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Mesoporous Architectures with Highly Crystallized Frameworks

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Porous materials have played an increasingly critical role in materials sciences and chemistry. From the viewpoint of applications, highly crystallized mesoporous architectures are very promising mainly due to their unique properties arising from the crystallized frameworks and many exciting applications in diverse fields. In this Highlight article, we summarize recent innovative researches in the creation of mesoporous architectures possessing crystalline pore walls. In particular, new strategies to synthesize highly crystallized mesoporous metals and metal oxides, metal–organic frameworks with large-sized mesopores, and zeolites with hierarchical mesoporosity are described. These mesoporous architectures show a lot of promise in energy and environment-related areas.

1. Introduction

Mesoporous architectures are of especial importance in both scientific and technological aspects because of their high surface area and large pore volume, as well as their abilities to accommodate and interact with nanoobjects (*i.e.*, ions, molecules, polymers, and clusters).[1-5] Progress in mesoporous silica materials is moving in a rapid pace covering several research topics including synthesis,[6] structural characterization,[7] morphological control,[8] and alignment control of mesochannels.[9] In addition, diversification of framework compositions has been made by incorporation of organic units and other metal atoms into the silica frameworks.[10,11] These silica-based mesoporous materials can be utilized not only for the conventional applications of porous materials such adsorption and catalysis but also for promising areas, for instance, chemical sensing, electronics, CO_2 capture, and drug delivery.[12,13] Along this avenue of research, the scope of mesoporous materials has been broadened to non-silica metal oxides, metals, carbons, organic polymers, zeolites, and metal–organic frameworks with promising properties and applications beyond the applicable windows of mesoporous silicas.[14-19]

In this article, we highlight recent progress in syntheses of mesoporous architectures with crystalline pore walls. The contents are organized based on the types of materials into three categories, that is, i) metals and metal oxides, ii) metal-organic frameworks, and iii) zeolites. In particular, we focus on ordered mesoporous metals and metal oxides, metal organic frameworks having large-sized pores, and zeolites with hierarchical porosity. The porous materials presented here are not limited to those with ordered mesostructures because the materials with irregularly porous structures can have uniform and narrow pore size distributions, and therefore are also useful in many applications where the structural order is of not critical importance. Introduction of mesopores into the materials with dense frameworks (*e.g.*, metals and metals oxides) can provide higher accessible and active surface areas, and thereby enhanced performances. For the materials with microporous frameworks such as zeolites and metal-organic frameworks, the solely presence of micropores in their frameworks often retards molecular diffusion. Introduction of mesopores into zeolites and metal-organic frameworks can resolve such molecular transport problems by enhancing micropore accessibility through the bypass-interconnected mesopores. These crystallized mesoporous architectures prove to be very useful in several applications in energy and environment-related areas.

2. Porous metals and metal oxides

Mesoporous metals and metal oxides are traditionally prepared by two distinguishable methods: hard- and soft-template.[15] The former technique comprises three main steps: i) infiltration of appropriate precursors into sacrificial hard templates, commonly mesoporous silica or carbon, ii) conversion of the precursors into the target materials, and iii) removal of the original templates. Although this hard-template technique is very useful and can be applied to various classes of materials, it is slightly intricate and has been thought to be unfavorable for large scale productions.[20] In the latter approach, lyotropic liquid crystals (LLCs) of surfactants act as direct, soft-templates. Formation of the target materials occurs by condensation or reduction of precursors embedded in the confined LLC spaces.[21] The soft-template method has several privileges over the hard-template; for example, it offers an efficient way for the microfabrication of mesoporous metals and metal oxides via the solvent-evaporation process.

Recently, Yamauchi *et al.* have demonstrated the formation of dendritic nanostructures of platinum and its hybrids exhibiting excellent performances in electrocatalysis for methanol oxidation reactions from very dilute micellar solutions.[22] The concentration of surfactants or template molecules is above a critical micelle concentration but below the point required for the formation of micellar cubic (I_1) LLC phase. They have further proposed the concept of "micelle assembly" as a novel route to fabricate mesoporous metal films by a simple electrodeposition technique.[23] These metallic mesoporous nanostructures were created with the assistance of micelle assembly in a dilute surfactant electrolyte. Significant progress has been made by integrating this novel procedure with the state-of-the-art layer-by-layer (LbL) approach to nanofabricate multilayer hybrid films consisting of alternated mesoporous platinum and palladium nanostructures (see Fig. 1).[24] Electrocatalytic activities of the resulting LbL films were substantially enhanced due to the synergistic effect of the high surface area and more accessible Pt−Pd heterointerfaces.

Research on mesoporous crystalline metal oxides have mainly been emphasized on aluminum oxide (alumina) and titanium oxide (titania).[25,26] A major problem in synthesis of such mesoporous crystalline oxides is the collapse of mesoporous structures, yielding materials with lower surface area and porosity, after crystallization of metal oxides by thermal treatment as the transformation of amorphous into crystallized frameworks generally causes a reduction in framework density and subsequently a shrinkage of mesopore walls.[14] One interesting way to overcome this challenge is the reinforcement of mesoporous structures by silicate-based species.[27] First, the mesoporous oxides with amorphous walls were synthesize by the conventional surfactant-directed sol−gel method. Before calcination at high temperature needing for crystallization of oxides, the amorphous walls were strengthened by coating with silicate species. The crystallization was performed by thermal treatment, followed by removal of the strengthening layers by treatment in alkali or hydrofluoric solutions, resulting the mesoporous crystalline metal oxides.

