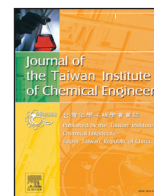




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# Construction Hierarchically Mesoporous/Microporous Materials Based on Block Copolymer and Covalent Organic Framework

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## ABSTRACT

Hierarchically ordered mesoporous materials have gained significant scientific attention due to their high surface areas, uniform porosity over various lengths scales, high-volume storage capability, shape selectivity, enhanced mass transport and diffusion. These materials have been widely applied in the fields of photocatalysis, separation, adsorption, photovoltaic solar cells, energy storage and conversion, chemical sensing, and drug delivery. In general, hierarchically porous materials can be generated in two ways: through sol-gel template approaches and a combination of surfactant-assisted procedures. In this review, we discuss recent progress in the preparation, properties, and potential applications of four hierarchically ordered porous materials: hierarchical mesoporous silica, mesoporous phenolic/carbon, nitrogen-doped mesoporous carbon, and mesoporous/microporous covalent organic frameworks.

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## 1. Introduction

Hierarchical mesoporous and microporous structures present in living organisms are known to be evolutionary tools in their favorable adaptation to changes in the environment [1]. Hierarchically porous materials have been attracted much attention and widely used in various fields, including energy storage, life science, gas separation, nanoscience, catalysis and sensors [2–20]. Typically, hierarchically porous materials are materials containing a multimodal hierarchically porous structure (interconnected pores) over various length-scales and having macro- (>50 nm), meso- (2–50 nm), and micro- (<2 nm) pore sizes. The multiple levels of these pores sizes can be divided into trimodalities (e.g., micro-meso-macro or meso-meso-macro structures) and bimodalities (e.g., micro-meso, meso-macro, or micro-macro structures) [21–25]. The ability to design hierarchically porous materials of various lengths is necessary for the preparation of functionalities desirable for many applications. Several

strategies have been utilized to construct hierarchically porous materials, including polymer templating, emulsion templating, freeze-drying, dual surfactant templating, bioinspired processes, colloidal crystal templating, phase separation, sol-gel controlling, selective leaching, post-treatment and spontaneous formation [26–29]. Recently, the morphologies of hierarchically porous materials have also been controlled under templating and physicochemical conditions [1]. For instance, the use of templating methods for two-dimensional (2D) films, polymer templating for one-dimensional fibers, self-formation for spheres, and phase-separation for three-dimensional (3D) monoliths. Besides, porous structures, as well as the structures of hierarchically porous materials in the range from the subnanometer to the micrometer, can be tuned through a combination of methods and can be integrated using nanounits [24]. Hierarchically porous materials have many applications because they display unique characteristics, such as well-controlled porosities over different lengths scales, shape selectivity, easy mass transport, high storage volume, and high contact surface areas [4,30–34]. Several literature reviews have described hierarchically porous materials prepared from organosilica, metal oxides and silica, as well as their applications in separation and absorption processes [35–39]. In general,

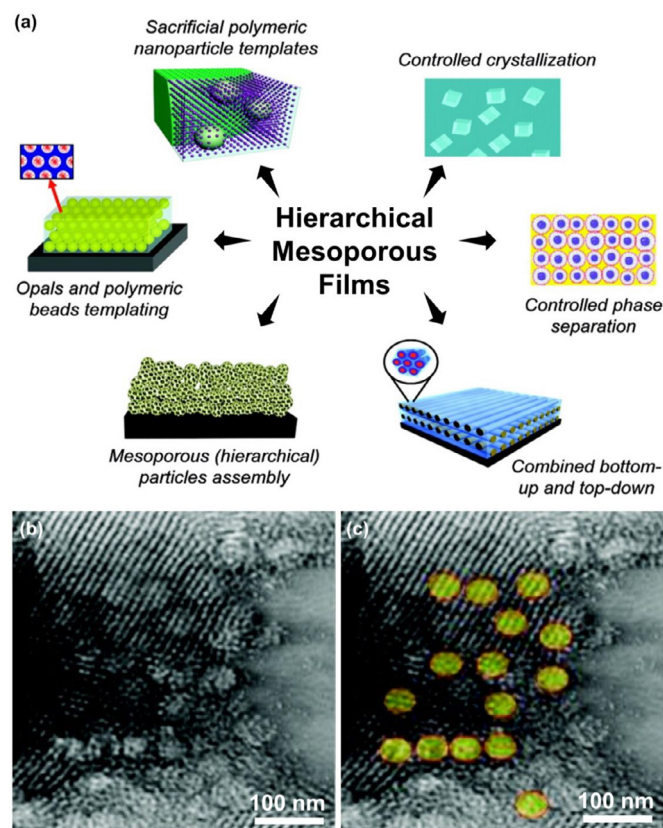
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E-mail addresses: [kevinwu@ntu.edu.tw](mailto:kevinwu@ntu.edu.tw) (K.C.-W. Wu), [kuosw@faculty.nsysu.edu.tw](mailto:kuosw@faculty.nsysu.edu.tw) (S.-W. Kuo).

