

REVIEW

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The rise of morphology-engineered microporous organic polymers (ME-MOPs): synthesis and benefits

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This review summarizes recent synthetic approaches for morphology-engineered microporous organic polymers (ME-MOPs). 0D, 1D, and 2D ME-MOPs were prepared by various hard and soft template methods. Silica spheres, metal-organic frameworks, zeolite particles, metal oxide nanoparticles, and water drops in organic media were utilized as templates for the synthesis of hollow MOPs. MOP films could be engineered using 2D plates as templates. Organic surfactants could induce the growth control of MOP nanoparticles. In some cases, ME-MOPs could be prepared by template-free synthesis. The ME-MOPs were utilized as templates for the synthesis of new ME-MOPs. Noncovalent self-assembly events were also utilized for the synthesis of ME-MOPs. The ME-MOPs provide various benefits over conventional MOPs. Due to the efficient mass transfer of reactants, hollow MOPs showed enhanced catalytic and energy storage performance. The ME-MOPs showed facile post-synthetic functionalization, compared with conventional MOPs. The ME-MOPs enabled the creation of new carbon and nanocomposite materials through the incorporation of precursors and heat-treatment. Moreover, the ME-MOPs provide the means to enable new applications including drug delivery systems, seed materials for polymer synthesis, and functional membranes for use in environmental and energy systems.

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1. Introduction

For the past two decades, microporous organic polymers (MOPs) have emerged as new functional materials.^{1–8} While covalent organic frameworks (COFs) are crystalline,⁹ MOPs are regarded as amorphous materials that present chemical stability, high surface areas, and microporosity with pore sizes

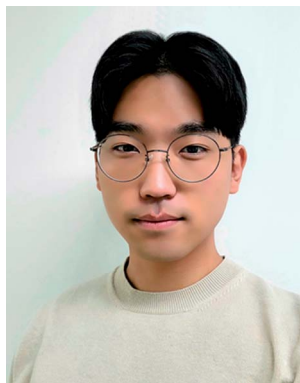
less than 2 nm.^{1–8} Moreover, the chemical structure of MOPs can be easily tuned by changing the organic building blocks.

Depending on the synthetic approaches, MOPs have been called by various terms (Fig. 1). For example, Tsyurupa and Davankov showed the synthesis of the first hypercrosslinked polymer (HCP).^{10,11} In their synthesis, polystyrene or polystyrene-*co*-divinylbenzene was further crosslinked with external crosslinkers bearing multi-chloromethyl moieties in the presence of Lewis acid catalysts, generating intrinsic microporosity in the HCPs.^{10,11} Later, Cooper *et al.* showed that monomeric

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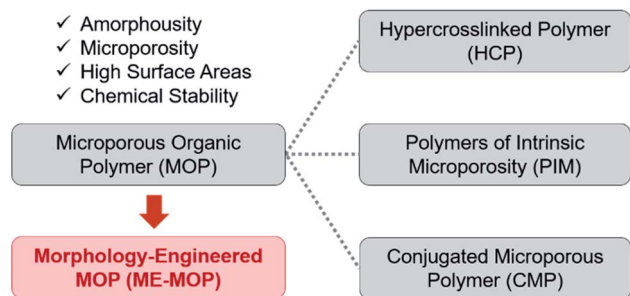


Fig. 1 The sub-classes of microporous organic polymers.

organic building blocks with multi-chloromethyl moieties can also be polymerized to HCPs in the presence of Lewis acid catalysts.^{12,13} In addition, Tan *et al.* showed the synthesis of HCPs using simple arenes and a formaldehyde dimethyl acetal crosslinker and called this the “knitting strategy” (Fig. 2a).¹⁴ Until now, numerous HCPs have been prepared through Friedel-Crafts chemistry using various organic building blocks.¹⁵

Another class of MOPs is polymers of intrinsic microporosity (PIMs) that were suggested by Budd and Mckeown *et al.*¹⁶ PIMs were prepared by the coupling of dicatchol building blocks with multi-fluoroarenes. For example, PIM-1 was prepared by the coupling of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-

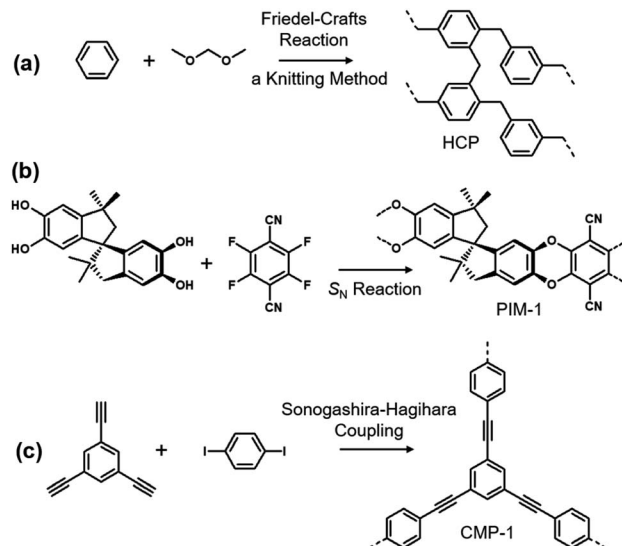


Fig. 2 Synthetic examples of (a) a hypercrosslinked polymer (HCP), (b) a polymer of intrinsic microporosity (PIM), and (c) a conjugated microporous polymer (CMP).

spirobisindane with 1,4-dicyano-2,3,5,6-tetrafluorobenzene, showing a surface area of 760 m² g⁻¹ (Fig. 2b).¹⁷ The microporosity of PIM-1 originates from a rigid polymer structure and the frustrated packing of polymer chains. The networked PIM, such as the Por-network-PIM, was also prepared by the coupling of tetrakis(tetrafluorophenyl)porphyrin building blocks with 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane.¹⁸

Another important class of MOPs is conjugated microporous polymers (CMPs) that were suggested by Cooper *et al.*¹ CMPs were prepared by the Sonogashira-Hagihara coupling of multi-haloarenes and multi-ethynylarenes.¹⁹ For example, CMP-1 was prepared by the Sonogashira-Hagihara coupling of 1,3,5-triethynylbenzene with 1,4-diiodobenzene, showing a surface area of 834 m² g⁻¹ (Fig. 2c).¹⁹ Various CMPs and CMP like nonconjugated MOPs have been prepared through the diverse coupling and condensation reactions of organic building blocks.¹

Recently, morphology-engineered MOPs (ME-MOPs) have appeared.²⁰ ME-MOPs were prepared by various hard and soft



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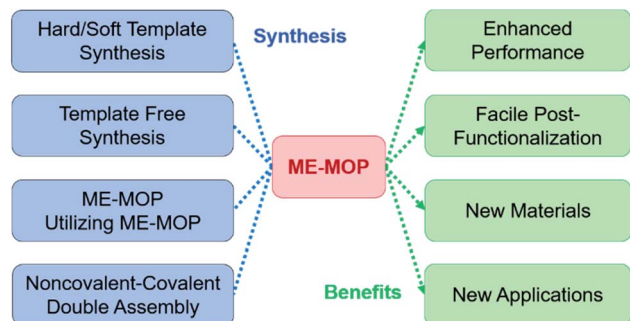


Fig. 3 Synthetic approaches for morphology-engineered microporous organic polymers (ME-MOPs) and their benefits.

template methods (Fig. 3).^{20b,21–37} Moreover, the template-free synthesis of ME-MOPs could also be found in the literature.^{38,39} In addition, unprecedented synthetic approaches have recently emerged for ME-MOPs, such as the synthesis of ME-MOPs utilizing ME-MOPs^{40–42} and noncovalent-covalent double assembly.^{20a,27,43–48}

ME-MOPs have shown various benefits over conventional MOPs (Fig. 3). First, the functional performance of ME-MOPs could be dramatically enhanced, compared with that of conventional MOPs,^{49,50} due to the material-economical synthesis and the morphology effect. In addition, the post-synthetic modification of ME-MOPs can be more facile due to the facile diffusion and efficient action of chemical reagents.^{51–53} ME-MOPs can be utilized as platform materials for the synthesis of new functional inorganic and nanocomposite materials.^{54–58} Moreover, ME-MOPs can open new application fields.^{59–66}

Whilst there have been recent reviews on the synthesis and application of MOPs,^{1–8,20} this review article focuses on the synthetic methods for ME-MOPs as well as the benefits provided over conventional MOPs.

2. Synthetic methods for morphology-engineered microporous organic polymers (ME-MOPs)

While the conventional synthesis of MOPs resulted in the formation of irregular particulate materials, a significant formation of ME-MOPs has been reported in the literature.^{20a,b,21–66} Usually, ME-MOPs have been prepared by template synthesis.^{20b,21–37} However, in some cases, ME-MOPs could be obtained by non-template synthesis.^{38,39} Moreover, new synthetic approaches have been suggested for ME-MOPs.^{40–48} The synthetic methods for ME-MOPs are summarized as follows:

2.1 Hard template synthesis

Hard template synthesis is a conventional method for the morphology engineering of functional materials.⁶⁷ The 0D hollow morphologies, 1D tubes, and 2D films of MOPs could be achieved by hard template methods.

2.1.1 Hollow MOP particles. Various hard templates could be utilized in the engineering of hollow MOPs (H-MOPs) (Fig. 4).^{20b,21–34} The conventional shell thicknesses of H-MOPs were observed in the range of 5–40 nm. One of the most common hard templates in materials science is silica materials. Moreover, by the well-recognized Stöber method, size-controlled monodisperse silica spheres can be easily obtained.⁶⁸ Through the adsorption of Pd and Cu catalysts, the silica spheres could be used for the engineering of the Sonogashira–Hagihara coupling-based H-MOPs (H-MOP-1) (Fig. 4a and f).^{20b} The inner silica spheres could be easily etched through the treatment with HF or NaOH solution. The outer shape of the H-

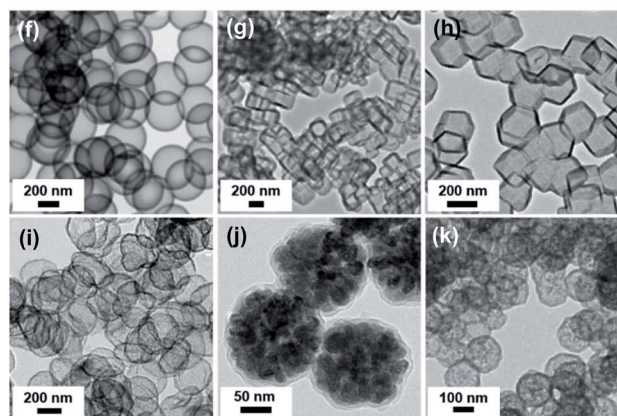
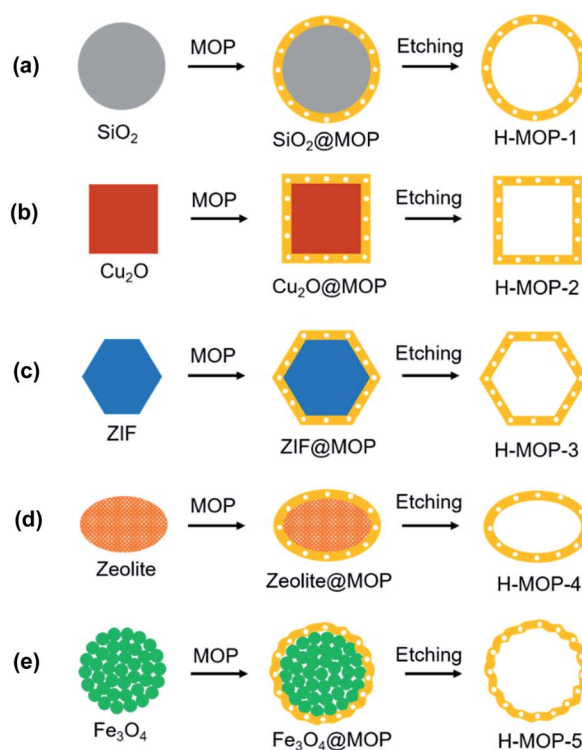


Fig. 4 Synthesis of hollow MOPs (H-MOP-1–5) using (a) SiO_2 , (b) Cu_2O , (c) ZIF, (d) zeolite, and (e) Fe_3O_4 nanoparticles as templates, respectively. TEM images of (f) H-MOP-1,^{20b} copyright 2013 ACS, (g) H-MOP-2,²² copyright 2017 RSC, (h) H-MOP-3,^{24a} copyright 2015 ACS, (i) H-MOP-4,²⁵ copyright 2015 RSC, (j) $\text{Fe}_3\text{O}_4@\text{MOP}$,^{26a} copyright 2014 RSC and (k) H-MOP-5,^{26a} copyright 2014 RSC.

