproduced with permission from Zhu et al. (2017a).
chlorotetracycline (CTC). The adsorption capacities of the adsorbent for TC and CTC can reach 806.60 and 876.60 mg/g in a wide pH range from 3.0 to 11.0, respectively. In addition, the adsorption equilibrium can be reached within 90 min for TC and 50 min for CTC (Lu et al., 2018). Zhu et al. (2015) fabricated multihollow magnetic imprinted microspheres by polymerization of Pickering double water in oil in water (W₁/O/W₂) emulsion. Hydrophobic Fe₃O₄ nanoparticles and Cellulose nanocrystals (CNCs) were used to stabilize the inner water in oil (W₁/O) interface and the outer oil in water (O/W₂) interface.

Fig. 12 – Fabrication of magnetic porous microspheres via (O₁/W)/O₂ double emulsion for fast removal of Cu²⁺ and Pb²⁺. Reproduced with permission from Zhu et al. (2016a).

Fig. 13 – Fabrication process of the molecularly imprinted nanomaterials of BA-MSNs (a) and the imprinted polymer foams of PGM-Pickering-BN (b). Reproduced with permission from Pan et al. (2017).
The adsorbents were used to selectively adsorb bifenthrin (BF). The selective recognition capability of BF with magnetic imprinted microspheres was proved to be more effective as compared with structural analogs. Wang et al. (2018c) reported a synthesis procedure of structured and molecularly imprinted multicore rattle-type microspheres through a facile Pickering emulsion polymerization using silica nanoparticles as the sole stabilizer. The imprinted spheres can be used to selectively adsorb bisphenol A (BPA) (Fig. 14).

2.3. Oil–water separation

Besides the soluble pollutants such as heavy metal ions, dyes and antibiotics, many insoluble or weakly soluble pollutants are also contained in the wastewater. These pollutants may be originated from industrial oily wastewater or oil spill accidents. These types of insoluble or weakly soluble pollutants are also known to be one of the most serious problems for water environment (Zhang et al., 2019). Generally, the separation of oil and water from oil/water mixture can be classified into three main categories: oil removal, water removal, and controllable separation of oil and water. Among them, oil-removing is the most attractive as compared to the other two because of its simplicity and easiness. Most of the traditional oil/water separation materials (e.g., active carbon, polypropylene sponge, zeolites and other adsorbents with microporous structures) are known to be disadvantageous, such as limited oil storage capacity, difficulties in oil recovery and poor material durability, which may restrict their practical application. On the other hand, three-dimensional monolithic porous materials such as aerogels, sponges and foams possess open and interconnected pores, which were regarded as more ideal oil adsorption materials because of their features of high oil adsorption capacities, easily recycling and reusing.

Zhang et al. (2016) prepared a poly(styrene-divinylbenzene) foam with the porosity as high as 98% by the Pickering HIPEs method through a one-step reaction process. The materials fabricated from different types of Fe3O4 particles had diverse hierarchical pore structures. Therefore, the microstructures of the polymer foams could be tailored by adjusting the morphology and size of Fe3O4 particles (Fig. 15). The adsorption capacity of the monolithic foam towards chloroform was as high as 57.00 g/g. The materials soaked with oil could be restored effectively by means of centrifugation with the oil recovery rate reaching 90%. Meanwhile, the monolithic Poly-HIPEs were subjected to 20 adsorption–centrifugation cycles and superior reusability was attained.

Yu et al. (2015) synthesized two types of monolithic supermacroporous polystyrene materials with closed-cell supermacroporous structure (CPPs) and highly interconnected macropores (IPPs) from water-in-oil Pickering emulsions. The CPPs were used as absorbents for oil–water separation with high absorption capacity and absorption rate for oil. These characteristics were attributed to their porous structures and the swelling property of polystyrene. Conversely, the IPPs were highly permeable for gases due to their interconnected macropores.

Porous structure is often required for adsorbents to achieve high oil absorption capacity (Adebajo et al., 2003). High pore volume will allow high oil absorption capacity (Azhar et al., 2017). However, the adsorbent with sufficiently high pore volume but closed pore structure cannot attain high oil absorption rate. In fact, there are few reports involving the study of porous material with fast oil absorption rate. It usually takes a couple of hours for current porous adsorbent to get to oil absorption saturation. Ma et al. (2014) synthesized a hierarchical porous resin via HIPEs for the purpose of high oil absorbency. The optimized adsorbents have the absorbency of 31.50 and 17.10 g/g for chloroform and toluene, respectively. Furthermore, duration of only 5 min is needed to reach their saturation absorption. The absorption/desorption cycling results proved the high repeatability of recovered resin. Zhang et al. (2017) prepared a hierarchically porous

![Fig. 14 – Schematic illustration for synthesis of MIP spheres containing multicores via Pickering emulsion polymerization. Reproduced with permission from Wang et al. (2018b).]
monolithic Fe₃O₄/polystyrene composite material via HIPEs technique emulsified by Span 20 together with Fe₃O₄ (Fig. 16). The oil adsorption capacity of the solid foam was 16 times its own mass even after 10 oil/water separation cycles.