there are two methods for preparing hierarchically porous materials: (1) sol-gel templated approaches and (2) the combination of surfactant-assisted procedures with physical and chemical methods.

In the first approach, dual or multiple templates are typically used. The advantages of this approach are that it requires a minimal number of reaction steps, occurs with high efficiency thereby allowing scale-up, operates under mild conditions and uses nontoxic solvents and precursors [1]. Two classes of templates are most often used to construct hierarchically ordered porous materials: soft templates (e.g., surfactant micelle arrays) and hard templates (e.g., rigid solid matrices, including ordered colloidal crystals or mesoporous silica or carbon) [1,36–40]. In the second approach, a surfactant-assisted procedure is combined with physical and chemical methods, including phase separation, post-treatment, and the introduction of microporous templates in the reaction media, to control the assembly of the mesostructured morphology [36]. For example, solvent evaporation-induced self-assembly (EISA) is a very simple and convenient method for the construction of ordered structured mesoporous materials, especially membranes, monoliths, and mesoporous thin films [41–45]. Brinker and co-workers first reported the EISA method in their synthesis of mesoporous silicas [46]. This method has been applied thereafter to the construction of hierarchically porous materials from amphiphilic triblock copolymers [e.g., poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO)], PEO-based diblock copolymers [e.g., poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS), poly(ethylene oxide)-*b*-polycaprolactone (PEO-*b*-PCL), and poly(ethylene oxide)-*b*-poly(methyl methacrylate) (PEO-*b*-PMMA)], poly(vinyl pyridine)-based diblock copolymers [e.g., poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP)], and cationic surfactants [e.g., cetyltrimethylammonium bromide (CTAB)] [24,47,48]. Ryoo *et al.* [49] successfully prepared crystalline mesoporous MFI zeolites by adding amphiphilic zeolite to alkaline zeolite. They found that the obtained zeolite material possesses pore size control, tunable mesoporosity (2–20 nm), large BET surface area and interconnected mesoporous with zeolitic pore walls. These materials exhibited excellent catalytic performance for conversion of methanol to gasoline and olefin. The same group also reported that the crystalline mesoporous molecular sieves with zeolitic framework which could be used as active catalyst for different acid-catalyzed reactions [50]. Bhaumik groups reported that hierarchical mesoporous Mn-ZSM-5 zeolite nanoparticles used as heterogeneous catalysts to obtain diphenyldithiol from benzenethiol [51]. Wang *et al.* revealed that hexagonal prism of ZSM-5/SBA-15 exhibited a higher breakthrough time, excellent cycling stability and toluene adsorption capacity compared with pure SBA-15 and ZSM [52]. Sinha *et al.* successfully synthesized hierarchical mesoporous Fe-ZSM-5 zeolite through adding Fe<sup>3+</sup> during the synthesis of mesoporous ZSM-5 and the materials displayed high selectivity and activity for the benzene hydroxylation with nitrous oxide to phenol [53]. In this review, we focus on recent progress in the preparation, properties, and applications of four different kinds of hierarchically meso- and microporous materials: (1) silica, (2) phenolic/carbon, (3) nitrogen-doped carbon, and (4) covalent organic frameworks (COFs).