Alternative to the above approach, the mesostructures can be stabilized during thermal crystallization of metal oxides by using highly thermally stable block copolymers containing polymer chains with sp^2-hybridized carbon moieties as soft-templates.[28] Before the transformation of amorphous precursors to crystalline metal oxides, the sp^2-hybridized carbon-containing polymer chains were carbonizied into amorphous carbon and accordingly could stabilize the mesostructures at higher temperatures where the crystallization of oxides takes place. This reinforced, amorphous carbon was subsequently removed by thermal oxidation (calcination) at even higher temperature. This approach has been proved to be effective for several metal oxides, including alumina,[28d] titania,[28a,c] and niobia,[28a] and mesoporous aluminum organophosphonates.[28b]

Another method to achieve mesoporous metal oxides with crystallized walls is to decrease the crystallization temperatures. This can happen by addition of metal oxide nanocrystals into the precursors. Bein and his colleagues have introduced a novel "brick and mortar" (Fig. 2) approach to synthesize mesoporous titania films as photocatalysts for NO oxidation and anodes in dye-sensitized solar cells.[29a] As shown in Fig. 2, in this approach, the preformed nanocrystalline titanias acting as bricks were assembled with the assistance of surfactant and then fused by the amorphous sol–gel titania as mortars. Upon calcination, the nanocrystalline bricks acting as seeds were further grown with the nutrients supplied from the amorphous mortars. Due to the presence of nanocrystalline seeds, the crystallization of metal oxides could be realized at lower temperature. The concept has been expanded to the fabrication of mesoporous titania–silica composite films[29b] and crack-free, thick films of mesoporous titania prepared by sequential deposition.[29c] Related approaches whereby the preformed oxide nanocrystals are assembled in the presence of surfactants were also applied to synthesize mesoporous materials of several oxides such as alumina and ceria.[30]

3. Metal–organic frameworks possessing large pore cavities

As a relatively new class of nanoporous materials, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have been expected to play important roles in several applications in which other nanoporous materials are not appropriate or do not provide satisfactory performances mainly because of their riches of synthetic chemistry with modular structures and functions.[31] Most MOFs reported to date are essentially microporous materials.[19] Construction of MOFs into the cage-type framework can generally result the structure with large pore cavities. Férey *et al.* reported the synthesis of MOFs possessing the MTN zeotype architecture with cage cavities in mesoscale domains, namely MIL-100[32a] and MIL-101.[32b] For example, MIL-101 constructed from supertetrahedral units consists of two types of mesoporous cages having internal free diameters of ~29 Å and 34 Å. Although both MOFs possess cage cavities in mesoporous scales, their pore windows are still in the range of micropores.

A series of MOF-74 or CPO-27 structures with pore apertures ranging from 14 to 98 Å was recently reported by Yaghi and co-workers.[33] As shown in Fig. 3, based on the concept of reticular chemistry, the pore apertures were systematically expanded by isomorphous substitution of the original linker with one phenylene ring in MOF-74 by ligands having two, three, four, five, six, seven, nine, and eleven phenylene rings, affording the isoreticular series of MOF-74. In particular, IRMOF-74-XI built from ligands containing eleven phenylene rings possesses its crystallographic pore apertures of 85 × 98 Å^2. Inclusion of several proteins into these large pore apertures MOFs was successfully demonstrated; for instance, vitamin B_{12} (largest dimension of 27 Å), myoglobin (spherical dimensions of 21 × 35 × 44 Å^3), and GFP (diameter of 34 Å and length of 45 Å) were accommodated in IRMOF-74-IV, IRMOF-74-VII, and IRMOF-74-IX, respectively.

Introduction of functionalized mesopores into MOFs through direct coassembly of metal ions, primitive ligands, and ligand fragments during MOFs synthesis have recently been proposed (Fig. 4, lower panel).[34] In general, the functionalization of MOF interiors via either pre-incorporation of functional ligands during MOF synthesis or post-synthetic modification of ligands tethering reactive groups can spoil the porosity with a reduction in pore sizes (Fig. 4, upper panel).[35] On the contrary, the new coassembly strategy yielded MOFs having desired functionalities with increased porosity. More importantly, mesopores were created in the MOF interiors when the ligand fragments having polar or ionic functional groups

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were introduced, affording the MOFs with hierarchical micro- and mesoporosity.[34]

Prussian blue (PB, $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$) is the first synthetic microporous coordination polymer constructed from coordination bonds between Fe^{II}/Fe^{III} and cyanide brides. Combing the liquid crystal concept with the PB synthesis, liquid-crystal-templated mesostructured PB analogues were synthesized from alkyl pyrazinium surfactants, yielding lamellar, cubic, or hexagonal mesostructures depending on the length of alkyl chains and M^{II} ions.[36] Unfortunately, the surfactants occluded in the mesoporous cavities could not be removed and accordingly the mesopores could not be fully utilized.

Alternatively, Yamauchi *et al.* introduced mesopores into PB and it analogues by selective etching of PB mesocrystals in the presence of poly(vinylpyrrolidone).[37] The strategic key is to use PB mesocrystals as a starting material because the acidic etching solution can be allowed to diffuse into the core of mesocrystals through small pores (like defects) in the aggregated PB mesocrystals, yielding PB nanoparticles having internal hollow cavities without the retention of crystallinity on the shells. The resulting hollow PB nanoparticles possessing mesopores on the crystalline shells and large hollow cavities showed interesting magnetic properties and superior cesium ion adsorption performance. Very recently, through step-by-step crystal growth and subsequent etching processes, various types of PB nanoparticles with shell-in-shell, yolk-shell, and yolk-double-shell hollow structures were successfully realized.[38] It is noteworthy that PB (meso)crystals are potential precursors for synthesis of various mixed oxide mesoporous materials by simple thermal calcination.[39]

