New Insight into the Synthesis of Large-Pore Ordered Mesoporous Materials

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ABSTRACT: Ordered mesoporous materials (OMMs) have received increasing interest due to their uniform pore size, high surface area, various compositions and wide applications in energy conversion and storage, biomedicine and environmental remediation, etc. The soft templating synthesis using surfactants or amphiphilic block copolymers is the most efficient method to produce OMMs with tailorable pore structure and surface property. However, due to the limited choice of commercially available soft templates, the common OMMs usually show small pore size and amorphous (or semicrystalline) frameworks. Tailor-made amphiphilic block copolymers with controllable molecular weights and compositions have recently emerged as alternative soft templates for synthesis of new OMMs with many unique features including adjustable mesostructures and framework compositions, ultralarge pores, thick pore walls, high thermal stability and crystalline frameworks. In this Perspective, recent progresses and some new insights into the coassembly process about the synthesis of OMMs based on these tailor-made copolymers as templates are summarized, and typical newly developed synthesis methods and strategies are discussed in depth, including solvent evaporation induced aggregation, ligand-assisted coassembly, solvent evaporation induced micelle fusion-aggregation assembly, homopolymer assisted pore expanding and carbon-supported crystallization strategy. Then, the applications of the obtained large-pore OMMs in catalysis, sensor, energy conversion and storage, and biomedicine by loading large-size guest molecules (e.g., protein and RNA), precious metal nanoparticles and quantum dots, are discussed. At last, the outlook on the prospects and challenges of future research about the synthesis of large-pore OMMs by using tailor-made amphiphilic block copolymers are included.

1. INTRODUCTION

Ordered mesoporous materials (OMMs) are an important kind of functional materials which possess regularly porous structure,

uniform pore size ranging from 2.0 to 50 nm, high surface area and diverse compositions such as silica, carbon, metals, and metal oxides.[1−9] OMMs were initially investigated to develop high-performance catalysts for heavy petroleum oil conversion due to their large pore channels, which was considered to be more suitable for mass transport than the commonly used microporous zeolites with a pore size less than 2.0 nm. Later on, OMMs have attracted intensive interest in various areas such as energy conversion and storage, environment remediation, and biomedical science due to their unique physicochemical properties.[8−20]

The most efficient approach to synthesize OMMs is the soft-templating approach using amphiphilic molecules (i.e., surfactants or amphiphilic block copolymers) as a template which can coassemble with organic (or inorganic) framework precursors.[21] Due to the unique hydrophobic interaction, the amphiphilic molecules can easily self-assemble into spherical or cylindrical micelles with hydrophobic core and hydrophilic shell in polar solvent (such as water, ethanol) at elevated concentration or temperature. These micelles can further assemble into thermo-dynamically stable ordered liquid crystalline phases with long-range mesostructure ordering. In the presence of framework precursors, these amphiphilic molecules can coassemble with organic (or inorganic) precursors to form hybrid composites ordered mesostructure. After cosolidification and selectively removing the template molecules, ordered mesoporous materials are obtained.

In the past 20 years, commercially available soft templates including surfactants (e.g., cetyltrimethylammonium bromide, CTAB) and amphiphilic block copolymers (e.g., poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide), PEO-b-PPO-b-PEO, such as Pluronic P123 and F127) have been intensively used to synthesize OMMs with variable morphologies. However, due to the limited choice of commercially available soft templates, the obtained OMMs usually show small pore sizes (<10 nm). It hampers their applications in many fields which require a fast mass transport and efficient loading of

large-size guest molecules (e.g., RNA, gene, and dye) and nanoparticles (e.g., noble metal nanoparticles).[22,23] In addition, ordered mesoporous metal oxides templated from these amphiphilic molecules usually exhibit amorphous or semicrystalline frameworks with a low thermal stability and poor electro-/photo- properties.[5] Consequently, various amphiphilic block copolymers with large molecular weights and special compositions have recently been explored, which now become an important supplementary kind of soft templates for OMMs with unique framework compositions and functionalities. These block copolymers can easily be synthesized via the well-established living polymerization methods such as atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer polymerization (RAFT). Even researchers who are not be familiar with polymers can prepare these block copolymers via these polymerization methods. However, most of them are not widely applied in both fundamental research and industry and have not been commercialized yet. Some of them are commercially available in only pretty small batches and are expensive, which makes it difficult to explore widely their applications in designed synthesis of OMMs. In principle, these block copolymers can be controllably synthesized in the lab in terms of the molecular weight, segment sequence and composition. To distinguish these polymers with commercially available Pluronic block copolymers, they are denoted tailor-made block copolymers in this Perspective.