MOP-1 followed the original spherical morphology of silica templates.

The nonspherical outer shapes of H-MOPs could also be achieved. For example, hollow MOP cubes (H-MOP-2) were obtained using Cu_2O nanocubes as templates (Fig. 4b and g).²² It was reported that Cu_2O can catalyze the azide-alkyne click reaction between aryl azides and ethynylarenes.^{69–71} Thus, in the engineering of H-MOP-2, Cu_2O nanocubes acted as catalysts and templates in the reaction of multi-azidoarenes and multi-ethynylbenzenes.²²

For the engineering of ME-MOPs, metal-organic frameworks and zeolitic imidazolate frameworks (ZIFs) were utilized as templates.^{23,24} UiO-66 or ZIF nanoparticles⁷² were coated with MOPs and were easily removed through acid-etching.^{23,24} Using ZIF-8 nanoparticles, hollow MOP octahedra (H-MOP-3) could be obtained (Fig. 4c and h).^{24a}

Nonspherical zeolite⁷³ or metal oxide nanoparticles have also been prepared by growth control and were successfully used as templates for the engineering of nonspherical hollow MOPs (H-MOP-4 and H-MOP-5) (Fig. 4d, e and i–k).^{25,26}

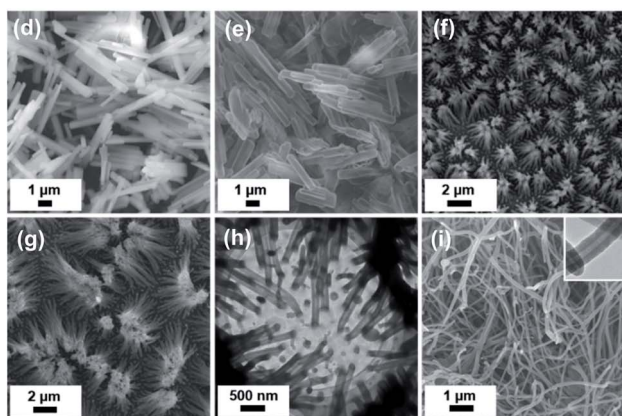
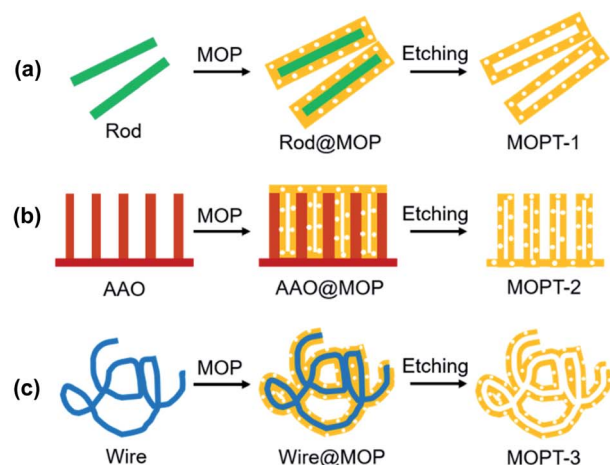


Fig. 5 Synthesis of (a) MOP tubes (MOPT-1), (b) aligned MOP tubes (MOPT-2), and (c) tubular MOP wires (MOPT-3) using rods, AAO, and wires as templates, respectively. SEM images of (d) [Et₃NH]Br rods,^{27a} copyright 2019 RSC, (e) MOPT-1,^{27a} copyright 2019 RSC, (f) short and (g) long MOPT-2,²⁸ copyright 2019 Wiley-VCH, and (i) MOPT-3,^{30a} copyright 2018 ACS. TEM images of (h) long MOPT-2,²⁸ copyright 2019 Wiley-VCH and (inset of i) MOPT-3,^{30a} copyright 2012 ACS.

2.1.2 Tubular MOPs. Tubular MOPs could be prepared by utilizing 1D templates (Fig. 5).^{20a,27–30} For example, nanorods were obtained through the electrostatic assembly of ammonium salts (Fig. 5a and d).^{27a} 1D salt rods were coated with MOPs. The etching of inner rods through dissolution resulted in the formation of MOP tubes (MOPT-1) (Fig. 5a and e). The shell thickness and the length of MOPT-1 were 50 nm and ~10 μm , respectively.

Anodic aluminum oxide (AAO) plates were utilized in the engineering of aligned MOP tubes (MOPT-2) (Fig. 5b and f–h).^{28,29} The hole diameter of AAO templates was a critical parameter for the successful engineering of MOPT-2. When the hole diameter of AAO plates was 160 nm, MOPs could not be formed inside holes due to the hindered diffusion of reagents into holes. In comparison, when the hole diameter was 300 nm, good quality MOPT-2 were obtained. The lengths of MOP tubes in MOPT-2 also were controlled in the range of 1–5 μm by controlling the thicknesses of AAO plates (Fig. 5f and g).

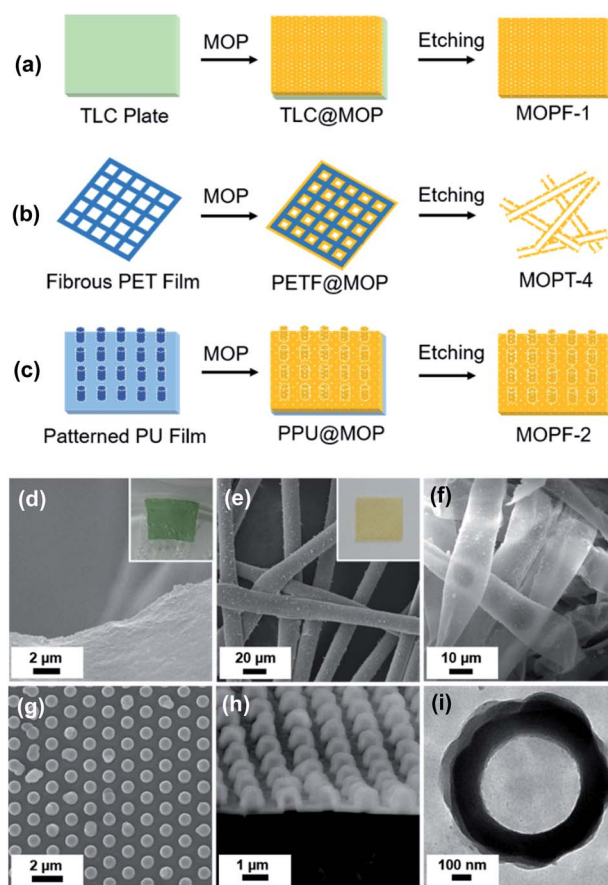


Fig. 6 Synthesis of (a) a MOP film (MOPF-1), (b) a fibrous PET@MOP film (PETF@MOP) and tubes (MOPT-4), and (c) a patterned MOP film (MOPF-2) using a TLC plate, a fibrous PET film, and a patterned PU film as templates, respectively. SEM images of (d) MOPF-1,^{31a} copyright 2015 RSC, (e) PETF@MOP,^{33b} copyright 2018 Wiley-VCH, (f) MOPT-4,^{33b} copyright 2018 Wiley-VCH, (g) a patterned PU@MOP film,³⁴ copyright 2019 ACS and (h) MOPF-2,³⁴ copyright 2019 ACS. (i) A TEM image of MOPF-2.³⁴ Copyright 2019 ACS. Photographs (insets of (d) and (e)) of MOPF-1,^{31a} copyright 2015 RSC and PETF@MOP films,^{33b} copyright 2018 Wiley-VCH.

Relatively long and tubular MOP wires (MOPT-3) with the length of 5–30 μm were obtained by using *in situ* generated salt wires as templates (Fig. 5c and i).^{27a,30} During the Sonogashira–Hagihara coupling of ethynylarenes with haloarenes in triethylamine, triethylammonium halide was *in situ* formed in a poor solvent such as toluene. The salt wires acted as *in situ* templates for the engineering of MOPT-3.

2.1.3 MOP thin films. MOP thin films have been engineered by using various 2D hard templates (Fig. 6).^{31–34} At first, thin layered silica plates could be used as templates for the formation of MOP layers on their surface.^{31a} The etching of silica layers induced the formation of MOP films (MOPF-1) (Fig. 6a and d).^{31a} MOP thin films were also introduced on the surface of the conducting electrode through the electropolymerization of organic building blocks.³²

Fibrous polymer membranes were utilized in the engineering of MOP films (Fig. 6b and e). For example, a fibrous poly(ethylene terephthalate) (PET) film was used for the engineering of MOPs on the surface of PET fibers (PETF).^{33a} The PETF hydrolysis of PETF@MOP resulted in MOP tubes (MOPT-4) (Fig. 6b and f). Polyurethane (PU) films with regular nanopatterns could also be used in the engineering of nanopatterned MOP films (MOPF-2).³⁴ Sonogashira–Hagihara coupling-based MOPs were introduced on the surface of PU films, replicating

the original regular nanopatterns of the PU templates (Fig. 6c and g–i).

2.2 Soft template synthesis

Soft templates have also been utilized in the engineering of ME-MOPs (Fig. 7). One of the conventional soft templates is surfactants.⁷⁴ When MOPs were formed in the presence of surfactants, size-controlled MOP colloidal nanoparticles (MOPNP-1) could be obtained due to the typical kinetic growth control by surfactants (Fig. 7a and d).³⁵ Water drops in organic media could act as templates for the synthesis of hollow MOPs (H-MOP-6) (Fig. 7b and e).³⁶ Organic–aqueous interfaces have also been utilized as soft templates for the synthesis of MOP films (MOPF-3) (Fig. 7c and f).³⁷

2.3 Template free formation of ME-MOPs

In some synthetic cases, ME-MOPs were prepared without specific templates (Fig. 8).^{38,39} For example, when tri(4-formylphenyl)amine and [1,1'-biphenyl]-4,4'-diacetonitrile were reacted under the conditions of the Knoevenagel condensation in tetrahydrofuran (THF), MOP nanorods (MOPRs) with an average thickness of 42 nm were obtained (Fig. 8a and c).^{38a} In this case, as the MOPs formed, their solubility in THF gradually decreased, hindering MOP growth and resulting in kinetically-controlled MOPRs.