4. Zeolites with hierarchical porosity

Zeolites, microporous crystalline aluminosilicates having pores and channels at molecular dimensions, are one of the most important materials for chemical industries for ion exchange, adsorption, membrane separation, and catalysis. Nonetheless, the solely presence of micropores in zeolite frameworks often limits molecular diffusion, and therefore, restricts the ability of bulky molecules to pass through or react within zeolite pores. This molecular transport problem currently become more critical because zeolites have been expected to be used as efficient catalytic materials for biomass conversions and upgrades where many reactions involve bulky substrates. This problem can be resolved by shortening the effective diffusion path lengths of zeolite crystals. Among many promising solutions, the construction of zeolites with hierarchical micro- and mesoporosity has gained particular attention due to the unique integration of the intrinsic micropores originated from zeolite frameworks and the bypass-interconnected mesopores, thereby improving the molecular traffic within the zeolite bodies.[40]

There are several methods to prepare hierarchical zeolites such as top-down desilication by alkali post-synthetic modification and bottom-up directed assembly by hard or soft templates.[18] Alkali treatment can selectively extract silicon atoms from the zeolite framework with the preservation of framework crystallinity, in contrast to the acid treatment in which aluminum atoms are removed from the zeolite structures. By treating zeolite with dilute alkali solutions under mild conditions, first comprehensive reports from Ogura *et al.* showed that uniform-sized mesopores could be generated in MFI zeolite without deterioration of crystallinity.[41] This desilication technique has been further studied intensively by Pérez-Ramírez and his co-workers and accordingly is now applicable for many zeolite frameworks (*e.g.*, MFI, FAU, MOR, *BEA, AST, and FER) in a wide range of Si/Al molar ratios.[42]

Akin to mesoporous metals and metal oxides (*vide supra*), hierarchical zeolites can also be achieved by the confined synthesis in hard templates. The successful development in preparation of bulk colloidal crystals assembled from monodisperse silica nanospheres with tunable diameters synthesized in an emulsion system containing basic amino acids has led to the significant progress on synthesis of hierarchical zeolites by the hard-template route.[43] As depicted in Fig. 5, three-dimensionally ordered mesoporous-imprinted single-crystal zeolites and size tunable zeolite nanocrystals were realized by steam-assisted crystallization in hard templates and utilized in catalysis and fabrication of ultrathin zeolite membrane.[44] The library of mesoporous-imprinted zeolites was expanded to various zeolites including *BEA, LTA, FAU, and LTL by direct hydrothermal crystallization under optimized conditions.[45]

Alternatively, zeolites having uniform mesopores can be achieved by the introduction of organic soft templates as mesopore-generating agents (mesoporogens) into typical zeolite synthesis solutions, which is currently the most fascinating way toward the single-step fabrication of hierarchical zeolites. This concept was innovated by the research group of R. Ryoo.[46] Silylated amphiphilic molecules were designed by combining hydrophilic zeolite structure-directing groups with hydrophobic alkyl chains (see Fig. 6; molecule **1**) to create hierarchical zeolites with tunable and uniform mesopososity.[47] Further modification of such bifunctional mesoporogens by fusing hydrophobic alkyl chains with zeolite stucture-directing groups (molecule **2** in Fig. 6) led to the formation of hierarchically assembled zeolite nanosheets, affording mesoporous zeolites with house-of-card-like structures.[48] Interestingly, the catalytic performance of these hierarchical nanosheets was reported to be promising for several industrial reactions such as cracking, methanol-to-gasoline conversion, and biomass conversion because thin crystalline zeolite layers with specific crystalline faces facilitate catalytic processes at exteriors or pore mouths, offering crystalline-face-dependent catalysis.[49]

The most significant innovation in synthesis of hierarchical zeolites by organic soft templates has been made by design of a series of Gemini-type multiammonium surfactants (*e.g.*, molecule **3** in Fig. 6). Molecule **3** can direct the formation the hexagonally ordered mesoporous zeolites. The mesopore walls of the resulting material consisted of the “truly” crystalline microporous zeolitic framework, while the hexagonally ordered mesopores resembled those of highly ordered mesoporous silicas.[50]

Recently, self-pillared zeolite nanosheets possessing hierarchical micro- and mesoporosity achieved by using a simple tetrabutylphosphonium cation as a zeolite organic structure-directing agent (SDA) have been reported by Tsapatsis and his colleagues.[51] Repetitive branching during crystal growth led to hierarchical zeolites made of orthogonally connected nanosheets with house-of-cards arrangement. However, the use of a phosphonium-based molecule may affect the physicochemical properties of the obtained zeolites because a certain amount of phosphorus debris species can sometimes remain in the zeolites after conventional thermal calcination. In addition, phosphonium-based SDAs can create greater industrial and environmental burdens than conventional ammonium-based SDAs because of their toxicity and hazardousness.

The mesoporogen-free approach was therefore extended to ammonium-based SDAs. Hierarchically organized MFI zeolites having three classes of porosity in one structure (*i.e.*, intrinsic microporosity originated from the zeolite framework, mesoporosity created within the zeolite plates, and macroporosity stemming from the complex intergrown structure) were achieved by sequential intergrowth using a simple, non-mesoporogen, SDA (Fig. 7).[52] The use of an appropriate SDA that is imperfectly fitted to the zeolite framework, yet can direct its formation, under optimized synthesis conditions being able to form plate-like zeolites with enhanced intergrowths was suggested to be a key component to realize such complex and unusual, hierarchical structure.