Until now, various PEO-based block copolymers, including PEO-*b*-polystyrene (PS), poly(methyl methacrylate) (PMMA), polyisobutylene (PIB) and poly(ethylene-*co*-butylene) (KLE), and poly(vinylpyridine)-based copolymers, such as poly(2-vinylpyridine)-*b*-polystyrene (P2VP-*b*-PS), were designed as templates to synthesize OMMs, and the relevant reports have recently been comprehensively reviewed.[16,21,22] Among these tailor-made block copolymers, PEO-*b*-PS (or PMMA) copolymers are representative ones and frequently studied because they can be conveniently synthesized. Their molecular weight can be easily controlled via the living radical polymerization process. Therefore, PEO-*b*-PS (or PMMA) block copolymers have intensively been used as a soft template for the controllable synthesis of OMMs with unique functionality. Due to the strong interactions (i.e., hydrogen bonding) between PEO segments and inorganic (or organic) precursors, the cross-linking and sol−gel process of the inorganic (or organic) oligomers usually occurs in the region of hydrophilic segments of block copolymers. By virtue of the rich phase behavior of these amphiphilic block copolymers, hybrid composites with variable mesostructures and different framework compositions can be obtained, which can be further converted into ordered mesoporous materials after selective removal of the block copolymer templates. The phase behavior of block copolymers changes with their compositions and molecular weight and other conditions (temperature, pH, additives); therefore, their coassembly with framework precursors needs to be further elaborated to realize controllable synthesis of OMMs. Moreover, the applications of the unique OMMs templated by these tailor-made block copolymers are yet to be further explored. In this Perspective, we discuss the synthesis and application of OMMs templated by the PEO-based block copolymers with a strong hydrophobic/hydrophilic contrast to elucidate the new synthesis methodology and principle, strategy for controlling the pore size and crystallization process of pore walls, and the applications of the resultant OMMs.

In this Perspective, we first demonstrate the unique properties of PEO-*b*-PS (or PMMA) such as strong hydrophobic/hydrophilic contrast, high glass transition temperature, and high content of sp^2 hybrid carbon atoms in contrast with the most frequently used commercial Pluronic block copolymers. Due to these differences, we then introduce some main progresses on the synthesis of OMMs using PEO-*b*-PS (or PMMA) as a template, including new synthesis methods such as evaporation induced aggregating assembly, the pore expansion method based homopolymer as a pore expander, and carbon-supported pore wall crystallization method for mesoporous metal oxides (TiO_2, WO_3, Nd_2O_5) with highly crystalline frameworks and large surface area. Because of the unique property, such as large pore size, high surface area, and well-crystalline framework (for metal oxides), these OMMs can be used as a host to incorporate large guest molecules such as protein, RNA and dye, metal nanoparticles, and quantum dots, which show excellent performance in different applications including catalysis, sensor, energy conversion and storage, and biomedicine. At last, we give a brief summary and perspective on the further research and development directions of OMMs, especially for tailor-made block copolymers templated OMMs that have large mesopores, semiconductor walls, stable frameworks and tunable surface properties.

2. DIFFERENCES BETWEEN PEO-*B*-PS (PMMA) AND COMMERCIAL PLURONIC BLOCK COPOLYMERS

In contrast to the most frequently used commercially available Pluronic block copolymers, PEO-*b*-PS (or PMMA) contains two highly immiscible blocks of hydrophilic PEO and hydrophobic PS (or PMMA), which endows them with strong hydrophobicity/hydrophilicity contrast, high glass transition temperature and high content of sp^2 hybrid carbon atoms.

First, PEO-*b*-PS (or PMMA) copolymers can be easily synthesized in lab through living radical polymerization methods. The block copolymers show tunable molecular weight (1−100 kg/mol) for both hydrophobic and hydrophilic blocks and narrow distributions of molecular weight (polydispersity index <1.1). Due to the distinct contrast between the hydrophobic and hydrophilic blocks, these block copolymers can easily self-assemble into micelles with PS (or PMMA) core and PEO shell in the polar solvent. In addition, as water is the selective solvent for the PEO-*b*-PS (or PMMA) copolymers, the microphase separation of these block copolymers can occur easily in the existence of water, which is favorable for the synthesis of OMMs in the water-involved sol−gel process (such as silicates). Furthermore, these block copolymers can form discrete single micelles in the water-rich phase in an ultralow concentration, which makes the assembly of single micelles possible during the synthesis. By contrast, Pluronic block copolymers are usually soluble in water and other polar organic solvent (such as ethanol, THF) and the formation of the micelles occurs at a very high concentration or temperature.

Second, PS (or PMMA) segments show a high glass transition temperature (T_g). As the molecular weight and composition can affect T_g of polymers, PS polymers (molecular weight around 10−40 kg/mol) have a T_g of about 100 °C. By contrast, the T_g of poly(propylene oxide) (PPO) is around −75 °C. Usually, the coassembly of the templates and precursors during the formation of OMMs occurs at 10−50 °C. At this temperature, PEO-*b*-PS can form a micelle with a rigid hydrophobic core (PS segment), like a "hard" template. Differently, the micelles formed from Pluronic block copolymers are not such robust or rigid, due to

the high mobility of both hydrophobic and hydrophilic segments. As a result, OMMs with rich compositions, unique frameworks and large pores could be obtained easily using the high-molecular weight PEO-*b*-PS as a template.

Third, as PS segment has a high content of sp^2 hybrid carbon atoms, the PEO-*b*-PS micelles can be in situ converted to residual carbon with high yields after carbonization in an inert atmosphere. The residual carbon can not only be used for further functionalization, but also act as a hard template to protect the ordered mesostructures during the crystallization process at a high temperature. Therefore, these amphiphilic templates not only direct the formation of ordered mesostructures, but also act as a "hard support" to suppress the shrinkage of the as-formed mesostructure caused by the framework cross-linking and crystallization at the coassembly stage and the aging process, and prevent the structural collapse during further treatment at high temperatures.