In another example, when 1,3,6,8-tetrabromopyrene and 1,4-bis(tributylstannyl)benzene were reacted under the conditions

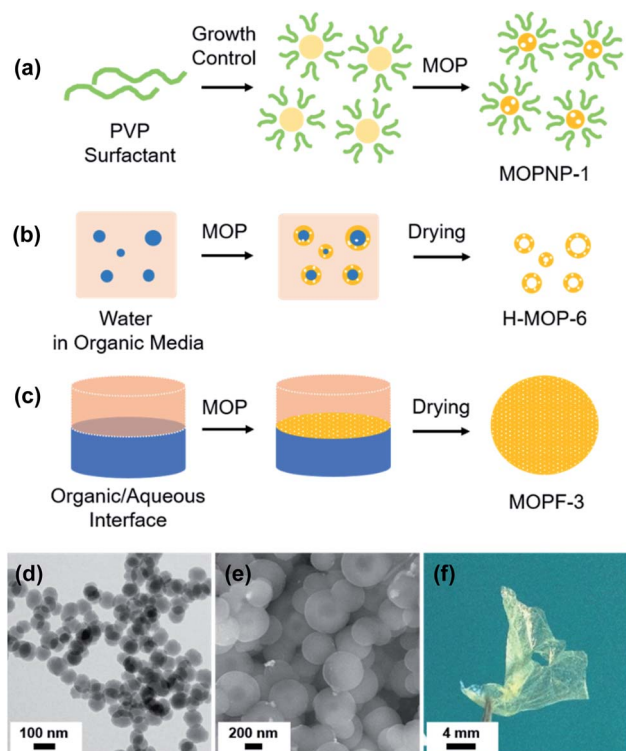


Fig. 7 Synthesis of (a) colloidal MOP nanoparticles (MOPNP-1), (b) hollow MOP spheres (H-MOP-6), and (c) a MOP film (MOPF-3) using a polyvinylpyrrolidone (PVP) surfactant, water drops in organic media, and an organic–aqueous interface as soft templates, respectively. A TEM image of (d) MOPNP-1.^{35a} Copyright 2018 ACS. A SEM image of (e) H-MOP-6.³⁶ Copyright 2015 Wiley-VCH. (f) A photograph of MOPF-3.³⁷ Copyright 2017 RSC.

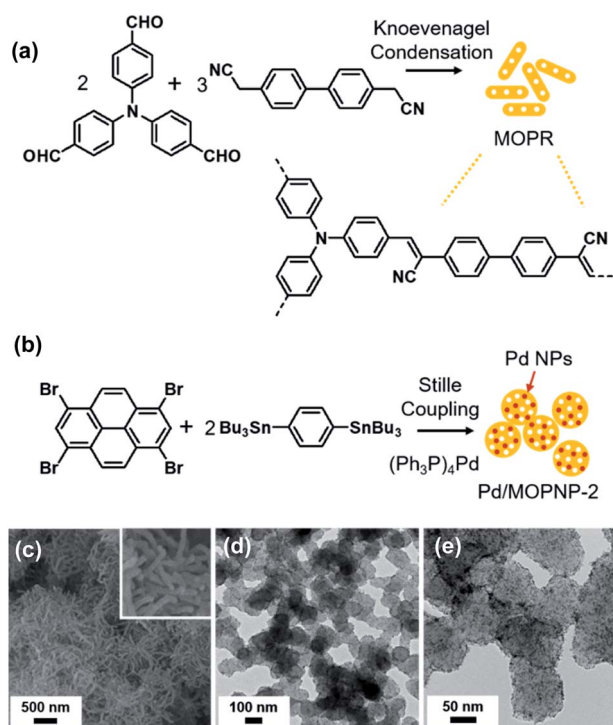


Fig. 8 Template-free formation of (a) MOP nanorods (MOPRs) and (b) MOP@Pd nanoparticles (Pd/MOPNP-2). SEM images of (c) MOPRs.³⁸ Copyright 2014 RSC. TEM images of (d and e) Pd/MOPNP-2.³⁹ Copyright 2020 RSC.

of the Stille coupling, monodisperse MOP nanoparticles (MOPNP) were formed.³⁹ In particular, 1–3 nm sized Pd nanoparticles were homogeneously deposited on the ME-MOPs to form Pd/MOPNP-2 (Fig. 8b, d and e). As the amount of (Ph₃P)₄Pd catalyst increased, the sizes of Pd/MOPNP-2 gradually decreased from 556 nm to 117 nm due to the increased number of nuclei at the early stage and the following MOP growth.

2.4 ME-MOPs utilizing ME-MOPs

ME-MOPs could be utilized as templates for the synthesis of secondary ME-MOPs (Fig. 9).^{40–42} First, Suzuki coupling-based CMPs (SCMPs) could be introduced on the surface of hollow MOP spheres using tetrabromodiphenylethylene and 1,4-benzene diboric acid as organic building blocks, resulting in hollow H-MOP@SCMPs (Fig. 9a).⁴⁰ While the average shell thickness of H-MOPs was 13 nm, those of H-MOP@SCMPs could be systematically controlled from 16 nm to 27 nm by controlling the organic building blocks of SCMPs. In addition, the original superhydrophobicity of H-MOPs with a water contact angle of 152° changed dramatically to the hydrophilic feature of H-MOP@SCMPs with a water contact angle of 31° due to the existence of defective and hydrophilic boronic acid moieties in SCMP shells.

In a similar way, HCPs could also be introduced on the surface of H-MOP spheres by the FeCl₃-catalyzed Friedel–Crafts reaction of 1,1'-bi-2-naphthol (BINOL) with formaldehyde dimethylacetal, resulting in H-MOP@HCPs (Fig. 9b).⁴¹ The shell thicknesses of H-MOP@HCPs were systematically controlled from 16 nm to 38 nm by the gradual increase of organic building blocks (Fig. 9c–e).

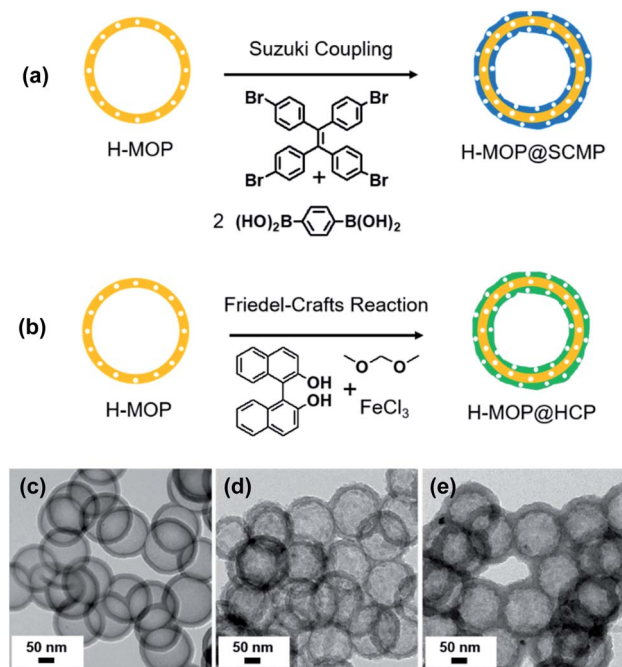


Fig. 9 Synthesis of (a) H-MOP@SCMPs and (b) H-MOP@HCPs using H-MOPs as templates. TEM images of (c) H-MOPs,⁴¹ copyright 2019 ACS, H-MOP@HCPs with the relatively (d) thin and (e) thick shell thickness,⁴¹ copyright 2019 ACS.

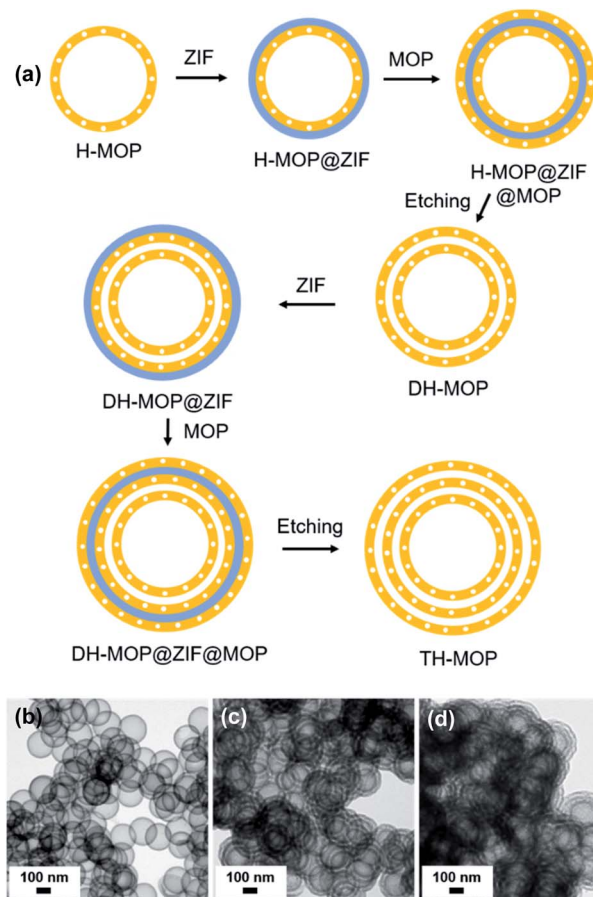


Fig. 10 (a) Synthesis of double and triple shell hollow MOP spheres (DH-MOPs and TH-MOPs) using the single shell hollow MOPs (H-MOPs) as templates.⁴² TEM images of (b) H-MOPs, (c) DH-MOPs, and (d) TH-MOPs.⁴² Copyright 2019 ACS.

Using H-MOPs as a structural platform, multi-layered hollow MOPs could also be engineered (Fig. 10a).⁴² First, ZIF-8 was incorporated on the H-MOPs to form H-MOP@ZIFs. Then, MOPs could be introduced on the surface of H-MOP@ZIFs by the Sonogashira–Hagihara coupling of tetra(4-ethynylphenyl) methane with 1,4-diiodobenzene. The acid etching of ZIF-8 layers from the H-MOP@ZIF@MOPs resulted in the formation of double-shell hollow MOPs (DH-MOPs) (Fig. 10b and c). ZIF-8 could be introduced again on the surface of the DH-MOPs. The coating of DH-MOP@ZIFs with the MOPs and the acid etching of the ZIF layers resulted in the formation of triple-shell MOPs (TH-MOPs) (Fig. 10d).

2.5 ME-MOPs utilizing noncovalent assembly

In general, the formation of MOPs is based on the formation of covalent bonds between organic building blocks during the networking process by various chemical reactions.^{1–8} Thus, the formation of MOPs can be described as an event of covalent assembly.

In comparison, various noncovalent interactions, such as dipole–dipole interaction, hydrogen bonding, and coulombic interaction, have been utilized in the formation of various self-

assembled materials.⁷⁵ Interestingly, these noncovalent self-assembly events could be successfully utilized for the engineering of ME-MOPs, resulting in a combined noncovalent and covalent assembly. Recently, corresponding examples have newly appeared in the literature for the engineering of various ME-MOPs.^{43–48} From the aspect of synthesis, the combined noncovalent and covalent assembly strategies for the engineering of ME-MOPs can be classified into three cases: self-template noncovalent-covalent synthesis, concomitant noncovalent and covalent synthesis, and step-by-step noncovalent and covalent synthesis.

2.5.1 Self-templated ME-MOPs. A noncovalent assembly-based self-templating strategy can be applied for the engineering of ME-MOPs (Fig. 11). For example, organic building blocks bearing salts were self-assembled into rods through the coulombic interaction of building blocks (Fig. 11a and c).^{20a,27a} The Sonogashira–Hagihara coupling of the assembled 1,4-di(4-bromophenyl)-3-methyl-1,2,3-triazolium iodide with tetra(4-ethynylphenyl)methane resulted in the formation of MOP tubes (MOPT-5) with lengths and a shell thickness of 400–800 nm and 140 nm, respectively (Fig. 11a and d).^{27a} For the gradual

formation of MOPT-5, the assembled rods of triazolium building blocks acted as self-templates.

Block copolymer chemistry can also be utilized in the engineering of hollow MOP tubes (MOPT-6).^{43–45} After block copolymers with ester connections were self-assembled into 1D columnar structures, the Friedel–Crafts chemistry-based knitting synthesis of outer materials induced the formation of HCPs (Fig. 11b). Then, the successive acidic hydrolysis of the ester connections between the outer HCPs and core materials resulted in the formation of tubular MOPs (Fig. 11e).