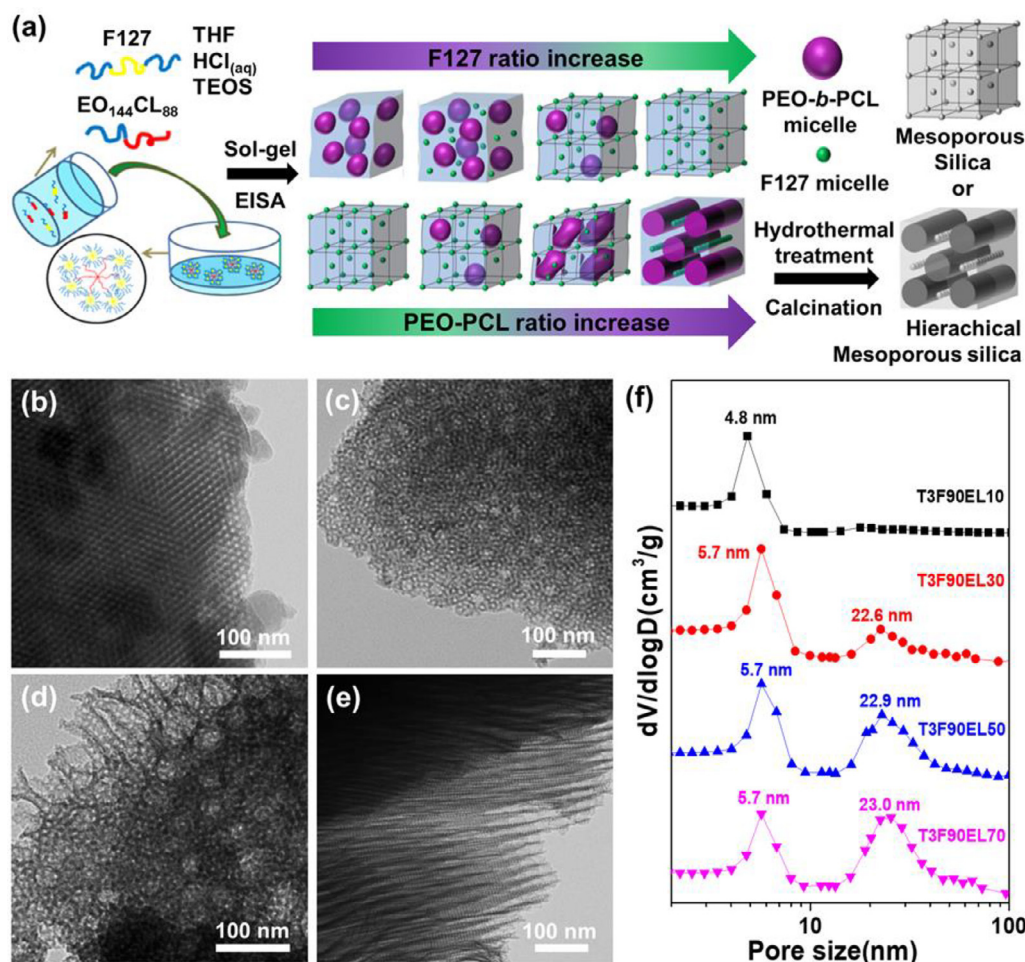
## 2. Hierarchical Mesoporous Silica

Hierarchically mesoporous silicas featuring high surface areas, large pore sizes, and unique pore structures have great potential applications in drug delivery, catalysis, and separation [54–56]. The solution phase and EISA methods have been used to prepare these materials [47,57–61]. Figure 1(a) displays the general approaches used to prepare hierarchically mesoporous silica materials through self-assembly with various templates, including nano and colloidal polymeric particles, mesoporous hierarchical particles, opal, and polymeric beads, as templates for mesoporous/macroporous structures, and shape-controlled salt crystals [61].