Conventional Pluronic block copolymers are particularly suitable for the synthesis of OMMs with amorphous frameworks (e.g., carbon and silica) and different structures in both aqueous and nonaqueous solutions, while PEO-*b*-PS (PMMA) block copolymers have the advantages in synthesizing OMMs with ultralarge pore size, thick pore wall, and/or crystalline framework and unique functionality which are highly desirable in various applications, such as immobilization of large functional nano-particles and guest molecules, electrochemical and photo-chemical process.

3. TEMPLATING SYNTHESIS BASED ON TAILOR-MADE AMPHIPHILIC BLOCK COPOLYMERS

3.1. Development of the Synthesis Method. Due to its water-insolubility, PEO-*b*-PS (or PMMA) is usually dissolved in organic solvent, such as THF, and the solvent evaporation induced self-assembly (EISA) method has to be employed to synthesize OMMs. However, for the synthesis of ordered mesoporous silica via such an EISA method, it is usually difficult to completely remove template via direct calcination or solvent extraction, resulting in inaccessible mesopores and undetectable surface area. The reason is that, considerable amount of ethanol can be produced during the hydrolysis of tetraethyl orthosilicate (TEOS), which can weaken the interaction between silicate species and PEO segments and thus cause PEO segments to retract from the silica walls.[24,25] As a result, PEO-*b*-PS spherical micelles are fully wrapped by the dense silica walls after the coassembly. To address this problem, we first developed a hydrothermal recrystallization strategy to create numerous "cracks" in the silica walls by micelle expansion. The "cracks" in the as-made samples serve as micropore channels in the silica walls which allow air to enter for removal of the organic template via combustion.[26] After calcination in air, ordered mesoporous silica with accessible large mesopores (~30.8 nm), high surface area (362 m^2/g), and large pore volume (0.66 cm^3/g) were finally obtained successfully.

Synthesis of OMMs, especially for silica, in water-rich phase using water-insoluble template is a great challenge. On the basis of the knowledge of Pluronic-templated ordered mesoporous silica, the aqueous solution synthesis can be applied to effectively adjust the morphology and porous structure, and meanwhile it is suitable for large-scale production. In this regards, a solvent evaporation induced aggregating assembly (EIAA) method has been developed (Figure 1) in our group.[27] PEO-*b*-PMMA was chosen as a typical water-insoluble template, which was first dissolved in THF/H$_2$O mixed solvent with volume ratio of 4:1 to
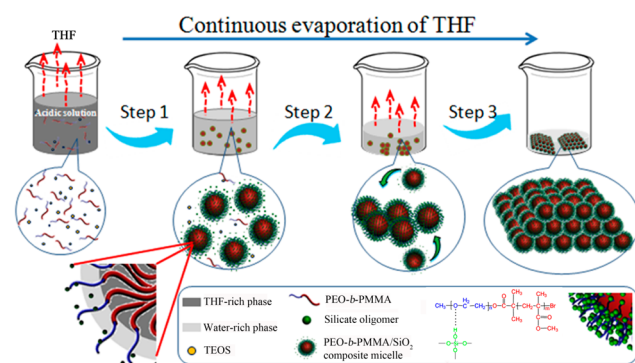
Figure 1. Schematic illustration of the synthesis of ordered mesoporous silica via a solvent evaporation induced aggregating assembly (EIAA) method. Reproduced with permission from ref 27. Copyright 2011 American Chemical Society.

form a clear and transparent solution in an open vessel. As THF evaporates, PEO-*b*-PMMA molecules experience a microphase separation to form spherical micelles with PMMA cores and PEO shells. The silica oligomers are located in the shells of uniform spherical micelles due to the hydrogen bonding with PEO segments. As THF further evaporates, the composite micelles tend to aggregate into a face-centered-cubic (*fcc*) closed-packing mesostructure to minimize the interface energy. Meanwhile, the cross-linking and condensation of silicate oligomers can fix the ordered mesostructure, and large crystal-like particles are obtained. As the PEO segments are inserted in the silica frameworks during EIAA process, plenty of micropores can be produced in the pore walls during calcination. These micropores facilitate the contact between O$_2$ molecules and hydrophobic segments, resulting in completely decomposing the hydrophobic segments (i.e., PMMA). After removing the templates, the obtained ordered mesoporous silica particles show unique crystal-like morphology with an *fcc* mesostructure, large pore size (~37.0 nm), large window size (~8.7 nm), high surface area (~508 m^2/g) and high pore volume (~1.46 cm^3/g).