2.5.2 Concomitant noncovalent and covalent assembly for ME-MOPs. ME-MOPs could be synthesized through the concomitant noncovalent and covalent assembly. For example, caffeine (CF) is known to be self-assembled into 1D crystals in poor media including triethylamine (TEA) (Fig. 12a and b).⁴⁶ Moreover, the CF showed time-dependent dynamic self-assembly in TEA, resulting in an increase in the aspect ratios of the self-assembled 1D materials. In the presence of caffeine, the Sonogashira–Hagihara coupling-based formation of MOPs in TEA resulted in the formation of 1D CF@MOPs (Fig. 12a). It is also noteworthy that caffeine is sublimable. Thus, after the morphology engineering of MOPs based on the concomitant noncovalent assembly of caffeine, the inner caffeine of CF@MOPs could be easily removed through sublimation,

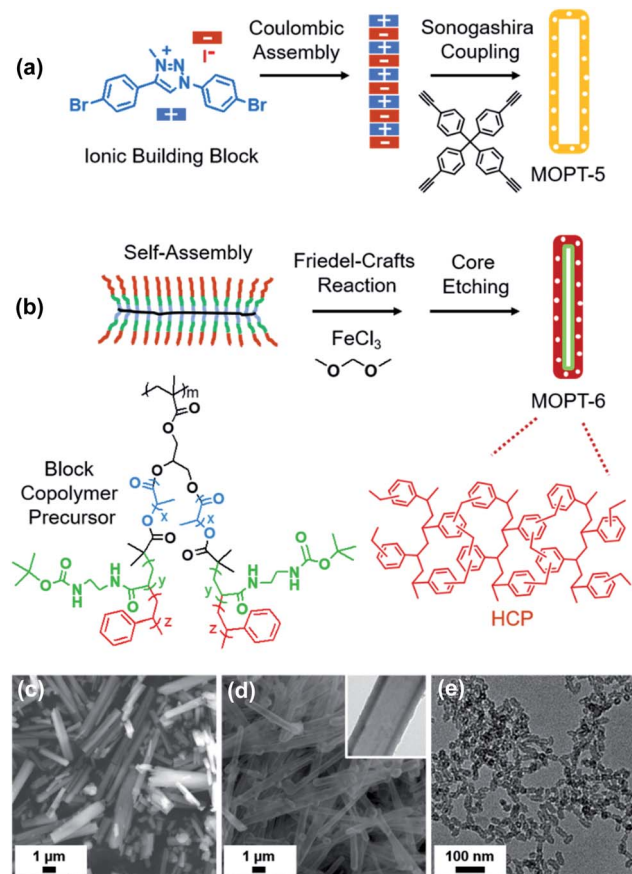


Fig. 11 Synthesis of MOP tubes (MOPT-5 and MOPT-6) through the self-assembly of (a) ionic building blocks,^{27a} copyright 2019 RSC and (b) block copolymer precursors, respectively. SEM images of (c) self-assembled ionic building block rods and (d) MOPT-5.^{27a} Copyright 2019 RSC. TEM images of (inset of d) MOPT-5,^{27a} copyright 2019 RSC and (e) MOPT-6,^{43a} copyright 2016 RSC.

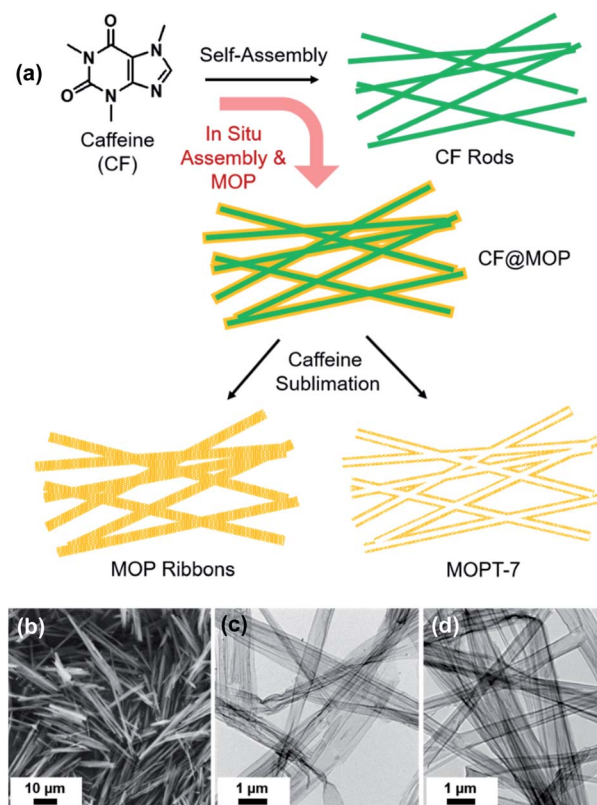


Fig. 12 (a) Synthesis of MOP ribbons and MOP tubes (MOPT-7) utilizing the concomitant noncovalent self-assembly of caffeine. (b) A SEM image of the assembled caffeine rods in triethylamine.⁴⁶ Copyright 2020 ACS. TEM images of (c) MOP ribbons,⁴⁶ Copyright 2020 ACS and (d) MOPT-7,⁴⁶ copyright 2020 ACS.

resulting in the formation of MOP ribbons and tubes (MOPT-7), depending on the amount of MOPs (Fig. 12a, c and d). In control tests, the formation of MOPs without caffeine resulted in conventional irregular MOP granules. The concomitant non-covalent/covalent assembly strategy for 1D MOPs could be applied to various functional organic building blocks bearing catalytic Zn-porphyrin species and aggregation-induced emissive (AIE) tetraphenylethylene moieties.

2.5.3 Step-by-step noncovalent and covalent assembly for ME-MOPs. Step-by-step noncovalent and covalent assembly is also a very efficient strategy for the more advanced engineering of ME-MOPs (Fig. 13). For example, through noncovalent interactions, uniform silica nanospheres can be self-assembled into opal structures on a glass plate. The silica opal structure was coated with CMPs by the Sonogashira–Hagihara coupling of tetra(4-ethynylphenyl)ethylene and tetra(4-bromophenyl)ethylene. Silica etching resulted in the formation of macroporous CMP films (MA-CMP-F) with a thickness of $\sim 2.9\ \mu\text{m}$, in contrast to the conventional solid CMP film (Fig. 13a and b–g).⁴⁷ The MA-CMP-F consisted of interconnected hollow CMP spheres with a shell thickness of 20 nm (Fig. 13f and g).

Another example of the step-by-step noncovalent and covalent assembly for the engineering of ME-MOPs is as follows: it

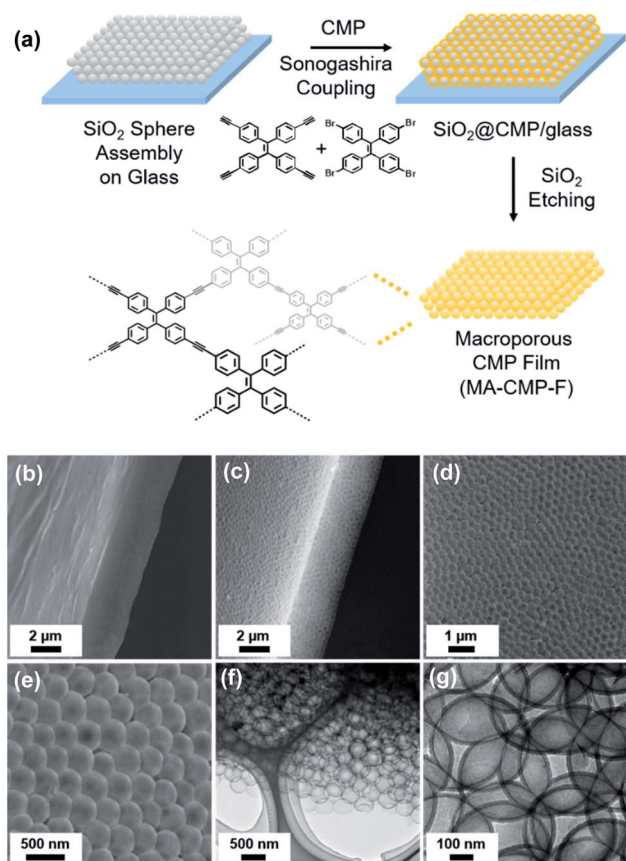


Fig. 13 (a) Synthesis of a macroporous CMP film (MA-CMP-F) using the self-assembled opal structure of silica spheres as a template.⁴⁷ Copyright 2018 RSC. SEM images of (b) a conventional CMP film and (c–e) MA-CMP-F. (f and g) TEM images of MA-CMP-F.⁴⁷ Copyright 2018 RSC.

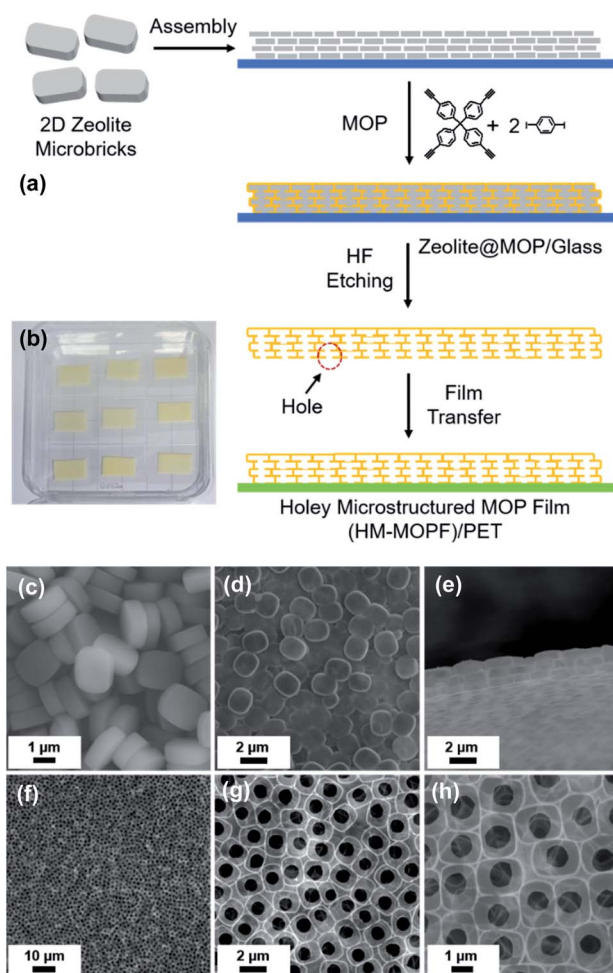


Fig. 14 (a) Synthesis of a holey microstructured MOP film on a PET film (HM-MOPF/PET) using the assembled 2D zeolites as templates.⁴⁸ Copyright 2017 RSC. (b) A photograph of HM-MOPF/PETs. SEM images of (c) 2D zeolite microbricks, (d) top view, (e) side view, and (f–h) bottom views of the HM-MOPF.⁴⁸ Copyright 2017 RSC.

was reported that 2D zeolite microbricks (silicalite-1) were assembled on solid supports such as a glass plate by simply rubbing them with a finger (Fig. 14a, c and d).⁷⁶ Due to a unique shape effect, the 2D zeolite microbricks were arranged on the glass plate with a b-orientation.