**Figure 1.** (a) Combinations of self-assembly and other template methods used to prepare the hierarchical mesoporous materials and (b, c) TEM images of mesoporous silica co-templated by PS nanoparticles and the triblock copolymer F127 where (c) the yellow pores were due to the removal of the PS nanoparticles and (b) the elliptical pores arose from the triblock copolymer F127. Reprinted with permission from Ref [61]. Copyright 2011 American Chemical Society.

Figures 1(b) and 1(c) provide examples of the synthesis of hierarchically mesoporous materials templated by PS nanoparticles and the triblock copolymer F127; these materials featured dual pore sizes: 70 nm from the PS nanoparticles and a mesoporous structure from the triblock copolymer F127 [61]. Zhao *et al.* employed EISA and solvent evaporation aggregating assembly (EIAA) as methods to prepare ordered mesoporous silicas (OMSSs) having various morphologies, with PEO-*b*-PMMA as the soft template, low-molecular-weight CTAB as the surfactant, and tetraethyl orthosilicate (TEOS) as the silica source. The ordered mesoporous silica obtained using both EISA and EIAA possessed face-centered cubic symmetry, based on TEM imaging, with a high surface area (482 m<sup>2</sup> g<sup>-1</sup>) and large pores (ca. 16 nm) [62]. We have also synthesized hierarchical mesoporous silicas through EISA, using two different templates (F127, PEO-*b*-PCL) and TEOS, as depicted in Figure 2(a). TEM images [Figures 2(b)–(e)] and N<sub>2</sub> adsorption/desorption isotherms [Figure 2(f)] revealed that we obtained these hierarchical mesoporous silicas in a regular spherical strip arrangement, with tetragonal cylinders having high specific surface areas and pore volumes (reaching 781 m<sup>2</sup> g<sup>-1</sup> and 0.99 cm<sup>3</sup> g<sup>-1</sup>, respectively). More interestingly, these materials exhibited ultra-low refractive indices (ca. 1.08) [63]. In addition to hierarchical mesoporous silicas being synthesized using two different templates, the application of a single template to prepare hierarchically mesoporous silicas is also interesting. For example, we prepared two different kinds of hierarchical mesoporous silicas—alternate body-centered cubic (BCC) and tetragonal cylinder with face-centered cubic (FCC) through the EISA method when using poly(ethylene-*b*-ethylene oxide)-*b*-caprolactone) triblock copolymers as single templates and various amounts of TEOS as the precursor [Figure 3(a–n)] [64]. We