The EIAA method can also be used to synthesize ordered mesoporous silica with different morphologies.[28,29] For example, by introducing ethanol as the additive in the EIAA system, unique mesoporous silica spheres with a diameter of 1−5 *μ*m, large pore size (~16.8 nm) and high surface area (~482 m^2/g) can be synthesized.[28] By tuning the solubility parameter through increasing water content, uniform silica hollow spheres (20−40 nm in diameter) and nanotubes (diameter of ~30 nm) can be obtained using templates with different molecular weight. By applying a shearing force during EIAA to induce the PEO-*b*-PS/silica spherical micelles to fuse into rod-like composite micelles, resulting in the formation of uniform silica nanotubes and even their closely packed hollow mesostructures.[29] As PEO-*b*-PMMA spherical micelles in the water-rich phase act as a "hard template", the introduction of small surfactant has little influence on the self-assembly process of the large tailor-made amphiphilic block copolymers. Consequently, using PEO-*b*-PMMA and CTAB as cotemplates, novel dual-pore mesoporous silica materials with large mesopores (~20 nm) and small worm-like mesopores (~2.5 nm) have successfully been synthesized. In the obtained materials, the smaller mesopores are homogeneously distributed in the pore walls of larger mesopores. These unique dual-pore mesoporous silica exhibits great potential for loading metal nanocrystals for catalysis.[30]

Recently, we have further extended the EIAA method to synthesize ordered mesoporous carbon with two-dimension

hexagonal mesostructure and large buckled pores by using PEO-*b*-PS as a template and resorcinol-based phenolic resin as a carbon source.[31] The coassembly process involves the formation of spherical composite micelles of PEO-*b*-PS/phenolic resin, their further fusion into rod-like composites and finally aggregation into two-dimension hexagonal mesostructured composite. After pyrolysis in nitrogen, the obtained ordered mesoporous carbons possess high specific surface area ($571-880$ m^2/g), large mesopores (up to 36.3 nm) and high density of active sites (i.e., carboxylic groups) of 0.188/nm^2. Gas sensor based on the ordered mesoporous carbons exhibits an excellent performance in sensing NH$_3$ at a low temperature with fast response (<2 min), ultralow limit of detection (<1 ppm), and good selectivity, due to the large pore sizes, high surface area and rich active sites in the carbon pore walls.

3.2. Tailoring Large Pores. Control over the pore size of OMMs is an important issue as it not only helps to understand the self-assembly process, but also directly relates to their performance for applications. Here we take the synthesis of ordered mesoporous carbon as an example to demonstrate the principle of the adjustment of pore size.

The self-assembly of resol (a low-molecular-weight phenol-formaldehyde resin, $M_w \approx 500$ g/mol) and commercial Pluronic block copolymers via EISA process to synthesize highly ordered mesoporous carbon has intensively been investigated.[32,33] However, the pore size is usually below 5.0 nm. Following EISA route, we reported ordered mesoporous carbons (FDU-18) with ultralarge accessible pores (22.6 nm) using PEO$_{125}$-*b*-PS$_{230}$ ($M_w = 29.7$ kg mol^{-1}) as a template (Figure 2).[26] The successful
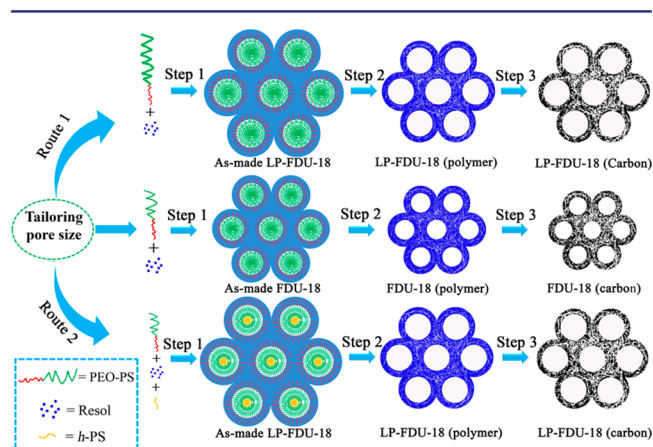

Figure 2. Synthesis of large-pore mesoporous carbon FDU-18 (LP-FDU-18) polymer and carbon via two routes: (1) increasing the molecular weight of hydrophobic segment of the tailor-made amphiphilic block copolymers; (2) incorporating hydrophobic homopolymer (*h*-PS) in the micelles of the block copolymers. Step 1, coassembly of the block copolymer templates and resol; Step 2, calcination at a low temperature (450 °C) to remove the templates; Step 3, carbonization at a high temperature (>800 °C) to obtain ordered mesoporous carbon.

synthesis of the large-pore OMMs implies that the pore size is largely related to hydrophobic volume of the block copolymer/resol composite micelles. Two efficient routes have thus been developed to adjust the hydrophobic volume and pore size of the resultant OMMs. The first one is to increase the molecular weight of hydrophobic segments (i.e., PS) of the block copolymers (Figure 2, route 1). As the molecular weight of PS segment increases, the hydrophobic volume of PEO-*b*-PS

spherical micelles can be enlarged, resulting in a large pore size after selective removing the templates. To prove this method, PEO-*b*-PS copolymers with the same hydrophilic segments but different chain length of hydrophobic segments (PEO$_{125}$-*b*-PS$_{120}$, -PS$_{230}$, and -PS$_{305}$) were used as the templates.[34] The pore size of the obtained ordered mesoporous carbon increases from 11.9 to 33.3 nm as the molecular weight of PS segment increases from 12 to 30.5 kg/mol.