The assembled 2D zeolite microbricks on the glass plate were coated with MOPs by the Sonogashira–Hagihara coupling of tetra(4-ethynylphenyl)methane with 1,4-diiodobenzene. Successive zeolite etching from the zeolite@MOP/glass plate resulted in the formation of a microstructured MOP film with interconnected hollow MOP sub-structures (Fig. 14a, d and e). Interestingly, the microstructured MOP films showed intriguing holes in each hollow MOP sub-structure (Fig. 14f–h).⁴⁸ It can be speculated that the holes formed through the limited diffusion of organic building blocks in the formation of MOPs due to the complete contact of 2D zeolite microbricks (Fig. 14a). The holey microstructured MOP film (HM-MOPF) could be transferred to another soft solid support such as a PET film. Due to the existence of holes, the HM-MOPF with a film thickness of 1.4–2.1

μm could be efficiently attached on the PET film (Fig. 14b). HM-MOPF/PET films were further utilized in the engineering of flexible current collectors through electroless Cu deposition.⁴⁸

3. Benefits of ME-MOPs

The morphology engineering of MOPs has provided various benefits. The morphology effects of ME-MOPs can enhance their functional performance.^{49,50} In addition, hollow MOPs can be easily post-modified due to the facilitated reaction of reagents.^{51–53} ME-MOPs can be utilized as platforms for the synthesis of new functional materials.^{54–58} For example, through the incorporation of various precursors into ME-MOPs, new inorganic and composite materials could be synthesized. Moreover, ME-MOPs can extend the application fields of MOPs.^{33,34,60–66}

3.1 Morphology effects on the functional performance of ME-MOPs

Compared with conventional MOPs, hollow MOPs are more beneficial in their functional performance, especially in catalysis, sensing, and energy storage.^{49,50} The first scientific principle is the facilitated mass transfer of reagents through the thin shells of hollow MOPs, enhancing reaction rates and inducing the efficient utilization of functional sites in the materials (Fig. 15a).⁷⁷ The second scientific principle is the atom-economical use of functional MOPs through the engineering of hollow MOPs or MOP nanoparticles. Using the same amount of MOPs, more hollow MOP nanoparticles can be

achieved, compared with conventional MOP powders (Fig. 15a). Thus, the functional performance of ME-MOPs per gram can be enhanced in catalysis⁴⁹ and energy storage applications⁵⁰ (Fig. 15b and c).

3.2 Efficient post-synthetic functionalization of ME-MOPs

Various tailored functions can be introduced into MOPs through a post-synthetic modification (PSM) approach.⁷⁸ However, the degree of PSM over whole MOPs is sensitive to their thicknesses. Bulk MOPs usually show incomplete functionalization because reagents cannot efficiently reach inner MOPs. If the thicknesses of MOPs are sufficiently thin, whole MOPs can be utilized in the PSM. In this regard, hollow MOPs with the thin thickness of 10–30 nm showed more efficient PSM, compared with conventional MOPs.^{51–53}

Moreover, hollow MOPs can be utilized as structural platforms for the synthesis of functional polymer materials through PSM (Fig. 16).⁵¹ Hollow and defective MOPs (H-DMOPs) prepared by the Sonogashira–Hagihara coupling of 1,4-dibromo-2,5-diethynylbenzene are rich in defective terminal alkynes that could be further utilized in the PSM (Fig. 16a and b). For example, the H-DMOPs could be further functionalized to terminal alkyne-enriched hollow MOPs (H-MOP@AB₂-TAs) (Fig. 16a and c) through the azide–alkyne click reaction using the AB₂ type building block, 3,5-diethynylbenzyl azide.⁵¹

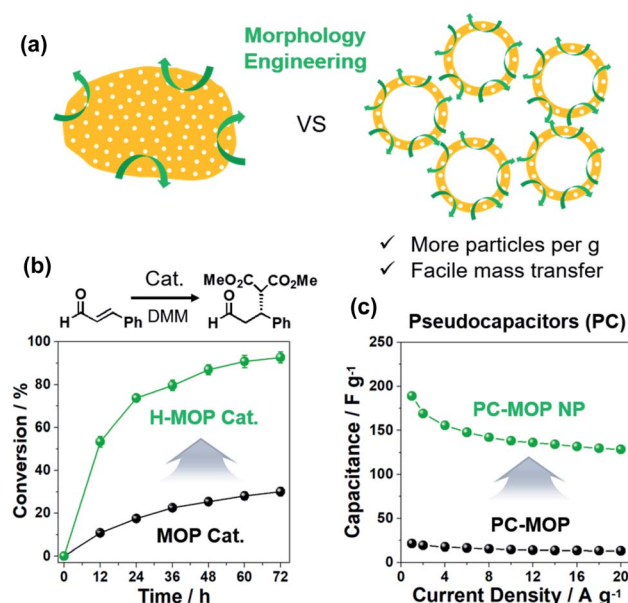


Fig. 15 (a) Scientific principles of the enhanced functional performance of hollow MOPs. (b) Enhanced catalytic performance of a hollow MOP catalyst (H-MOP Cat.) for organocatalytic dimethylmalonate (DMM) addition to cinnamaldehyde.⁴⁹ Copyright 2017 RSC. (c) Enhanced energy storage performance of pseudocapacitive MOP nanoparticles (PC-MOP NPs) in coin-cell type supercapacitors.⁵⁰ Copyright 2020 Wiley-VCH.

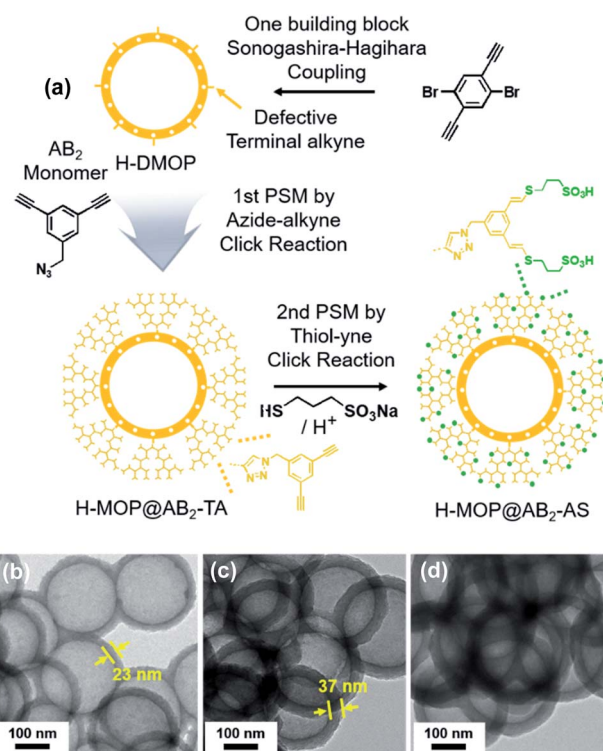


Fig. 16 (a) Post-synthetic modification of hollow MOPs bearing defective terminal alkynes (H-DMOPs) by the azide–alkyne click reaction of AB₂ type monomers to form terminal alkyne (TA)-enriched H-MOPs (H-MOP@AB₂-TAs) and aliphatic sulfonic acid (AS)-enriched H-MOPs (H-MOP@AB₂-ASs). TEM images of (b) H-DMOPs, (c) H-MOP@AB₂-TAs, and (d) H-MOP@AB₂-ASs.⁵¹ Copyright 2020 RSC.

Moreover, the H-MOP@AB₂-TAs were further functionalized to the aliphatic sulfonic acid-enriched hollow MOPs (H-MOP@AB₂-ASS) (Fig. 16a and d).

3.3 Synthesis of new materials utilizing ME-MOPs

ME-MOPs can be utilized in the synthesis of new functional materials such as carbon nanomaterials or inorganic-carbon nanocomposites (Fig. 17).^{26,54–58} First, the heat-treatment of the azide-alkyne click-based hollow MOP cubes under argon

resulted in N-doped carbon nanocubes, showing excellent energy storage performance as electrode materials for supercapacitors (Fig. 17a and f).⁵⁴

Second, microporosity and high surface areas allowed for inorganic precursors to be efficiently incorporated into ME-MOPs. When hollow or nanoparticulate MOPs with MoS₂ precursors were heated under argon, hollow or nanoparticulate MoS₂/carbon composites could be synthesized, respectively (Fig. 17b, c and g–i).^{55,56} While hollow MoS₂/carbon composites showed excellent lithium storage performance for lithium ion batteries,⁵⁵ MoS₂/carbon nanoparticles showed excellent adsorption behaviors toward pollutants in water.⁵⁶

Third, core-shell materials bearing MOPs were utilized as precursor materials for the synthesis of nanocomposites.^{26,57} For example, when ZIF-67@MOPs or Fe₃O₄@MOPs were heated under argon, Co@C⁵⁷ and Fe₃O₄@C nanocomposites^{26a} were prepared, respectively (Fig. 17d, e and j, k). While Co@C nanocomposites showed excellent performance as magnetic adsorbents for pollutants in water,⁵⁷ Fe₃O₄@C materials showed enhanced anode performance for lithium ion batteries due to the buffer effect of the carbon matrix.^{26a}

Fourth, ME-MOPs were utilized in the synthesis of metal oxide nanomaterials (Fig. 18).^{20b,58} For example, iron and cobalt carbonyls were incorporated into the pores of H-MOP spheres or MOP tubes. The heat-treatment of H-MOP@Co or MOPT@Fe in air resulted in the formation of hollow Co₃O₄ spheres and Fe₂O₃ nanotubes, respectively (Fig. 18a–e).^{20b,58} Interestingly, both hollow Co₃O₄ spheres and Fe₂O₃ nanotubes consisted of interconnected metal oxide nanoparticles (Fig. 18d). Due to the nanoparticulate feature, the hollow Co₃O₄ spheres and Fe₂O₃ nanotubes showed

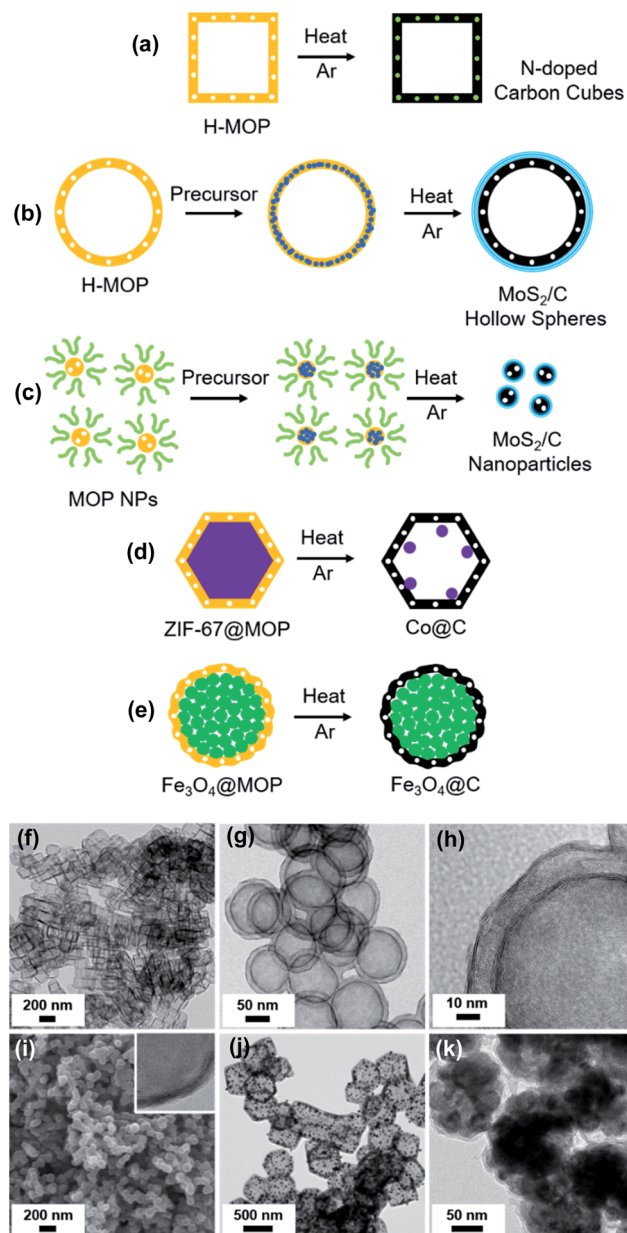


Fig. 17 Synthesis of (a) N-doped carbon cubes, (b) MoS₂/C hollow spheres, (c) MoS₂/C nanoparticles, (d) Co@C, and (e) Fe₃O₄@C using ME-MOPs. TEM images of (f) N-doped carbon cubes,⁵⁴ copyright 2018 ACS, (g and h) MoS₂/C hollow spheres,⁵⁵ copyright 2015 RSC, (j) Co@C,⁵⁷ copyright 2015 RSC, and (k) Fe₃O₄@C,²⁶ copyright 2014 RSC. A SEM image of (i) MoS₂/C nanoparticles.⁵⁶ Copyright 2019 Wiley-VCH.