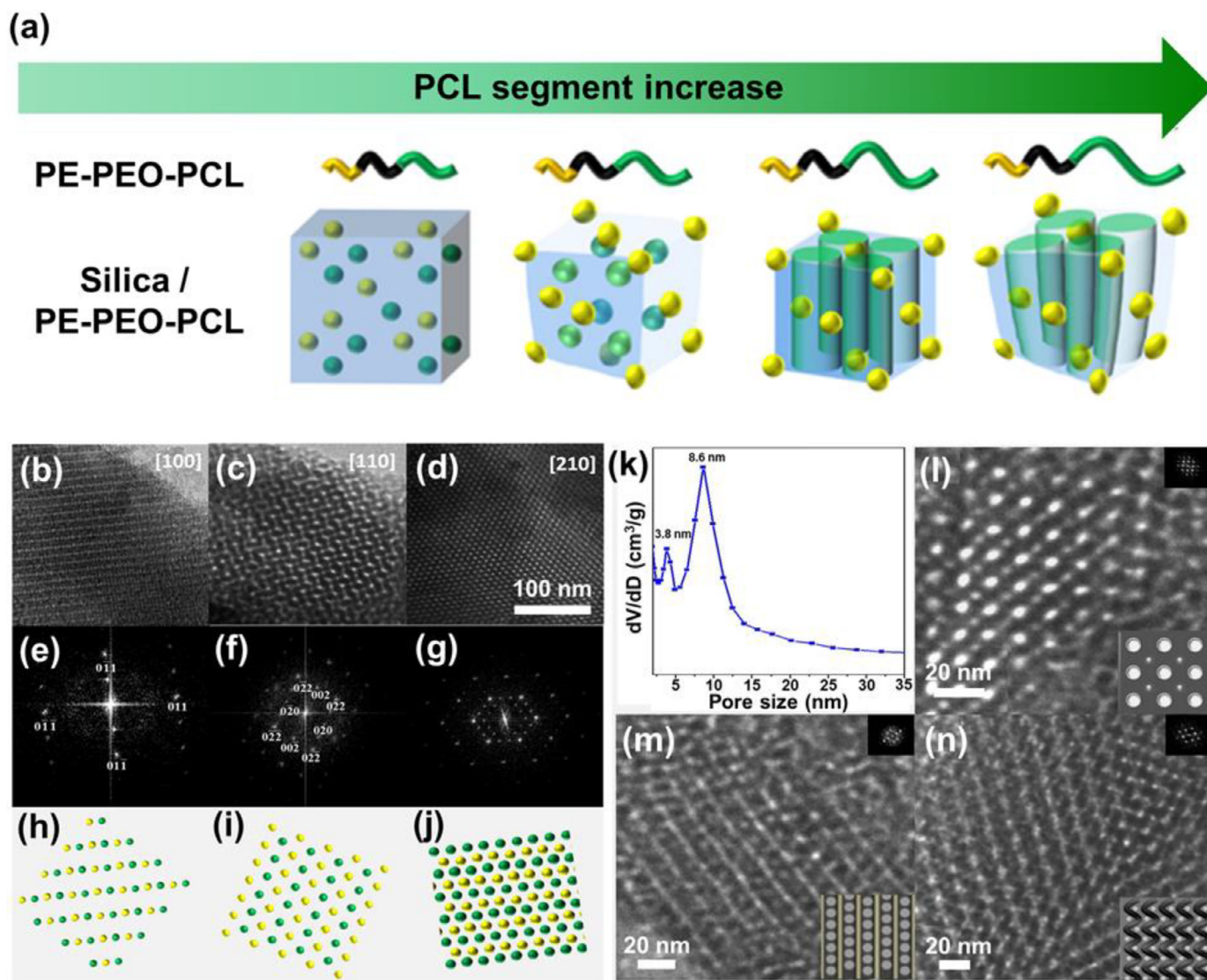


**Figure 2.** (a) Preparation of hierarchical mesoporous silicas co-templated by F127 and PEO-*b*-PCL. (b–e) TEM images and (f) pore size distribution curves for four hierarchical mesoporous silicas prepared with different PEO-*b*-PCL weight fractions at a fixed TEOS/F127 ratio of 30:9. Reprinted with permission from Ref [63]. Copyright 2014 Royal Society of Chemistry.

obtained similar results when using poly(ethylene-*b*-ethylene oxide-*b*-lactide) triblock copolymer as a single template and used the resulting hierarchical mesoporous silicas for drug loading [65]. Cho et al. prepared hierarchically bimodal mesoporous silicas when using poly(lactic acid-*co*-glycolic acid)-*b*-poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(lactic acid-*co*-glycolic acid) pentablock copolymers as single templates and TEOS as the silica precursor. Though they obtained hexagonally ordered mesoporous silicas featuring a bimodal pore size distribution (2–9 nm) when using PLGA-PEO as the template, the presence of this pentablock copolymer as the template yielded core/shell-type mesoporous silicas having large pores (20 nm), based on Brunauer–Emmett–Teller (BET) analysis [66]. Yamauchi et al. fabricated Pt-decorated mesoporous silica through an EISA approach using an asymmetric PS-*b*-P2VP-*b*-PEO triblock copolymer as the pore directing agent, TEOS as the silica precursor, and platinum(II)-2,4-pentanedionate. They observed a strong interaction between the Pt and the hydrophobic PS core and the incorporation of TEOS on the P2VP shell through acid-catalyzed polymerization, with the resulting materials exhibiting excellent activity for the oxidation of carbon monoxide (CO) [67]. In addition, we have fabricated mesoporous silica templates through EISA from polytyrosine (PTyr), biodegradable PEO-*b*-PCL, and TEOS in MeOH. The polypeptide-functionalized mesoporous silicas displayed a propensity for the adsorption of methylene blue hydrate from aqueous solution, based on UV spectroscopic analysis [68].