5. Summary and prospect

The continuing research and development of mesoporous materials possessing crystallized pore walls can provide promising platforms having nanospace in mesoscale domains for several potential applications that other nanoporous materials are not appropriate or do not provide satisfactory performances. As summarized in this highlight article, the scope of mesoporous materials has been broadened beyond mesoporous silica to several crystalline materials. Significant efforts have been made to realize mesoporous metals, metal oxides, metal–organic frameworks, and zeolites. Traditionally, there are two major distinguished approaches to synthesize mesoporous materials having the aforementioned crystalline frameworks, that is, hard- and soft-template methods. Learning from the progress in these two methods, non-template approaches have been demonstrated to achieve such mesoporous crystalline materials. Innovative strategies highlighted here include fabrication of metallic mesoporous films by micelle assembly, synthesis of MOF hollow nanoparticles with mesocavities by selective etching, and mesoporogen-free, one-pot synthesis of hierarchical zeolites by controlling crystal intergrowth.

However, there are still a number of subjects needed to be explored for eventual applications of these materials. Attempts should be donated to fabricate mesoporous metal alloys and bi- or tri-metallic nanostructures with pronounced heterointerfaces for enhancing activities in electrocatalytic alcohol oxidation and oxygen reduction, which are main reactions in direct alcohol fuel cells. The library of mesoporous metal oxides should be more extended because several transition metal oxides and hydroxides exhibit excellent performance as pseudo-capacitance electrodes and acid catalysts. In addition, mesoporous metal oxides having basic sites are increasingly interested for CO_2 capture from dilute gas stream and base-catalyzed conversions of biomass.

Although as described above some interesting methods to introduce mesopores into MOF structures have been demonstrated, such techniques could not likely be applicable for every MOF. There is remaining need to develop more general ways to construct mesoscopic architectures of MOFs. In addition, unique applications of mesoporous MOFs such as magnetoelectronics and optoelectronics are rare and needed to be realized. Since hierarchical zeolites have been expected to be utilized with improved performance in petrochemical and biomass processes, construction of hierarchical architectures of zeolites other than the most studied MFI and *BEA frameworks is needed, particularly by a low-cost and scalable process.

Although not emphasize in this article, there are other interesting and useful mesoporous materials with crystallized walls that should also be paid attention such as aluminum organophosphonates.[28b,53,54] The readers, who are interested in this type of non-siliceous materials, are recommended to learn from the recent comprehensive reviews.[53] Last but not least, it is clearly demonstrated that mesoporous crystalline materials are of scientific and technological importance. We truly believe that innovative research on synthesis and application, particularly in the fields of energy and environment, of such materials, highlighted here as examples, will cast new light on the rational developments for eventual applications in practical scales.

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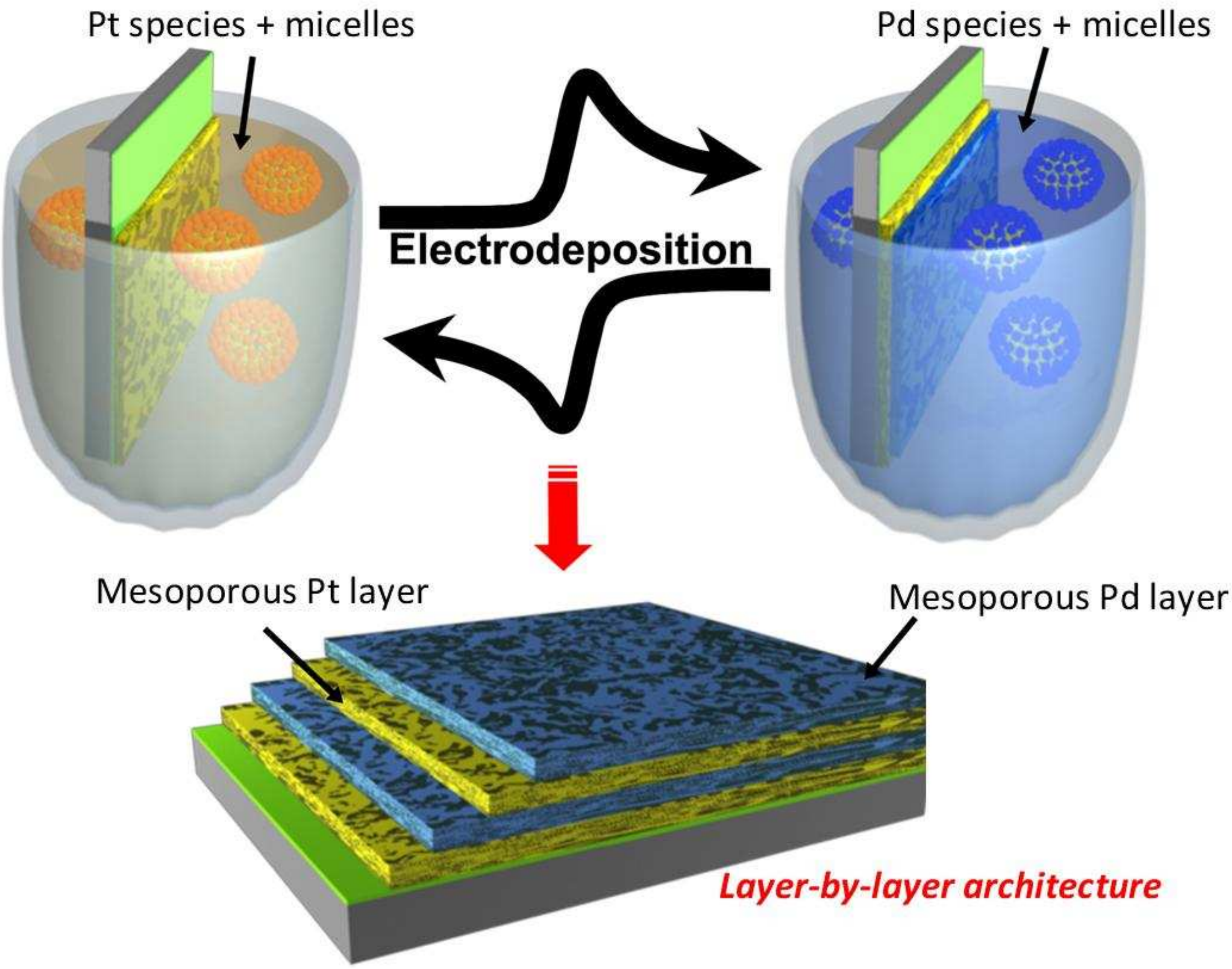

Fig. 1 Fabrication of multilayer films of alternated mesoporous Pt/Pd for electrocatalysis application.