The second route is to incorporate small hydrophobic molecules into the micelles of tailor-made amphiphilic block copolymers to expand the hydrophobic volume (Figure 2, route 2). In the synthesis of large-pore mesoporous silica, some hydrophobic solvents such as benzene and its alkyl-substituted derivatives (e.g., 1,3,5-trimethybenzene), cyclic or/and linear hydrocarbons and long-chain amines were used as a pore expander in the CTAB or Pluronic block copolymers-based synthesis systems, which could easily enter the hydrophobic core of the template micelles and increase the volume of hydrophobic core of micelles.[35] This method is usually used in the water-phase synthesis conditions. However, such a pore expanding synthesis is not compatible in the typical EISA system for the synthesis of ordered mesoporous carbons because these organic molecules would also evaporate like the volatile organic solvent; therefore, they are not suitable to be used to expand the micelles. In addition, the interactions between the pore expander and organic solvent are much stronger than that between the expander and block copolymer micelles. As a result, these small molecules could not enter the hydrophobic domain of the composites micelles, failing in expanding the volume of micelles. Hence, it is of great interest and important to explore a new pore expanding agent, particularly for the EISA process. The hydrophobic homopolymer (i.e., *h*-PS) is demonstrated to be a good swelling agent to increase the hydrophobic volume and lead to a large-pore mesoporous carbon.[36] Briefly, using PEO$_{125}$-*b*-PS$_{230}$ as a template, homopolystyrene (*h*-PS$_{49}$) as a pore expander, ordered mesoporous carbon with adjustable pore sizes can be synthesized through the well-established EISA approach. As the addition of *h*-PS$_{49}$ increases from 0 to 20 wt % relative to PEO$_{125}$-*b*-PS$_{230}$, the pore size can be continuously tuned from 22.9 to 37.4 nm. The *h*-PS$_{49}$ can enter in the hydrophobic PS domains of the mesostructured PEO-*b*-PS/resol composites because of strong interactions between *h*-PS$_{49}$ and PS segment via $\pi-\pi$ stacking interaction. Apart from the pore size, the pore wall thickness and mesostructure can also be finely controlled by changing the property of tailor-made amphiphilic block copolymers.[37-40]

3.3. Highly Crystalline Frameworks. For the ordered mesoporous metal oxides (e.g., TiO$_2$), the high surface area and crystalline framework are difficult to be achieved simultaneously because of the collapse of mesostructure during the crystallization process of pore walls.[41-43] The commercially available block copolymers usually fail to synthesize ordered mesoporous metal oxides mainly due to their small differences in hydrophilicity/hydrophobicity contrast and low glass transition temperature, which makes it impossible to generate "rigid" micelles to maintain and preserve the ordered mesostructure during the aging and crystallization process of inorganic frameworks. Even through carefully controlling the synthesis conditions, the obtained ordered mesoporous metal oxides usually have a semicrystalline framework, small mesopore (typically <5 nm) and poor thermal stability. To solve this problem, Lee et al. developed a new method to synthesize mesoporous metal oxides with highly crystalline and thermally stable frameworks by combining soft structure-directing assemblies and hard-templating process
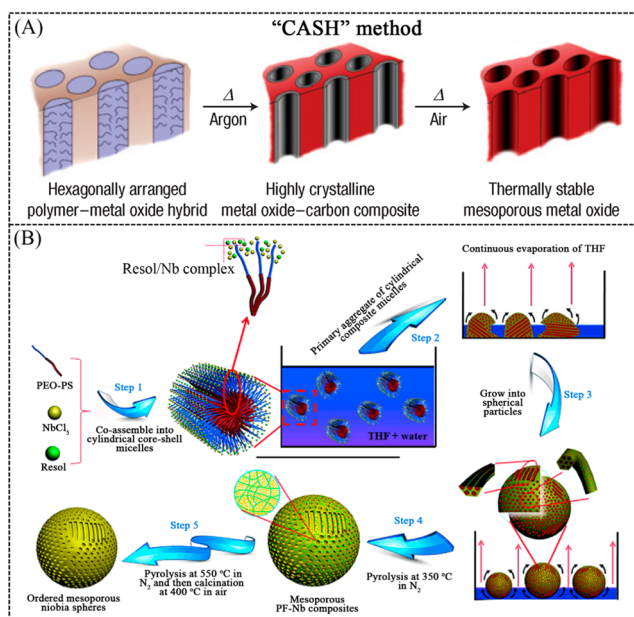
Figure 3. Synthesis of ordered mesoporous metal oxides with a highly crystalline framework and large surface area using (A) "CASH" and (B) Resol-assisted coassembly method. Reproduced with permission from ref 44 and 46. Copyright 2008 Nature Publishing Groups and 2013 Wiley.

(called "CASH" method, Figure 3A). The PEO-*b*-PI template contains sp^2-hybridized carbon atoms in the PI segment, which can be first converted to carbon.[44] The residual carbon serves as a rigid support and prevents mesostructure collapse during the framework crystallization at a high temperature. Finally, the residual carbon is removed by calcination in air. The PS segments of PEO-*b*-PS have a benzene ring structure, which can be converted into graphitic carbon more easily, comparing to PI with isolated C═C bonds. Using PEO-*b*-PS as a template, highly ordered mesoporous TiO$_2$ with a high surface area (112 m^2/g), crystalline framework and high thermal stability (700 °C) was synthesized.[45]