### 3. Hierarchical Mesoporous Phenolic/Carbon Materials

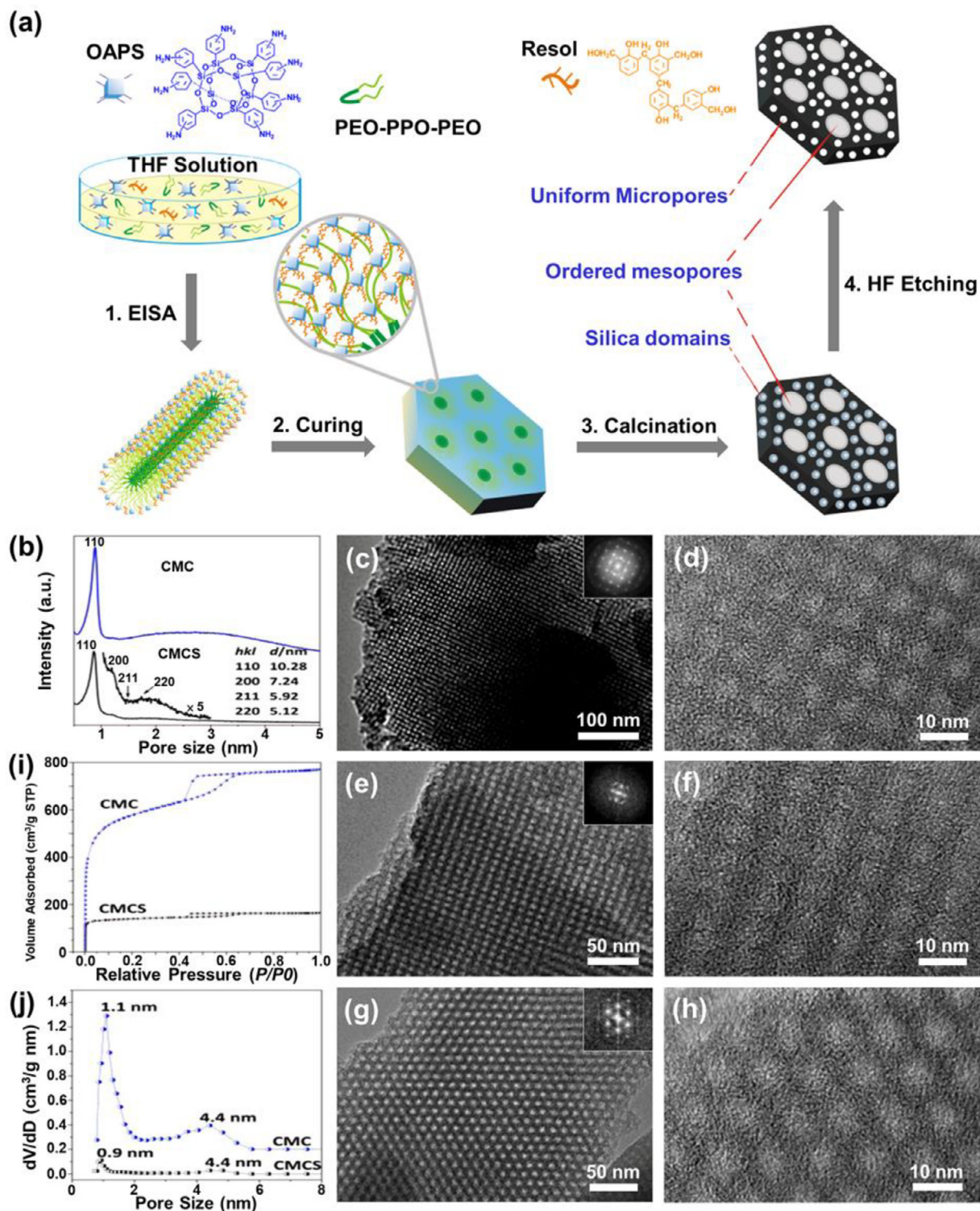
The preparation of ordered mesoporous materials from carbon or phenolic resins with high BET surface area, good mechanical stability and large pore volume, have been attracted and received much attention because of their amazing application in drug delivery, separation, catalysis, adsorption and photonics. As known, there are two types from phenolic resins; novolac and resol based materials. The generation of nanostructures based on resol materials through in situ phenolic crosslinking in mixtures of block copolymers, water, phenol, and formaldehyde. The nanostructures strongly depend on the self-assembly of block copolymers, cross-linking and vitrification of the resols and solvents evaporation. We reported the preparation of closed-loop mesoporous phenolic resins having pore sizes of 7.5–12.4 nm by exploiting the competitive hydrogen bonding between triple-crystalline PEO-*b*-PCL-*b*-PLLA triblock copolymers and phenolic resin as the homopolymer; the formation of the cylinder, gyroid, and disordered spherical phenolic resins resulted from the three strong competitive hydrogen bonding interactions [69]. In addition, we obtained long-range-ordered mesoporous phenolic resins after blending PEO-*b*-PCL, resol, and hexamethylenetetramine (HMTA, as the curing agent) with various amounts of a star-shaped PEO-octa functionalized polyhedral oligomeric silsesquioxane (POSS); the hexagonally packed cylinder structure changed into a bicontinuous gyroid structure after the addition of the star PEO-POSS into the PEO-*b*-PCL template [70]. Wang et al.