Zhang et al. (2017) prepared polyHIPEs monoliths from light-induced polymerization of an ionomer for effective reclamation of spilled oil. The HIPEs can be stabilized by sulfonated polystyrene, seawater and economically efficient monomers such as butyl acrylate and tetraethyl or thosilicate (TEOS) which acted as the dispersed aqueous phase and continuous phase, respectively. The adsorbent demonstrated excellent performance for oil spill reclamation, which included high absorption capacity to a wide variety of organic solvents or oil, high absorption rate (reaching saturated absorption in 3–5 min), a high recovery rate of over 85% and a high reusability of over 20 cycles. To further enhance the efficiency of monoliths, Zhang and Guo (2017) designed a continuous process for oil spill recovery (Fig. 17). The SPS-polyHIPEs monoliths are firstly packed into a bunch and the bunches are then connected to form a cycle. Certain bunches at the right position can absorb spilled oil from oil water mixture, and the absorbed bunches are drawn back into the boat. Meanwhile, new bunches enter the oil water mixture, the absorbed oil is recovered by a simple squeezing process and the polyHIPEs monoliths are then reused, achieving continuous collection of oil from oil water mixture (Fig. 18).

3. Conclusions and future prospects

Porous materials prepared using emulsion template methods have been attracting much attention for various applications in many fields. In comparison with the emulsion stabilized with surfactants, Pickering emulsion has much more advantages, including higher stability, low cost and enhanced mechanical stability of Pickering emulsion. Besides, new characteristics and properties can be introduced into the porous materials by stabilizing the emulsion with different types of particles. We have reviewed the current research progress of the porous materials prepared from Pickering emulsion stabilized with synthetic particles and natural particles. The shape, size, morphology and strength of synthetic particles are more controllable. At the same time, the pore structure, pore size distribution, mechanical strength and the performance of the
corresponding porous materials can also be tuned by varying the nature of particles. However, the synthetic particles also have some disadvantages such as high cost. On the contrary, natural particles have the advantages of high yield, substantial reserves due to wide distribution of resources and lower cost as compared to synthetic particles. However, the controllability of natural particles is weaker than that of synthetic particles. Despite the abovementioned drawbacks, porous materials prepared through the emulsion template were still highly concerned by researchers and plenty of excellent works have been reporting on the preparation of Pickering HIPEs and their resulting macroporous materials (named poly-Pickering-HIPEs) to establish foundations to address those potential issues.

3.1. High consumption of organic phase

Emulsion templating polymerization is proven to be an effective method to prepare interconnected porous polymer monoliths with controlled morphologies. However, the recent studies are still more focused on the HIPEs. For the W/O HIPEs, only little amount of organic solvent in the preparation process is needed while for the O/W emulsion, massive organic phases such as benzene, toluene, and long chain alkane need to be used. The organic solvents are usually poisonous and the treatment of these harmful solvents is still an issue to be addressed. Cyclic utilization of these organic solvent is a choice worth consideration but the solvent needs to be refined prior to the subsequent step. In order to minimize usage of poisonous organic solvent, most reported polyHIPEs are prepared from W/O emulsion. However, if the porous materials are used to remove the heavy metal, the porous adsorbent has to be hydrophilized. The adsorption capacities for the heavy metal are significantly affected by the hydrophilic process. There are two suggested alternative methods: replacement of the organic solvent with natural oil such as flaxseed oil and reduction of the disperse phase from high internal phase ($V \geq 74.05\%$) to medium internal phase ($30\% \leq V < 74\%$) and even to low internal phase ($V < 30\%$).

3.2. Poor mechanical strength

The vast majority of cases concerning high internal phase emulsions (HIPEs) have a dispersed phase volume greater than 74%. The practical application of the product polyHIPEs...
Fig. 17 – Schematic illustration of the preparation of SPS-polyHIPE monoliths (a) and reclamation of spilled oil with SPS-polyHIPEs (b). Reproduced with permission from Zhang and Guo (2017).

Fig. 18 – Schematic representation of the procedures adopted for the preparation of porous polymeric monoliths through 3D printing of stable gel emulsions. Reproduced with permission from Liu et al. (2019).
often suffers from poor mechanical properties because of their low density. Various strategies have been implemented to notably increase the mechanical strength of polyHIPEs. These approaches include incorporation of organic or inorganic charges into the polymer matrix (Menner et al., 2008), proper selection of the monomers (Hus and Krajnc, 2014), and reinforcements of these porous structures by increasing the content of monomer in the emulsion. However, a more attractive method is switching from high to medium or low internal phase emulsions (MIPEs and LIPEs) (Mathieu et al., 2016).

3.3. The closed pore structure

Since polyHIPEs are porous materials that are highly tunable, Pickering HIPEs template materials often have a closed-cell pore structure, which may lead to a very low permeability. Currently, a common strategy is to decrease the droplet size and weaken the barrier at oil-water interface by adding a large quantity of surfactants to co-stabilize HIPEs. However, in this method, surfactants are still involved, which can cause secondary pollution in the adsorption process. Additionally, creation of polyHIPEs with interconnected porosity becomes more difficult when pore sizes become greater than 50 μm (Wong et al., 2011; Susec et al., 2013). Since some methods have been used to form interconnected pores such as reactive lignin particles and specific poly(urethane urea) stabilizer, they are not versatile in most HIPEs. Recent progresses in additive manufacturing have demonstrated the ability to optimize mechanical function as well as mass transport through designed porous architectures (Martins et al., 2009). For this purpose, researchers have recently explored methods based on stereo lithographic apparatus (SLA) to fabricate constructs with precise architectures from emulsion-template materials. The combination of the highly porous polyHIPEs materials and an additive manufacturing design process would enable a vast array of complex geometries and hierarchical porosity (Johnson et al., 2013; Sherborne et al., 2018). Furthermore, the employment of other technologies such as 3D printing to the emulsion template is also a significant research direction. As illustrated in Fig. 18, this 3D printed polyHIPEs constructs benefit from the tunable pore structure of emulsion templated materials where 3D printing is capable of the detailed control over complex geometries which is not possible with traditional manufacturing techniques (Liu et al., 2019).

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Appendix A. Supplementary data

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REFERENCES