Another problem with the synthesis of ordered mesoporous metal oxides is the fast hydrolysis and condensation of the metal precursors. It is unfavorable for the coassembly of amphiphilic copolymer templates and precursors and usually results in poorly ordered mesostructures. To overcome this obstacle, a resol-assisted solvent evaporation induced self-assembly method has been recently developed to synthesize ordered mesoporous niobium oxide spheres (Figure 3B).[46] Resol has multiple phenolic hydroxyl groups and can polymerize into rigid phenolic formaldehyde (PF) resin upon heating. In this approach, the resol molecules act as a building block to coassemble with amphiphilic block copolymers and Nb^{5+} species by hydrogen bonding without strictly controlling over the synthetic conditions, such as humidity and evaporation rate of solvent. Moreover, the resol-derived carbon can retain the mesostructure during crystallization like the "CASH" method. The obtained mesoporous niobia spheres have a large pore size (11.4 nm), high surface area (131 m^2 g^{-1}) and large pore volume (0.26 cm^3·g^{-1}). Similarly, ordered mesoporous WO$_3$ with a high surface area and crystalline framework have been synthesized by using PEO-*b*-PS as a template by carefully regulating the self-assembly process and calcination conditions.[47]

4. APPLICATIONS

4.1. Catalysis. Due to the large pore size and high surface area, OMMs derived from the tailor-made amphiphilic block copolymers are an ideal catalyst support. The loading of

nanoparticles has little influence on the pore accessibility and the transport of guest reactant molecules. For example, ordered dual-mesoporous silica materials with a large mesopore size of ~20 nm and small worm-like mesopore (~2.5 nm) homogeneously distributed in the large pore walls were used as a nanoreactor by introducing Au nanoparticles with a diameter of sub-5 nm into the large mesopores.[30] The large mesopores serve as a nanoreactor while small mesopores in the pore walls provide an open channel for molecule transport. The obtained catalysts exhibited a high catalytic performance for selective epoxidation of styrene with a high conversion (95.4%) and selectivity (82.6%) for styrene oxide. Interestingly, apart from the introduction of guest molecules, the tailor-made amphiphilic block copolymers themselves can be used as catalysts after functionalization. For example, the as-made PEO-*b*-PS/silica composites with highly ordered meso-structures could first be converted to carbon/silica hybrid composites through carbonization.[48] The template-derived carbon nanoparticles were in situ formed in the large pores of mesoporous silicas. After further sulphonation treatment, sulfonic carbon nanoparticles loaded in ordered mesoporous silica were obtained, which was demonstrated to be an interesting solid acid catalyst with excellent catalytic performance, high selectivity and conversion (93%) and good stability for the condensation reaction of benzaldehyde with ethylene glycol.

4.2. Sensor. Ordered mesoporous metal oxides can also be used as a sensor for detection of toxic gases by utilization of their semiconducting properties. For example, ordered mesoporous WO$_3$ materials templated from PEO$_{117}$-*b*-PS$_{198}$ show a large pore size (ca. 10.9 nm), high surface area (ca. 121 m^2/g) and crystalline framework, and excellent performance for H$_2$S gas sensing at a very low concentration (0.25 ppm) with ultrafast response (2 s) and recovery (38 s) even in interfering gases.[47] Due to the large pore size and unique framework, some active proteins such as hemoglobin (Hb) with molecular size of 5.0 × 5.5 × 6.5 nm can be easily loaded in the pores of ordered mesoporous niobia to fabricate a H$_2$O$_2$ sensor. The Hb/ordered mesoporous niobia biosensor can achieve 95% of the steady-state current within 5 s, and the amperometric response shows a good linear relationship with H$_2$O$_2$ concentration in both low concentration range of 5.0−60 mM and high concentration of 80 μM-11 mM, which indicates an excellent electrochemical sensing of H$_2$O$_2$ with a high sensitivity and fast response.[46]

4.3. Energy Conversion and Storage. Ordered mesoporous TiO$_2$ with large pore size, high surface area, and highly crystalline framework is one of important materials for solar cells. By employing PEO-*b*-PS templated TiO$_2$ as the photo anode in a dye-sensitized solar cell, a high power-conversion efficiency (5.45%) can be achieved in combination with a commercial dye N719.[45] Combing the self-assembly and dip-coating method, highly ordered mesoporous TiO$_2$ films with a thickness from 150 nm to several micron meters were also synthesized.[49] The small-bandgap semiconductor nanoparticles (e.g., CdS quantum dots) could be easily deposited into the mesopore channels for enhanced performance of photoelectrochemical water splitting. Apart from the postdeposition approach, we have recently demonstrated a new site-inserted approach to in situ incorporate sub-5 nm sized graphitic pencil nanodots (PND) into ordered mesoporous titania frameworks for fabricating optoelectronic materials via a coassembly process.[50] Due to the hydrophilic groups, the PND can be directly dispersed in aqueous solutions and retained for subsequent ordered self-inserted supra-assembly, overcoming size effects on the coassembly of inorganic precursors by incorporation of exogenous materials. The hydrogen