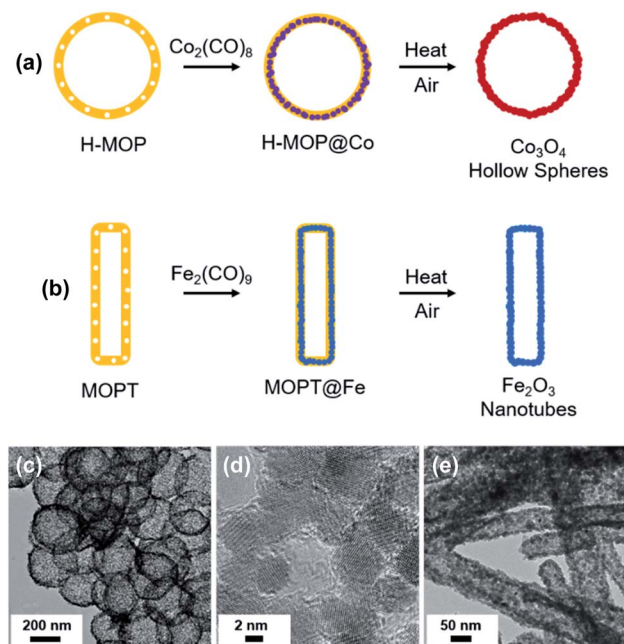


Fig. 18 Synthesis of (a) Co₃O₄ hollow spheres and (b) Fe₂O₃ nanotubes using ME-MOP precursor materials. TEM images of (c and d) Co₃O₄ hollow spheres,^{20b} copyright 2013 ACS and (e) Fe₂O₃ nanotubes,⁵⁸ copyright 2012 Wiley-VCH.

excellent catalytic activities and energy storage performance as anode materials for lithium ion batteries, respectively.^{20b,58}

3.4 New applications of ME-MOPs

While MOPs have been applied to various purposes including adsorbents, catalysis, and energy storage materials,^{1–8} ME-MOPs have opened paths for new applications. Examples of new applications of ME-MOPs include biomedical applications,^{42,59–62} antifouling polymer synthesis,^{63,64} and new membranes for environmental and energy applications.^{33,34,48,65,66}

3.4.1 Biomedical applications of ME-MOPs. ME-MOPs could be applied to biomedical fields.^{42,59–62} First, H-MOPs were decorated with folate groups and applied as drug delivery vehicles for cancer cells with folate acceptors.⁵⁹ Second, the triple shell H-MOPs showed more efficient drug delivery performance than conventional single shell H-MOPs due to the efficient interaction of inner shells with doxorubicin (DOX).⁴² Third, hollow MOPs bearing folate groups, emissive tetraphenylethylenes, and Fe_3O_4 nanoparticles (FVM-FAs) could be engineered for multifunctional drug delivery systems (Fig. 19a–d).⁶² While the hollow space and micropores of FVM-FAs carried DOX, the folate groups and tetraphenylethylenes in the shells were utilized for targeting cancer cells and emissive imaging,

respectively (Fig. 19a). In particular, inner iron oxides can induce a magneto-thermal therapy through magnetic field-induced heat generation (Fig. 19e and f).

3.4.2 Antifouling polymer synthesis using ME-MOPs. ME-MOPs can be applied in polymer production technology (Fig. 20).^{63,64} In the conventional synthesis of polymers, reactor fouling is a critical and technical problem (Fig. 20a and d).^{79,80} The polymers sticking on the surface of the reactors induced not only poor quality of polymers but also an increase of costs due to additional efforts to remove the stuck polymers. To solve this problem in polymer production, seed-mediated polymer synthesis can be an efficient way (Fig. 20a). In this case, after the reaction, polymers can be formed around the seeds, resulting in the formation of polymer particles without a reactor fouling phenomenon.

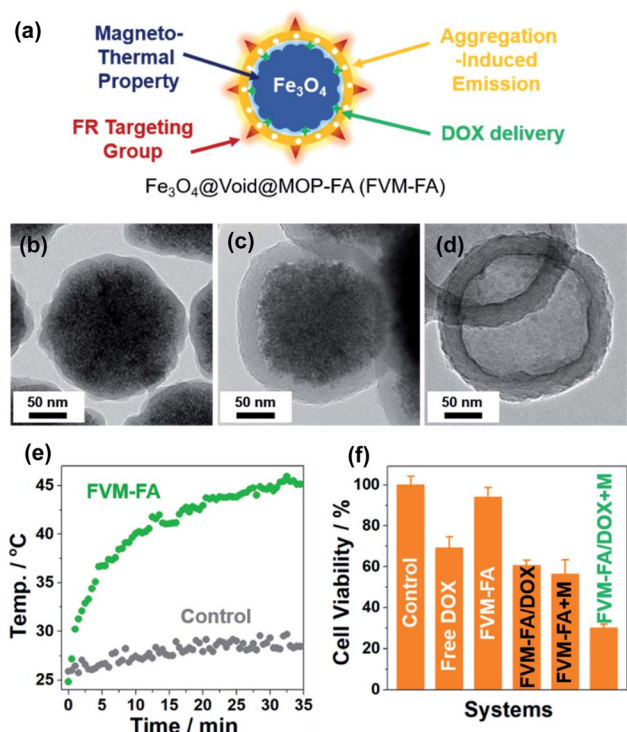


Fig. 19 (a) Multifunctional drug delivery systems based on the Fe_3O_4 @Void@MOP-FAs (FVM-FAs).⁶² Copyright 2020 ACS. TEM images of (b) Fe_3O_4 @ SiO_2 , (c) FVM-FAs, and (d) hollow MOP-FAs.⁶² Copyright 2020 ACS. (e) Magneto-thermal behavior (magnetic field: 109.3 kHz, 31.3 kA m^{-1}) and (f) a combined chemo and hydrothermal therapy of KB cancer cells by FVM-FAs (DOX and M imply doxorubicin and magnetic field, respectively).⁶² Copyright 2020 ACS.

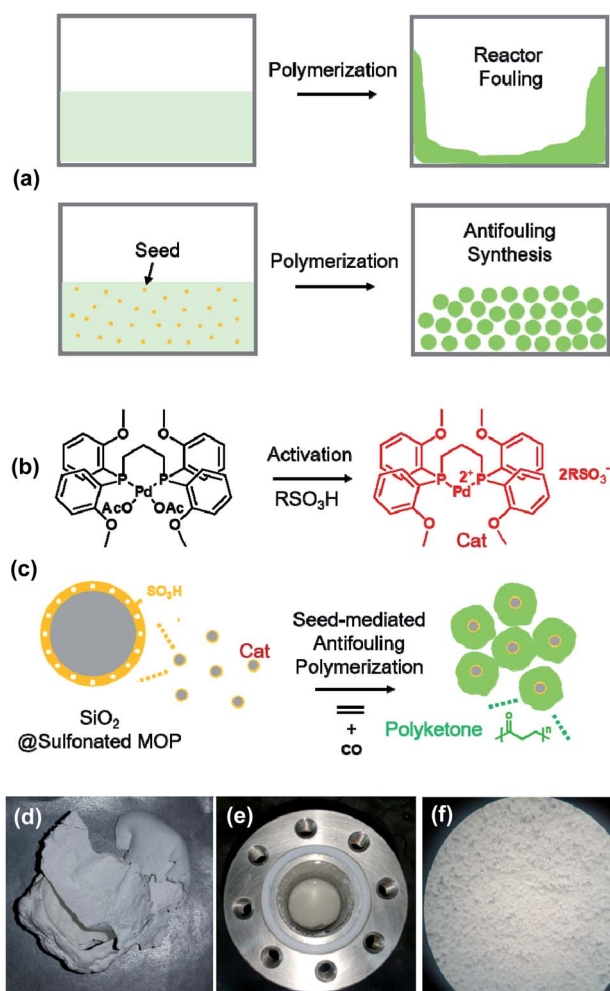


Fig. 20 (a) Illustration of a conventional reactor fouling issue vs. seed-mediated antifouling polymer synthesis. (b) Activation of a Shell's catalyst precursor by a reaction with sulfonic acid.⁶² (c) Activation of a Shell's catalyst precursor on the surface of the SiO_2 @sulfonated MOP nanoseeds and seed-mediated antifouling polyketone synthesis from ethylene and carbon monoxide. Photographs of (d) polyketones obtained with reactor fouling, (e) antifouling polyketone synthesis using SiO_2 @sulfonated MOP nanoseeds, and (f) polyketone powders obtained through seed-mediated antifouling polymerization.⁶⁴ Copyright 2017 ACS.

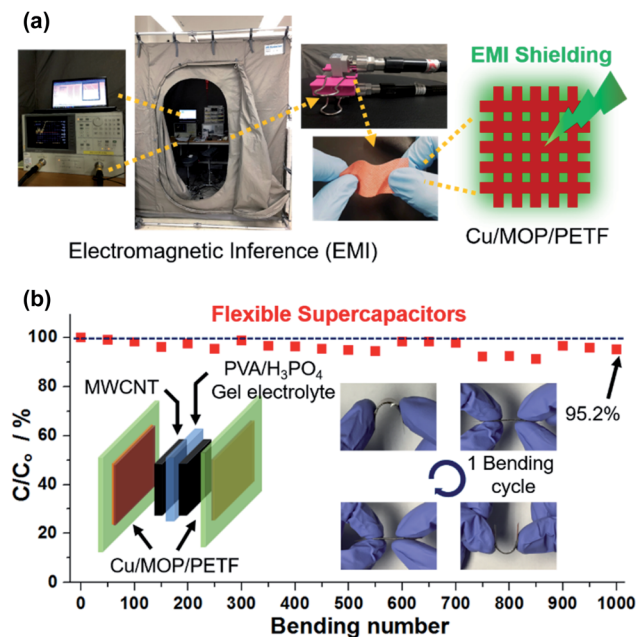


Fig. 21 (a) Electromagnetic interference shielding (EMI) using a fibrous Cu/MOP/PET.⁶⁵ Copyright 2020 ACS. (b) Electrochemical performance of the flexible supercapacitors fabricated using Cu/MOP/PETs.⁴⁸ Copyright 2017 RSC.