**Figure 3.** (a) Possible change in the mesoporous structure of hierarchical mesoporous silicas templated by the triblock copolymer PE-*b*-PEO-*b*-PCL with different degrees of polymerization of the PCL block segment and alternative BCC structure templated by PE<sub>13</sub>-*b*-PEO<sub>42</sub>-*b*-PCL<sub>9</sub>; (b-d) TEM images, (e-g) FFT patterns, and (h-j) phase diagrams from the (b, e, h) [100], (c, f, i) [110], and (d, g, j) [210] directions. Tetragonal cylinders with FCC structure templated by PE<sub>13</sub>-*b*-PEO<sub>42</sub>-*b*-PCL<sub>31</sub>: (k) pore size distribution curve and (l-n) TEM images viewed from the (l) [001], (m) [10], and (n) [11] directions (inset: FFT pattern). Reprinted with permission from Ref [64]. Copyright 2013 Royal Society of Chemistry.

fabricated large, tunable-pore-size, mesoporous carbon nanoparticles (MCNs) by using PEO-*b*-PS as a soft template and resorcinol-formaldehyde as the carbon source. Based on BET analysis and scanning electron microscopy (SEM), their MCNs possessed small diameters (100–126 nm), high specific surface areas (646 m<sup>2</sup> g<sup>-1</sup>), and pore sizes distributed in the range 13–32 nm and they applied the resulting MCNs as nano carriers to deliver biomolecule drugs into cancer cells [71]. Li et al. prepared hierarchically ordered mesoporous carbons (OMCs) by using aminophenyl-functionalized POSS as silica and carbon source and Pluronic F127 as the template [Figure 4(a)]. When using block copolymers of different molecular weights, the structure of the mesopores could be tuned from BCC (Im3m) and 2D hexagonal structures (P6m) [Figure 4(b-j)]. In addition, the hierarchically mesoporous carbons derived from POSS possessed high surface areas (ca. 2000 m<sup>2</sup> g<sup>-1</sup>), large pore volumes (1.19 cm<sup>3</sup> g<sup>-1</sup>), and high specific capacitances (160 and 210 F g<sup>-1</sup> in ionic liquid and 1 M H<sub>2</sub>SO<sub>4</sub>, respectively) [72]. We have prepared activated cylinder and gyroid mesoporous carbon structures having pore sizes in the range 14.1–15.6 nm when using specific weight ratios of phenolic resin and PEO-PCL