bond-driven hydrolysis and condensation of precursors can occur on PND, and further assemble into ordered composite micelles. The mesoporous N-doped carbon nanodots/TiO_2 is then used as a photo anode for optoelectronic studies. The optical photos show that the composites have a unique blue-green color emission under ultraviolet light excitation (Figure 4a, b).
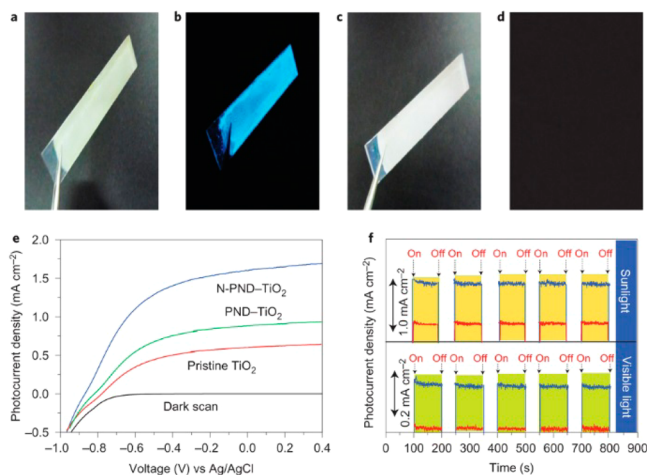
Figure 4. (a, b) Photographs of the N-doped pencil-derived carbon nanodot-TiO_2 (N-PND-TiO_2) under visible light (a) and ultraviolet light (b). (c, d) Photographs of the pristine mesoporous TiO_2 under visible light (c) and ultraviolet light (d). (e) Photocurrent densities versus voltage measured from the pristine mesoporous TiO_2, PND-inserted mesoporous TiO_2 and N-PND-TiO_2. (f) Amperometric $I-t$ curves for N-PND-TiO_2 and pristine mesoporous TiO_2 under simulated sunlight (top) and visible-light (bottom) illumination. Reproduced with permission from ref 50. Copyright 2016 Nature Publishing Groups.

By comparison, the mesoporous TiO_2 without carbon nanodots has no emission (Figure 4c, d). The incorporation of carbon nanodots, especially N-doped carbon nanodots can effectively enhance the photocurrent densities (Figure 4e). Moreover, the time-dependent photocurrent measurements of the N-doped carbon nanodots/TiO_2 show a highly stable and sensitive photocurrent density under on/off cycles of simulated solar illumination without observable degradation (Figure 4f). Different from the postdeposition approach, such coassembly route can make the semiconductor nanoparticles more dispersible in the TiO_2 frameworks. Notably, through this general site-inserted superassembly method, various nanoparticles can be incorporated into the ordered mesoporous frameworks for different applications.

The catalysts for the cathode reaction (i.e., oxygen reduction reaction, ORR) are one of the key components in polymer electrolyte membrane fuel cells. The development of nonprecious metal catalysts such as carbon-based catalysts with a low-cost, high activity and stability for ORR to replace commercial Pt/C is urgent for large-scale applications of fuel cells even in car.[51] Due to the large pore size and high surface area, ordered mesoporous carbon composites templated from the tailor-made amphiphilic block copolymer are ideal candidates due to the enhanced mass transport and fully exposed active sites. Recently, Tang et al. synthesized N-doped mesoporous carbon spheres by casting an N-containing polymer (e.g., polydopamine) on the PEO-*b*-PS microstructure followed by carbonization.[52] The obtained N-doped mesoporous carbon spheres were used as a metal-free electrocatalysts and showed a high performance for oxygen reduction in alkaline conditions (Figure 5). Lee et al. demonstrated the effect of the pore size and the dopingsite
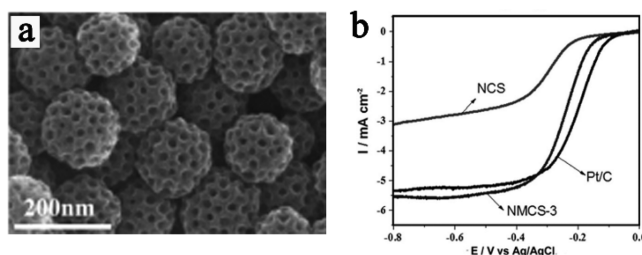
Figure 5. (a) SEM image of N-doped mesoporous carbon (NMCS-3). (b) Polarization curves of the N-doped carbon and Pt/C in O_2-saturated 0.1 M KOH solution with a rotating speed of 1600 rpm. Reproduced with permission from ref 52. Copyright 2015 Wiley.

positions of heteroatoms (N and P) on the single-cell performance of metal-free catalysts using ordered mesoporous carbon templated from PEO-*b*-PS.[53] The single-cell tests prove that the pore size and doping-site position can directly affect the cell performance by changing the mass-transport properties and the numbers of the available catalytic active sites in the catalyst layer. The N, P-doped ordered mesoporous carbon with precisely controlled doping sites to be near the large mesopores exhibited a high onset potential and achieved 70% of the maximum power density of Pt/C.

Due to the large pore size, good conductivity, high surface area and pore volume, ordered mesoporous carbon templated from tailor-made amphiphilic block copolymer has been considered as an idea support for loading active materials such as metal or metal oxide nanoparticles for lithium-ion batteries. The large porous structure can facilitate the electrolyte and ions transport and stabilize the active materials during charge and discharge. For example, Hwang et al. reported Sn nanowires and nanoparticles embedded in mesoporous carbon/silica composites through the coassembly of precursors of carbon, silica and Sn with PEO-*b*-PS via EISA process.[54] The resultant Sn/C/SiO_2 exhibits high specific capacities (600 mA h/g at a current density of 45 mA/g) and a good cyclability of over 100 cycles with a high Coulombic efficiency.