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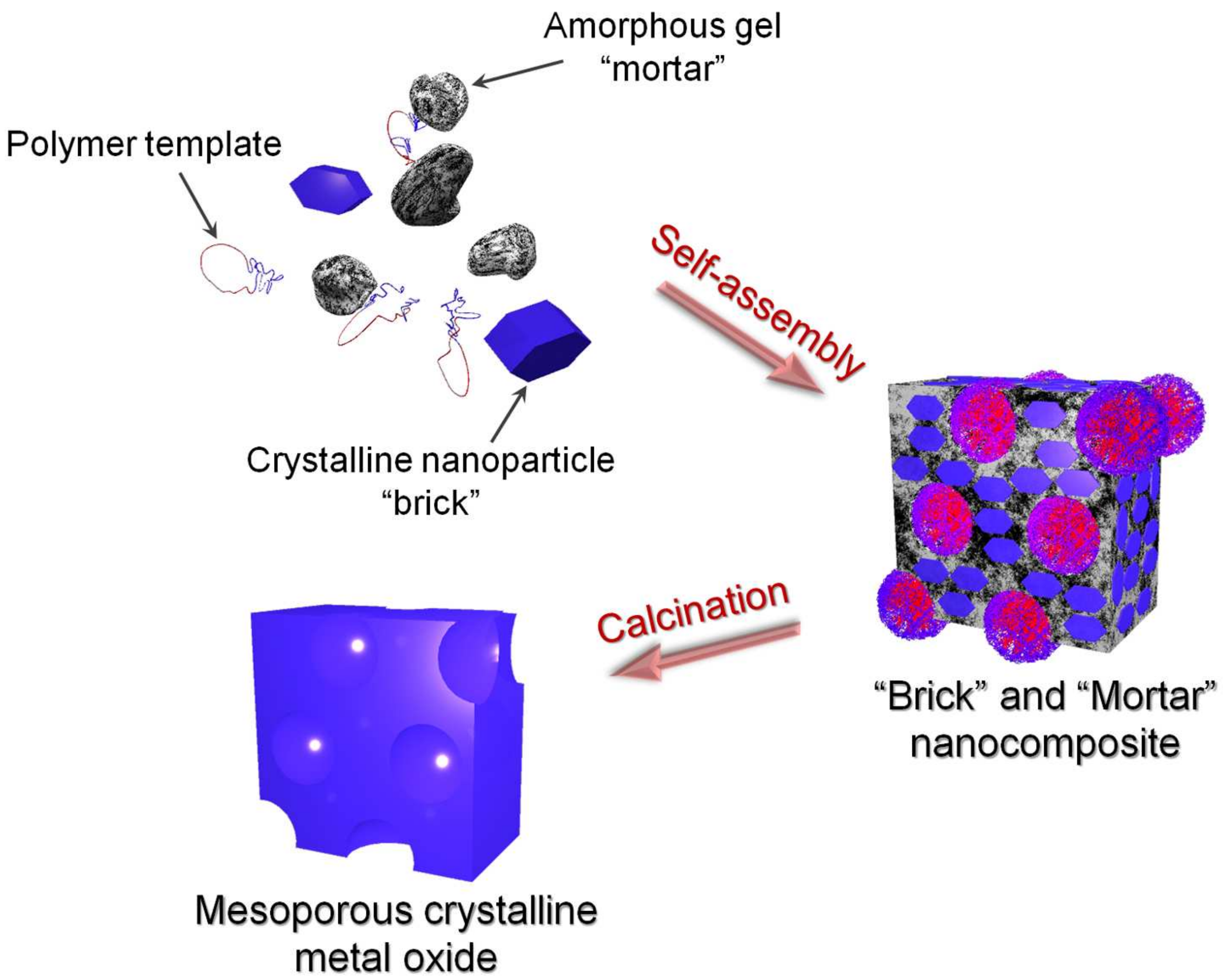

Fig. 2 Strategy for the preparation of mesoporous crystalline metal oxides through a "brick" and "mortar" approach.