For example, ME-MOPs were applied to engineer seed materials for polyketone (PK) synthesis (Fig. 20b–f).^{63,64} Recently, PK has attracted significant attention of scientists because PK contains 50 wt% carbonyl groups that originate from carbon monoxide.⁸¹ Shell's Pd catalyst is known to show high activity in the PK synthesis.⁸² Usually, the Shell's Pd catalyst precursor with acetates should be activated by the reaction with sulfonic acid, generating active Pd sulfonates (Fig. 20b). The size-controlled silica spheres were coated with MOPs and further sulfonated with chlorosulfonic acid. The SiO₂@-sulfonated MOP seed materials could activate the Shell's Pd catalyst precursors and induced the seed-mediated antifouling synthesis of high-quality PK (Fig. 20c–f).⁶⁴

3.4.3 Functional membranes based on ME-MOPs for environmental and energy applications. Recently, particulate matter (PM) has been a serious environmental problem.⁸³ Fibrous films have been applied for the adsorptive removal of PM.⁸⁴ The efficient interaction of the fibers with PM is critical to be efficient systems. In this regard, when MOPs were introduced onto the surface of a fibrous PET film, fibrous PET@MOPs showed enhanced adsorptive removal performance towards PM.^{33,34}

Fibrous PET@MOP films could be utilized in the electroless deposition of metals.^{65,66} The resultant PET@MOP@Cu membranes could be applied for electromagnetic interference shielding (Fig. 21a).⁶⁵ In addition, PET@MOP@Cu and PET@MOP@Ni could be utilized as flexible current collectors for the engineering of flexible batteries and supercapacitors (Fig. 21b).^{48,66}

4. Conclusions and perspectives

MOPs have become a very important class of functional materials and recently, advanced ME-MOPs emerged in the literature. Various synthetic approaches have been explored to realize ME-MOPs. From the aspect of synthesis, we think that there is much room to further explore ME-MOPs. First, the established hard and soft template synthesis can be applied for the synthesis of more various ME-MOPs using tailored building blocks. Second, further post-functionalized ME-MOPs can be prepared using ME-MOPs for tailored functionalization. Third, new ideas for the utilization of noncovalent assembly can be explored for the engineering of ME-MOPs. Fourth, various nanostructured MOP films can be realized using new 2D templates.

From the aspect of applications, first, we think that more various heterogeneous catalysts can be developed based on hollow and nanoparticulate MOPs. Second, high-performance energy-related materials based on carbon and inorganic/carbon nanocomposites can be further designed and synthesized using ME-MOPs as structural platforms. Third, tailored functional MOP membranes for environmental and energy applications can be engineered. We expect that there will be continuous studies on the synthesis of new ME-MOPs and such novel applications.

Author contributions

S. U. Son: conceptualization, supervision, writing original draft, and review & editing. K. Cho, C. W. Kang, S. H. Ryu, and J. Y. Jang: review & editing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 J.-S. M. Lee and A. I. Cooper, *Chem. Rev.*, 2020, **120**, 2171–2214.
- 2 Y. Gu, S. U. Son, T. Li and B. Tan, *Adv. Funct. Mater.*, 2020, **31**, 2008265.
- 3 B. Zheng, X. Lin, X. Zhang, D. Wu and K. Matyjaszewski, *Adv. Funct. Mater.*, 2020, **30**, 1907006.
- 4 N. Chaoui, M. Trunk, R. Dawson, J. Schmidt and A. Thomas, *Chem. Soc. Rev.*, 2017, **46**, 3302–3321.
- 5 S. Das, P. Heasman, T. Ben and S. Qiu, *Chem. Rev.*, 2017, **117**, 1515–1563.
- 6 J.-K. Sun, M. Antonietti and J. Yuan, *Chem. Soc. Rev.*, 2016, **45**, 6627–6656.

- 7 Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012–8031.
- 8 F. Vilela, K. Zhang and M. Antonietti, *Energy Environ. Sci.*, 2012, **5**, 7819–7832.
- 9 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.
- 10 V. A. Davankov, S. V. Rogoshin and M. P. Tsyurupa, *J. Polym. Sci., Polym. Symp.*, 1974, **47**, 95–101.
- 11 V. A. Davankov, G. I. Timofeeva, M. M. Ilyin and M. P. Tsyurupa, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 3847–3852.
- 12 C. D. Wood, B. Tan, A. Trewin, H. Niu, D. Bradshaw, M. J. Rosseinsky, Y. Z. Khimyak, N. L. Campbell, R. Kirk, E. Stöckel and A. I. Cooper, *Chem. Mater.*, 2007, **19**, 2034–2048.
- 13 C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou and A. I. Cooper, *Adv. Mater.*, 2008, **20**, 1916–1921.
- 14 B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, C. Hu and B. Tan, *Macromolecules*, 2011, **44**, 2410–2414.
- 15 L. Tan and B. Tan, *Chem. Soc. Rev.*, 2017, **46**, 3322–3356.
- 16 N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675–683.
- 17 P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.*, 2004, 230–231.
- 18 N. B. McKeown, S. Hanif, K. Msayib, C. E. Tattershall and P. M. Budd, *Chem. Commun.*, 2002, 2782.
- 19 J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem., Int. Ed.*, 2007, **46**, 8574–8578.
- 20 (a) H. C. Cho, H. S. Lee, J. Chun, S. M. Lee, H. J. Kim and S. U. Son, *Chem. Commun.*, 2011, **47**, 917–919; (b) N. Kang, J. H. Park, M. Jin, N. Park, S. M. Lee, H. J. Kim, J. M. Kim and S. U. Son, *J. Am. Chem. Soc.*, 2013, **135**, 19115–19118; (c) Q. Li, S. Razzaque, S. Jin and B. Tan, *Sci. China: Chem.*, 2017, **60**, 1056–1066; (d) H. Bildirir, V. G. Gregoriou, A. Avgeropoulos, U. Scherf and C. L. Chochos, *Mater. Horiz.*, 2017, **4**, 546–556.
- 21 (a) X. Zhuang, D. Gehrig, N. Forler, H. Liang, M. Wagner, M. R. Hansen, F. Laquai, F. Zhang and X. Feng, *Adv. Mater.*, 2015, **27**, 3789–3796; (b) K. Wang, L. Huang, S. Razzaque, S. Jin and B. Tan, *Small*, 2016, **12**, 3134–3142; (c) L. Li, C. Cui, W. Su, Y. Wang and R. Wang, *Nano Res.*, 2016, **9**, 779–786; (d) Z. Jia, K. Wang, B. Tan and Y. Gu, *ACS Catal.*, 2017, **7**, 3693–3702; (e) S. Wu, Z. Zhu, C. Liu, Y. Su, F. Wang, W. Bai, H. Sun and W. Liang, *J. Colloid Interface Sci.*, 2021, **586**, 152–162.
- 22 D. Kang, J. H. Ko, J. Choi, K. Cho, S. M. Lee, H. J. Kim, Y.-J. Ko, K. H. Park and S. U. Son, *Chem. Commun.*, 2017, **53**, 2598–2601.
- 23 J. Chun, S. Kang, N. Park, E. J. Park, X. Jin, K.-D. Kim, H. O. Seo, S. M. Lee, H. J. Kim, W. H. Kwon, Y.-K. Park, J. M. Kim, Y.-D. Kim and S. U. Son, *J. Am. Chem. Soc.*, 2014, **136**, 6786–6789.
- 24 (a) J. H. Park, J. H. Ko, S. Hong, Y. J. Shin, N. Park, S. Kang, S. M. Lee, H. J. Kim and S. U. Son, *Chem. Mater.*, 2015, **27**, 5845–5848; (b) Z. Wei, D. Wang, Y. Liu, X. Guo, Y. Zhu, Z. Meng, Z.-Q. Yu and W.-Y. Wong, *J. Mater. Chem. C*, 2020, **8**, 10774–10780.
- 25 S. Kang, J. Chun, N. Park, S. M. Lee, H. J. Kim and S. U. Son, *Chem. Commun.*, 2015, **51**, 11814–11817.
- 26 (a) B. Lim, J. Jin, J. Yoo, S. Y. Han, K. Kim, S. Kang, N. Park, S. M. Lee, H. J. Kim and S. U. Son, *Chem. Commun.*, 2014, **50**, 7723–7726; (b) H.-J. Zhang, J.-H. Wang, Y.-H. Zhang and T.-L. Hu, *J. Polym. Sci., Polym. Chem.*, 2017, **55**, 1329–1337.
- 27 (a) C. W. Kang, J. H. Ko, S. M. Lee, H. J. Kim, Y.-J. Ko and S. U. Son, *J. Mater. Chem. A*, 2019, **7**, 7859–7866; (b) Q. Li, S. Jin and B. Tan, *Sci. Rep.*, 2016, **6**, 31359.
- 28 S. H. Ryu, D. H. Lee, Y.-J. Ko, S. M. Lee, H. J. Kim, K. C. Ko and S. U. Son, *Macromol. Chem. Phys.*, 2019, **220**, 1900157.
- 29 S. H. Ryu, C. W. Kang, J. Choi, Y. Myung, Y.-J. Ko, S. M. Lee, H. J. Kim and S. U. Son, *ACS Appl. Mater. Interfaces*, 2018, **10**, 6815–6819.
- 30 (a) J. Chun, J. H. Park, J. Kim, S. M. Lee, H. J. Kim and S. U. Son, *Chem. Mater.*, 2012, **24**, 3458–3463; (b) W. Fan, X. Liu, Z. Zhang, Q. Zhang, W. Ma, D. Tan and A. Li, *Microporous Mesoporous Mater.*, 2014, **196**, 335–340; (c) Z. Xiang, H. Sun, Z. Zhu, W. Liang, B. Yang and A. Li, *RSC Adv.*, 2015, **5**, 24893–24898; (d) P. Mu, W. Bai, Z. Zhang, J. He, H. Sun, Z. Zhu, W. Liang and A. Li, *J. Mater. Chem. A*, 2018, **6**, 18183–18190; (e) Z. Zhu, P. Mu, Y. Fan, W. Bai, Z. Zhang, H. Sun, W. Liang and A. Li, *Eur. Polym. J.*, 2020, **126**, 109560.
- 31 (a) J. H. Ko, J. H. Moon, N. Kang, J. H. Park, H.-W. Shin, N. Park, S. Kang, S. M. Lee, H. J. Kim, T. K. Ahn, J. Y. Lee and S. U. Son, *Chem. Commun.*, 2015, **51**, 8781–8784; (b) B. Liang, H. Wang, X. Shi, B. Shen, X. He, Z. A. Ghazi, N. A. Khan, H. Sin, A. M. Khattak, L. Li and Z. Tang, *Nat. Chem.*, 2018, **10**, 961–967; (c) Z. Liu, Y. Yin, F. Xiu, X. Wang, S. Ju, M. Song, Q. Chang, J. Chen, J. Liu and W. Huang, *J. Mater. Chem. C*, 2018, **6**, 7295–7301; (d) S. Ju, Y. Ding, Y. Yin, S. Cheng, X. Wang, H. Mao, Z. Zhou, M. Song, Q. Chang, C. Ban, Z. Liu and J. Liu, *RSC Adv.*, 2019, **9**, 17399–17404.
- 32 (a) C. Gu, Y. Chen, Z. Zhang, S. Xue, S. Sun, K. Zhang, C. Zhong, H. Zhang, Y. Pan, Y. Lv, Y. Yang, F. Li, S. Zhang, F. Huang and Y. Ma, *Adv. Mater.*, 2013, **25**, 3443–3448; (b) C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu and D. Jiang, *Angew. Chem., Int. Ed.*, 2014, **53**, 4850–4855; (c) C. Gu, N. Huang, Y. Wu and D. Jiang, *Angew. Chem., Int. Ed.*, 2015, **54**, 11540–11544; (d) C. Gu, N. Huang, Y. Chen, L. Qin, H. Xu, S. Zhang, F. Li, Y. Ma and D. Jiang, *Angew. Chem., Int. Ed.*, 2015, **54**, 13594–13598; (e) C. Gu, N. Huang, Y. Chen, H. Zhang, S. Zhang, F. Li, Y. Ma and D. Jiang, *Angew. Chem., Int. Ed.*, 2016, **55**, 3049–3053; (f) A. Palma-Cando and U. Scherf, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11127–11133.
- 33 (a) C. W. Kang, Y.-J. Ko, S. M. Lee, H. J. Kim and S. U. Son, *Adv. Mater. Interfaces*, 2018, **5**, 1800628; (b) J. Lee, J. G. Kim and J. Y. Chang, *Sci. Rep.*, 2017, **7**, 13568; (c) K. Yuan,