4.4. Biomedicine. The large pore size and high pore volume of OMMs have been proved to be promising carriers for application of drug delivery because of their high capability in loading drug and gene molecules. However, most of PEO-*b*-PS (or PMMA) templated OMMs show particles size of a few micrometres, which is incompatible with cells. Recently, Liu et al. synthesized mesoporous carbon nanoparticles with a small diameter of 100−126 nm, pore size of 13−32 nm, and high surface area (646 m^2/g) by using PEO-*b*-PS as a template.[55] As a proof-of-concept, dye-labeled oligoDNA (Cy3-oligoDNA) was chosen as a model molecule. The resultant mesoporous carbon nanoparticles can efficiently deliver the biomolecules into different cancer cells. In addition, the mesoporous carbon nanoparticles show a negligible toxicity in both HCT-116 and KHOS cells at concentrations from 10 to 80 μg/mL.

5. CONCLUSIONS AND PERSPECTIVE

The use of tailor-made amphiphilic block copolymers (e.g., PEO-*b*-PS, PEO-*b*-PMMA) as a template for the synthesis and applications of ordered mesoporous materials with a large accessible pore and unique functionality is summarized. As water is a selective solvent for these block copolymers, these block copolymers could form stable single micelles in the water-rich phase.[27] On this basis, the evaporation induced aggregating assembly (EIAA) method has been applied to synthesize OMMs with

various compositions and mesostructures, controllable pore size and morphologies. As the molecular weight of the hydrophobic segments can be easily adjusted, the pore size (18−45 nm for silica and 10−37 nm for carbon) of the obtained OMMs can be tailored. Different from the commercially available Pluronic block copolymers, the tailor-made amphiphilic block copolymers exhibit high glass transition temperature and thermal stability, as well as high content of sp^2 hybrid carbon atoms. They are more suitable for the synthesis of ordered mesoporous metal oxides with large pore size, high surface area and well-crystalline framework. The large-pore OMMs could be used as a support to load large-size guest molecules (e.g., protein, RNA, dye), metal nanoparticles and quantum dots, which could be applied in catalysis, sensor, energy conversion and storage, and biomedicine. In addition, the large pore size can also enhance the mass transport, which is promising in electrocatalysis. To date, although significant advances have been made, many challenges are still facing researchers particularly in the field of mesoscale science, including supramolecular assembly, and mesostructured materials.

First, it is challenging and desirable to synthesize ordered mesoporous materials with new compositions such as metal carbides, nitrides and sulfides that can hardly be achieved by the commercial Pluronic templates. These new compositions are attractive in various fields and can greatly broaden applications of OMMs.[56,57] For example, Robbins et al. have recently developed three-dimensionally continuous gyroidal mesoporous niobium nitrides by using PI-b-PS-b-PEO as a template.[58] These niobium nitride materials have been proved to be a good superconductor with a critical temperature of about 7−8 K.

Second, large-pore functional OMMs with the low-dimensional nanoscale structure and morphology such as spheres, fibers (or rods), thin films and nanosheets are much more desired than their bulk counterparts. Most of the large-pore OMMs reported before usually show large particles size with a few micrometres, which hinders their wide applications such as drug delivery. OMMs with nanospherical, nanofibrous or nanosheet morphologies can also shorten the mass transport path, which is highly appealing for energy conversion and storage. More importantly, these nanostructures could also be easily integrated with other components to fabricate functional devices. Moreover, it is desirable to explore new methods or pathways to construct complex nanostructures with preprogramed functions and compositions starting from the single micelles of the tailor-made copolymers, such as single sheets of graphene-like carbon with mesopores, one-dimensional or nanofibers or nanowires assembled by single micelle arrays.

Third, the incorporation of other functional components (e.g., nanoparticles and guest biomolecules) into the OMMs to fabricate their multicomposites for various applications is even more important and challenging. Currently, the post deposition route is widely used, which can inevitably result in the heterogeneous distributions even aggregations of the guest components. Most of nanoparticles or nanocrystals are capped with hydrophobic molecules, and it is difficult to be inserted into the mesoporous frameworks. How to realize an artful assembly of nanocrystals of different functions into high-surface-area mesoporous materials in a "one-pot" manner is attracting. The design of block copolymers with special side-chain groups may become a direction in the controlled assembly with inorganic species would fabricate various organic/inorganic hybrid materials for different applications. However, the compatibility between the existing synthesis methods and guest components

needs be reconsidered, and new strategies to tune the assembling interfaces are yet to be developed to realize complex assembly systems.[59]

Last but not least, though PEO-b-PS (or PMMA) is mainly discussed in this Perspective, other tailor-made amphiphilic block copolymers should be also paid much attention. And through controlling the compositions and molecular weight of the tailor-made block copolymers, new liquid-crystal phases such as L3 and LMM could be accessible in principle, which can enrich the family of OMMs and show some new properties. Some other tailor-made copolymers-templated mesoporous materials with morphologies or mesostructures that mimic the assembly structures of DNA or other biomacromolecules are yet to be explored, such as vesicles, chiral structures, folding and bending structure.

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Notes
The authors declare no competing financial interest.

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