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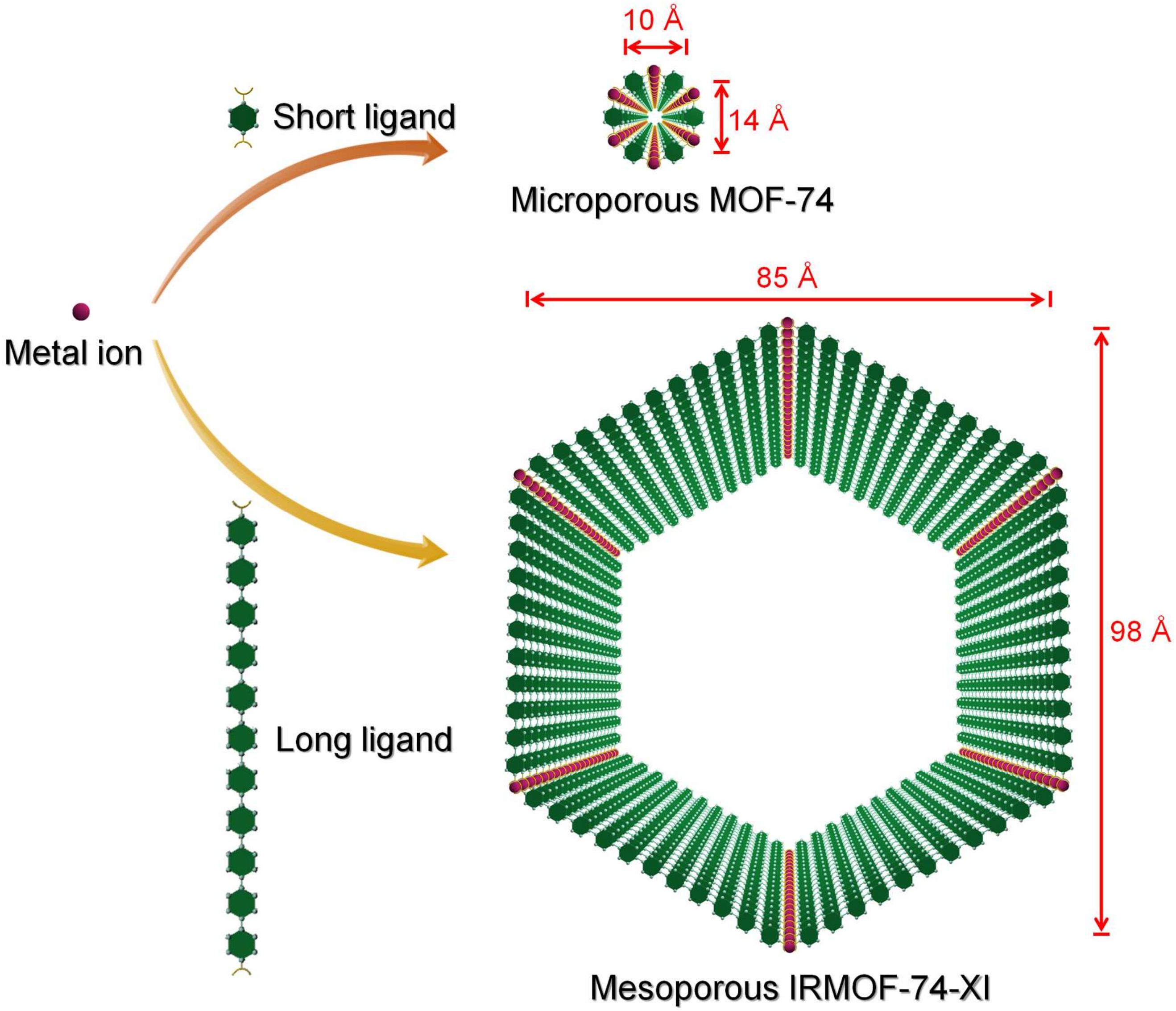

Fig. 3 Synthetic schemes for microporous MOF-74 *versus* mesoporous IRMOF-74-XI.