- P. Guo-Wang, T. Hu, L. Shi, R. Zeng, M. Forster, T. Pichler, Y. Chen and U. Scherf, *Chem. Mater.*, 2015, **27**, 7403–7411.
- 34 C. W. Kang, J. Jin, Y.-J. Ko, S. M. Lee, H. J. Kim and S. U. Son, *ACS Appl. Mater. Interfaces*, 2019, **11**, 1748–1753.
- 35 (a) D. H. Lee, K. C. Ko, J. H. Ko, S. Y. Kang, S. M. Lee, H. J. Kim, Y.-J. Ko, J. Y. Lee and S. U. Son, *ACS Macro Lett.*, 2018, **7**, 651–655; (b) S. Bandyopadhyay, P. Pallavi, A. G. Anil and A. Patra, *Polym. Chem.*, 2015, **6**, 3775–3780.
- 36 W. Zhou, H. Gao and J. B. Goodenough, *Adv. Energy Mater.*, 2016, **6**, 1501802.
- 37 Z. Chen, M. Chen, Y. Yu and L. Wu, *Chem. Commun.*, 2017, **53**, 1989–1992.
- 38 (a) J. H. Park, K. C. Ko, N. Park, H.-W. Shin, E. Kim, N. Kang, J. H. Ko, S. M. Lee, H. J. Kim, T. K. Ahn, J. Y. Lee and S. U. Son, *J. Mater. Chem. A*, 2014, **2**, 7656–7661; (b) S. K. Kundu and A. Bhaumik, *ACS Sustainable Chem. Eng.*, 2015, **3**, 1715–1723; (c) A. Modak, P. Bhanja and A. Bhaumik, *Chem.–Eur. J.*, 2018, **24**, 14189–14197.
- 39 S. H. Ryu, S. J. Choi, J. H. Seon, B. Jo, S. M. Lee, H. J. Kim, Y.-J. Ko, K. C. Ko, T. K. Ahn and S. U. Son, *Catal. Sci. Technol.*, 2020, **10**, 5535–5543.
- 40 S. H. Ryu, D. H. Lee, S. M. Lee, H. J. Kim, Y.-J. Ko, K. C. Ko and S. U. Son, *Chem. Commun.*, 2019, **55**, 9515–9518.
- 41 S. J. Choi, E. H. Choi, C. Song, Y.-J. Ko, S. M. Lee, H. J. Kim, H.-Y. Jang and S. U. Son, *ACS Macro Lett.*, 2019, **8**, 687–693.
- 42 J. Y. Jang, T. M. D. Le, J. H. Ko, Y.-J. Ko, S. M. Lee, H. J. Kim, J. H. Jeong, T. Thambi, D. S. Lee and S. U. Son, *Chem. Mater.*, 2019, **31**, 300–304.
- 43 (a) H. Zhang, L. Xiong, Z. He, A. Zhong, T. Wang, Y. Xu, M. Zhou and K. Huang, *Polym. Chem.*, 2016, **7**, 4975–4982; (b) M. Zhou, H. Zhang, L. Xiong, Z. He, T. Wang, Y. Xu and K. Huang, *Polym. Chem.*, 2017, **8**, 3721–3730; (c) L. Xiong, H. Zhang, Z. He, T. Wang, Y. Xu, M. Zhou and K. Huang, *New J. Chem.*, 2018, **42**, 1368–1372.
- 44 Z. He, A. Zhong, H. Zhang, L. Xiong, Y. Xu, T. Wang, M. Zhou and K. Huang, *Macromol. Rapid Commun.*, 2016, **37**, 1566–1572.
- 45 (a) Y. Xu, T. Wang, Z. He, A. Zhong and K. Huang, *RSC Adv.*, 2016, **6**, 39933–39939; (b) H. Zhang, M. Zhou, L. Xiong, Z. He, T. Wang, Y. Xu and K. Huang, *J. Phys. Chem. C*, 2017, **121**, 12771–12779; (c) Y. Xu, T. Wang, Z. He, M. Zhou, W. Yu, B. Shi and K. Huang, *Polym. Chem.*, 2018, **9**, 4017–4024.
- 46 C. W. Kang, S. M. Lee, H. J. Kim, Y.-J. Ko and S. U. Son, *ACS Sustainable Chem. Eng.*, 2020, **8**, 13900–13907.
- 47 C. W. Kang, D. H. Lee, Y. J. Shin, J. Choi, Y.-J. Ko, S. M. Lee, H. J. Kim, K. C. Ko and S. U. Son, *J. Mater. Chem. A*, 2018, **6**, 17312–17317.
- 48 C. W. Kang, J. Choi, J. H. Ko, S.-K. Kim, Y.-J. Ko, S. M. Lee, H. J. Kim, J. P. Kim and S. U. Son, *J. Mater. Chem. A*, 2017, **5**, 5696–5700.
- 49 K. Cho, J. Yoo, H.-W. Noh, S. M. Lee, H. J. Kim, Y.-J. Ko, H.-Y. Jang and S. U. Son, *J. Mater. Chem. A*, 2017, **5**, 8922–8926.
- 50 S. Y. Park, C. W. Kang, S. M. Lee, H. J. Kim, Y.-J. Ko, J. Choi and S. U. Son, *Chem.–Eur. J.*, 2020, **26**, 12343–12348.
- 51 S. K. Chae, K. Cho, S. M. Lee, H. J. Kim, Y.-J. Ko and S. U. Son, *Polym. Chem.*, 2020, **11**, 789–794.
- 52 J. Choi, E. S. Kim, J. H. Ko, S. M. Lee, H. J. Kim, Y.-J. Ko and S. U. Son, *Chem. Commun.*, 2017, **53**, 8778–8781.
- 53 J. H. Ko, S. M. Lee, H. J. Kim, Y.-J. Ko and S. U. Son, *ACS Macro Lett.*, 2018, **7**, 1353–1358.
- 54 J. Lee, J. Choi, D. Kang, Y. Myung, S. M. Lee, H. J. Kim, Y.-J. Ko, S.-K. Kim and S. U. Son, *ACS Sustainable Chem. Eng.*, 2018, **6**, 3525–3532.
- 55 J. Jin, B. Kim, M. Kim, N. Park, S. Kang, S. M. Lee, H. J. Kim and S. U. Son, *Nanoscale*, 2015, **7**, 11280–11285.
- 56 S. Y. Kang, C. W. Kang, D. W. Kim, Y. Myung, J. Choi, S. M. Lee, H. J. Kim, Y.-J. Ko and S. U. Son, *Chem.–Asian J.*, 2019, **14**, 3173–3180.
- 57 S. Hong, J. Yoo, N. Park, S. M. Lee, J.-G. Park, J. H. Park and S. U. Son, *Chem. Commun.*, 2015, **51**, 17724–17727.
- 58 N. Kang, J. H. Park, J. Choi, J. Jin, J. Chun, I. G. Jung, J. Jeong, J.-G. Park, S. M. Lee, H. J. Kim and S. U. Son, *Angew. Chem., Int. Ed.*, 2012, **51**, 6626–6630.
- 59 J. Y. Jang, H. T. T. Duong, S. M. Lee, H. J. Kim, Y.-J. Ko, J. H. Jeong, D. S. Lee, T. Thambi and S. U. Son, *Chem. Commun.*, 2018, **54**, 3652–3655.
- 60 D. W. Kim, D. H. Kim, J. Y. Jang, Y.-J. Ko, S. M. Lee, H. J. Kim, K. Na and S. U. Son, *J. Mater. Chem. B*, 2019, **7**, 4118–4123.
- 61 D. W. Kim, T. M. D. Le, S. M. Lee, H. J. Kim, Y.-J. Ko, J. H. Jeong, T. Thambi, D. S. Lee and S. U. Son, *ChemNanoMat*, 2020, **6**, 1104–1110.
- 62 D. H. Kim, D. W. Kim, J. Y. Jang, N. Lee, Y.-J. Ko, S. M. Lee, H. J. Kim, K. Na and S. U. Son, *ACS Appl. Mater. Interfaces*, 2020, **12**, 37628–37636.
- 63 N. Park, Y. N. Lim, S. Y. Kang, S. M. Lee, H. J. Kim, Y.-J. Ko, B. Y. Lee, H.-Y. Jang and S. U. Son, *ACS Macro Lett.*, 2016, **5**, 1322–1326.
- 64 S. Y. Kang, Y. N. Lim, Y.-J. Cheong, S. M. Lee, H. J. Kim, Y.-J. Ko, B. Y. Lee, H.-Y. Jang and S. U. Son, *Ind. Eng. Chem. Res.*, 2017, **56**, 10235–10241.
- 65 S. I. Park, C. W. Kang, S. Y. Cho, S. M. Lee, H. J. Kim, Y.-J. Ko, J. Choi and S. U. Son, *Langmuir*, 2020, **36**, 8745–8752.
- 66 C. W. Kang, J. Choi, Y.-J. Ko, S. M. Lee, H. J. Kim, J. P. Kim and S. U. Son, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36936–36943.
- 67 Y. Liu, J. Goebel and Y. Yin, *Chem. Soc. Rev.*, 2013, **42**, 2610–2653.
- 68 W. Stöber, A. Fink and E. J. Bohn, *Colloid Interface Sci.*, 1968, **26**, 62–69.
- 69 R. Huisgen, *Proc. Chem. Soc.*, 1961, 357–396.
- 70 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
- 71 M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2953–3015; P. L. Golas and K. Matyjaszewski, *Chem. Soc. Rev.*, 2010, **39**, 1338–1354.
- 72 L. He, L. Li, S. Zhang, S. Xing, T. Wang, G. Li, X. Wu, Z. Su and C. Wang, *CrystEngComm*, 2014, **16**, 6534–6537.
- 73 Y.-P. Guo, T. Long, Z.-F. Song and Z.-A. Zhu, *J. Biomed. Mater. Res., Part B*, 2014, **102**, 583–591.
- 74 A. Heuer-Jungemann, N. Feliu, I. Bakaimi, M. Hamaly, A. Alkilany, I. Chakraborty, A. Masood, M. F. Casula, A. Kostopoulou, E. Oh, K. Susumu, M. H. Stewart,

- I. L. Medintz, E. Stratakis, W. J. Parak and A. G. Kanaras, *Chem. Rev.*, 2019, **119**, 4819–4880.
- 75 A. J. Savyasachi, O. Kotova, S. Shanmugaraju, S. J. Bradberry, G. M. Ó'Máille and T. Gunnlaugsson, *Chem*, 2017, **3**, 764–811.
- 76 T. Cao, T. Pham, H. S. Kim and K. B. Yoon, *Science*, 2011, **334**, 1533–1538.
- 77 G. Prieto, H. Tüysüz, N. Duyckaerts, J. Knossalla, G.-H. Wang and F. Schüth, *Chem. Rev.*, 2016, **116**, 14056–14119.
- 78 M. Kalaj and S. M. Cohen, *ACS Cent. Sci.*, 2020, **6**, 1046–1057.
- 79 J. Urrutia and J. M. Asua, *Ind. Eng. Chem. Res.*, 2021, **60**, 10502–10510.
- 80 M. N. Cardoso and A. G. Fisch, *Ind. Eng. Chem. Res.*, 2016, **55**, 9426–9432.
- 81 C. Bianchini and A. Meli, *Coord. Chem. Rev.*, 2002, **225**, 35–66.
- 82 C. Bianchini, A. Meli and W. Oberhauser, *Dalton Trans.*, 2003, 2627–2635.
- 83 H. Liu, C. Cao, J. Huang, Z. Chen, G. Chen and Y. Lai, *Nanoscale*, 2020, **12**, 437–453.
- 84 C. Liu, P.-C. Hsu, H.-W. Lee, M. Ye, G. Zheng, N. Liu, W. Li and Y. Cui, *Nat. Commun.*, 2015, **6**, 6205.