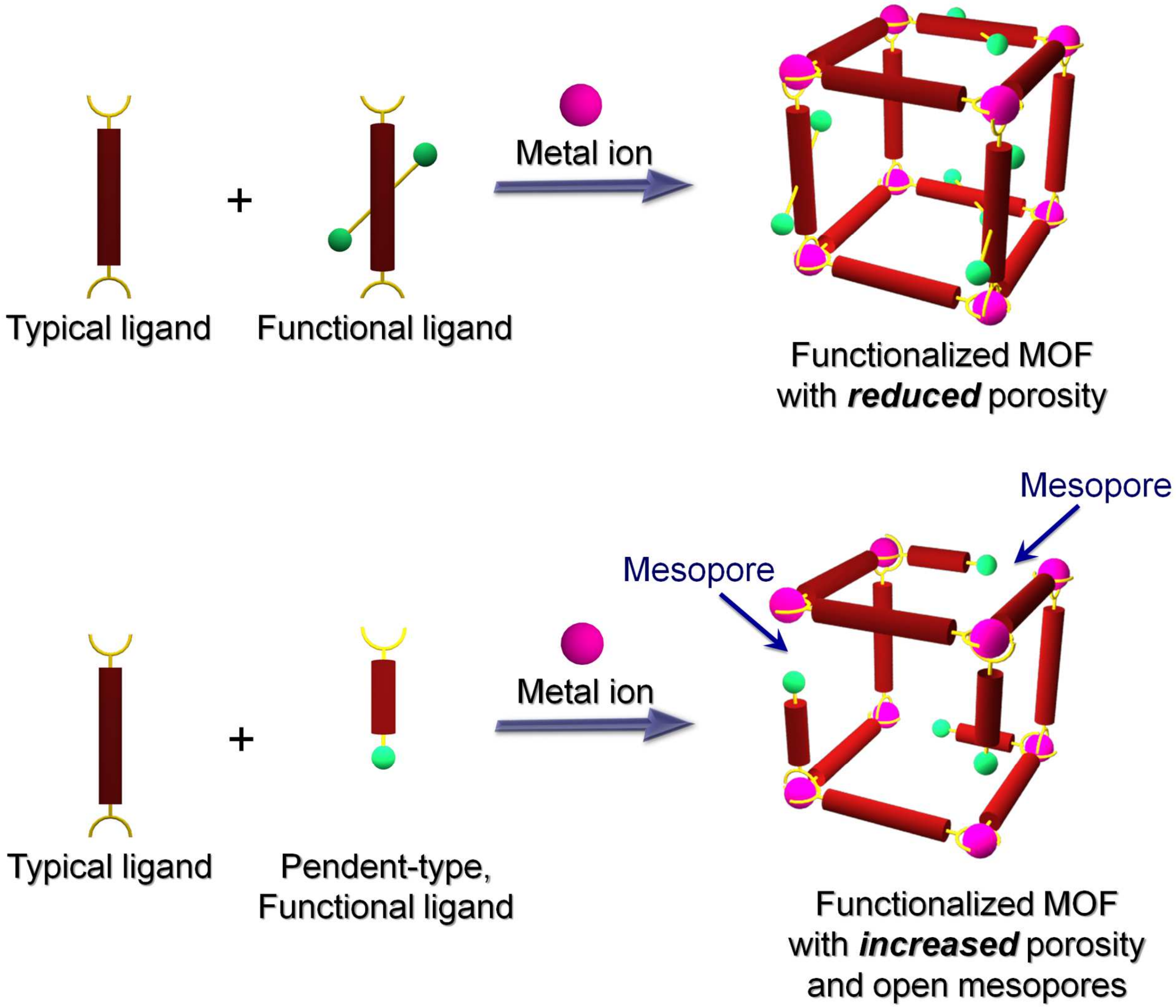

Fig. 4 MOF having functionalized mesopores through coassembly of metal, ligand, and ligand fragment.

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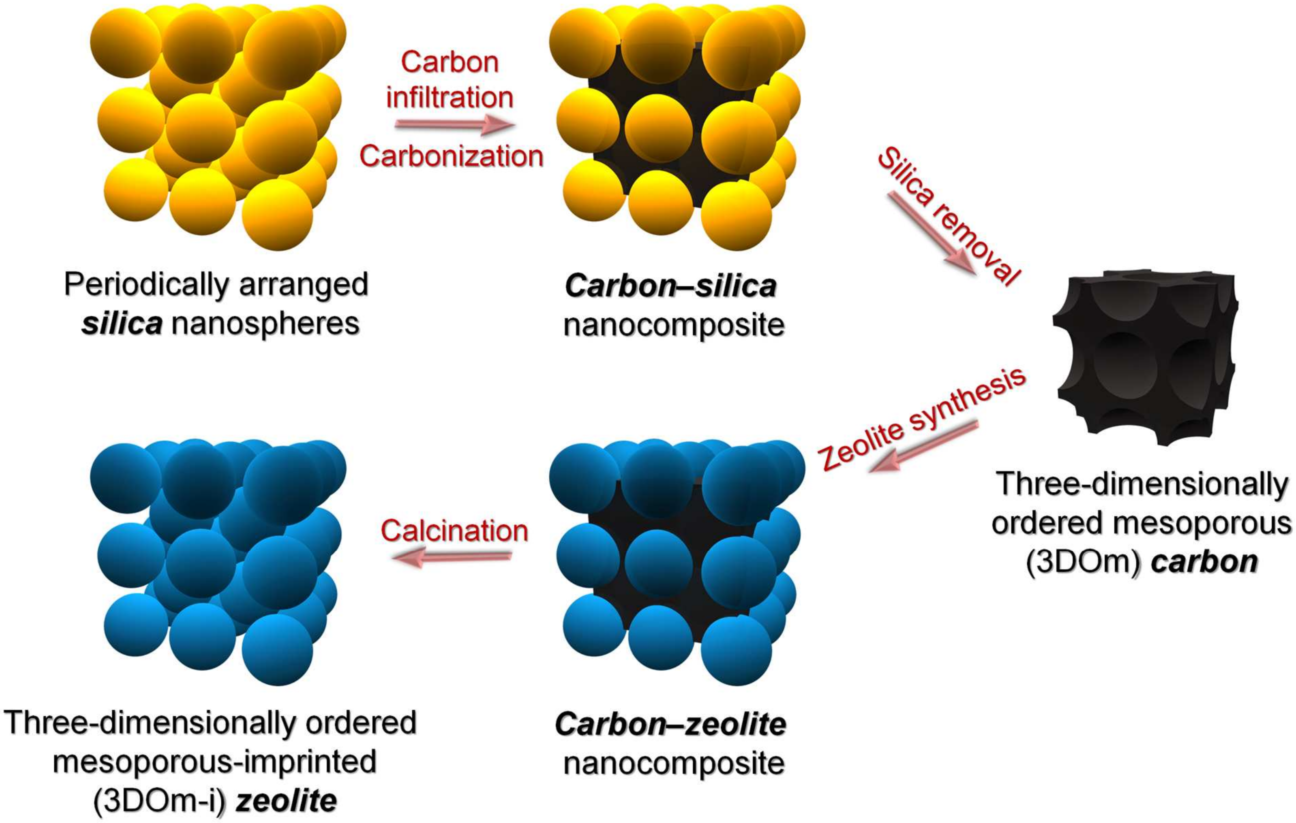

Fig. 5 Schematic of the formation of 3DOm-i zeolite confined in the mesopore space of 3DOm carbon.

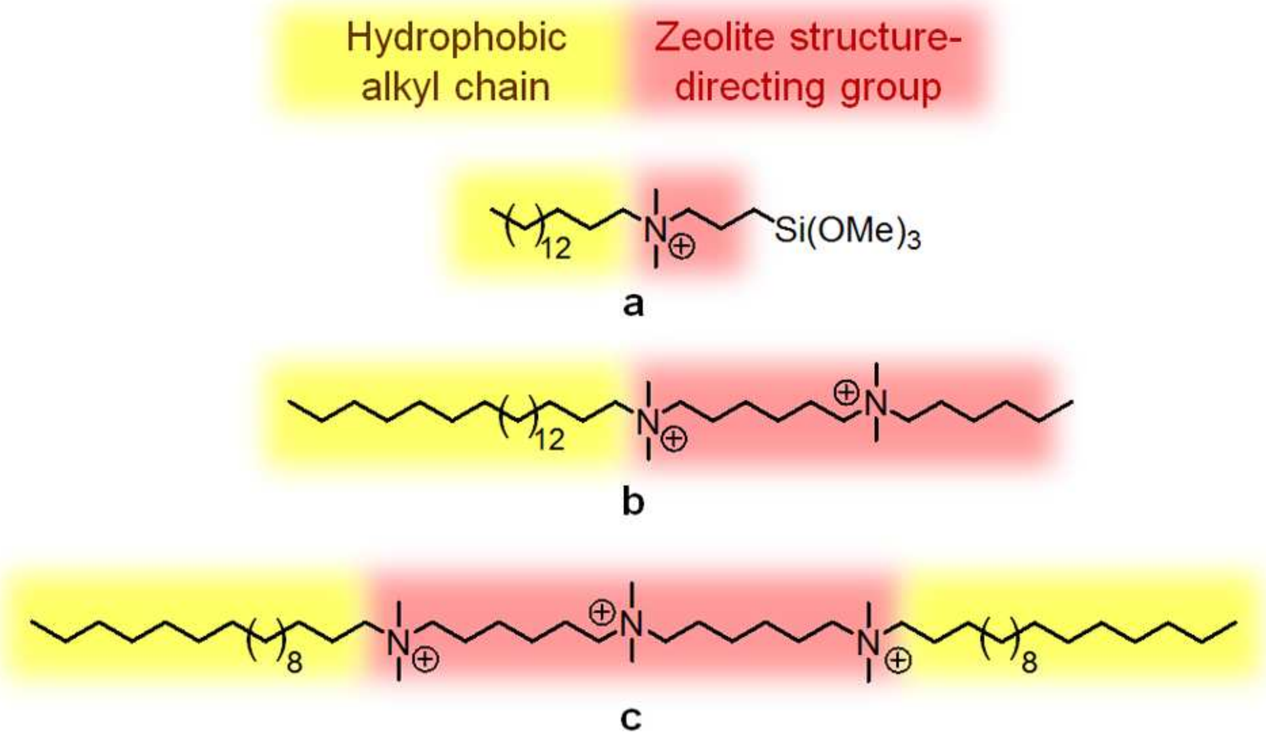

Fig. 6 Examples of bifunctional amphiphilic mesopore-generating agents consisting of long hydrophobic alkyl chain and hydrophilic zeolite structure-directing group developed in the R. Ryoo lab.

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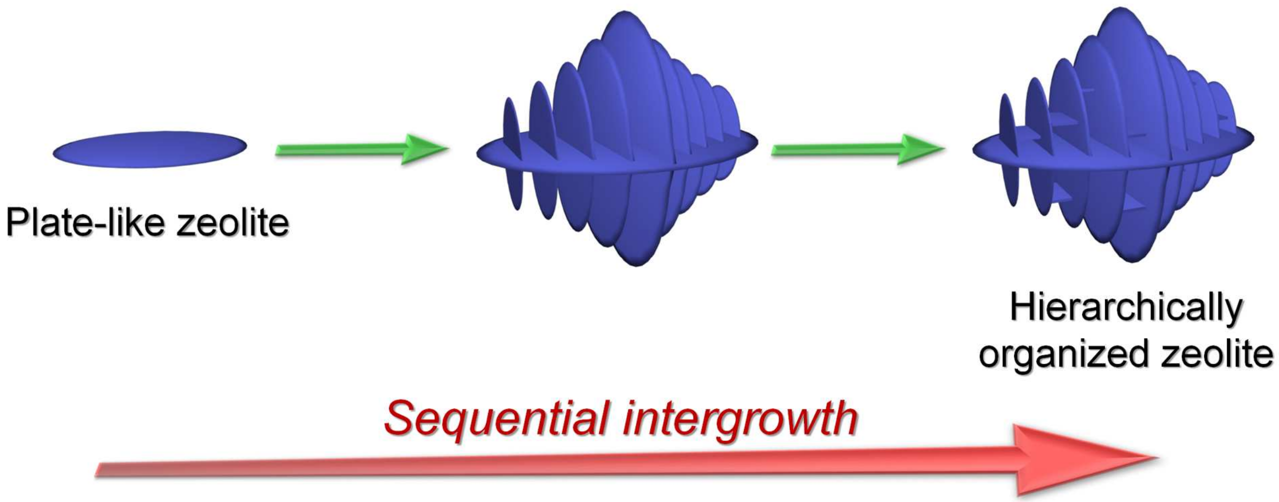

Fig. 7 Formation scheme for the formation of hierarchically organized zeolite by sequential intergrowth.

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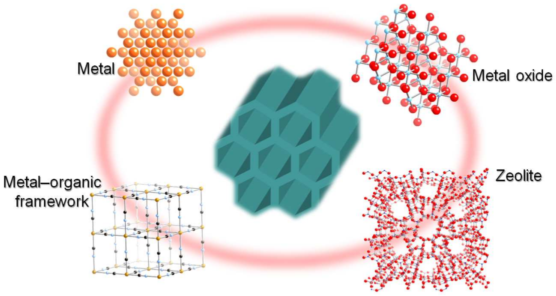
TOC graphic



5 In this highlight article, we summarize the current research trends in synthesis of mesoporous materials possessing crystallized pore wall. In particular, the innovative methods toward mesoporous metal, mesoporous metal oxide, metal–organic framework, and zeolite are highlighted.