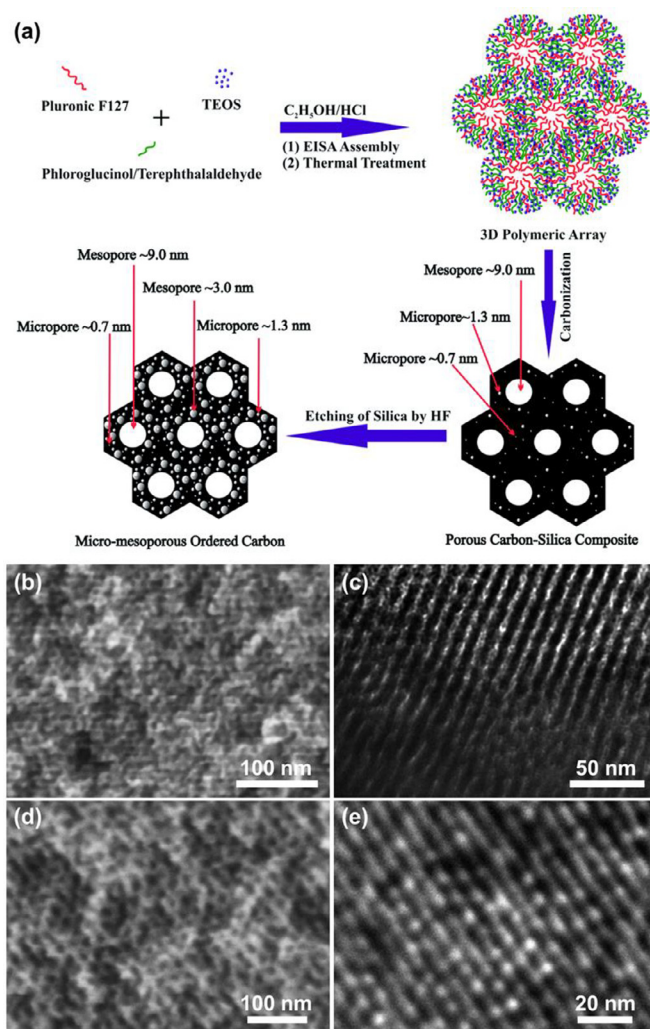
Electrochemical measurements revealed that, when used as electrodes, the gyroid mesoporous carbon nanostructure displayed supercapacitor performance superior to that of the cylinder mesoporous carbon structure [73]. Zhao et al. synthesized OMCs through hydrothermal processing and carbonization (700°C) of β-cyclodextrin, as the carbon precursor, with PEO-*b*-PPO-*b*-PEO. These OMCs displayed high specific surface areas (ca. 781 m<sup>2</sup> g<sup>-1</sup>), a uniform pore size (ca. 4.5 nm), and a 2D-ordered hexagonal mesostructure, as well as high specific capacitance (157 F g<sup>-1</sup>) and excellent electrochemical stability [74]. Furthermore, Zhao et al. also fabricated amino-functionalized OMCs from a bimodal mesoporous carbon as the matrix, through a chemical process of oxidation, acylation, and amidation. These materials displayed an ordered bimodal mesoporous structure (pore sizes of 2.3 and 4.8 nm), a high specific surface area (1063 m<sup>2</sup> g<sup>-1</sup>), and a large pore volume (0.7 cm<sup>3</sup> g<sup>-1</sup>); More importantly, they exhibited outstanding adsorption capabilities for the removal of microcystin-LR in batch and column experiments due to their positively charged amino groups [75]. Zhao et al. obtained activated OMCs through the activation of FDU-15, which was prepared on a large scale through EISA of



**Figure 4.** (a) Hierarchically mesoporous carbons co-templated by F127 and OAPS nanoparticles and (b) SAXS patterns of CMCS and CMC. (c–h) TEM images viewed from the (c, d) [100], (e, f) [110], and (g, h) [111] directions, (i) N<sub>2</sub> adsorption/desorption isotherms, and (j) pore size distribution curve. Reprinted with permission from Ref [72] Copyright 2016 Elsevier.

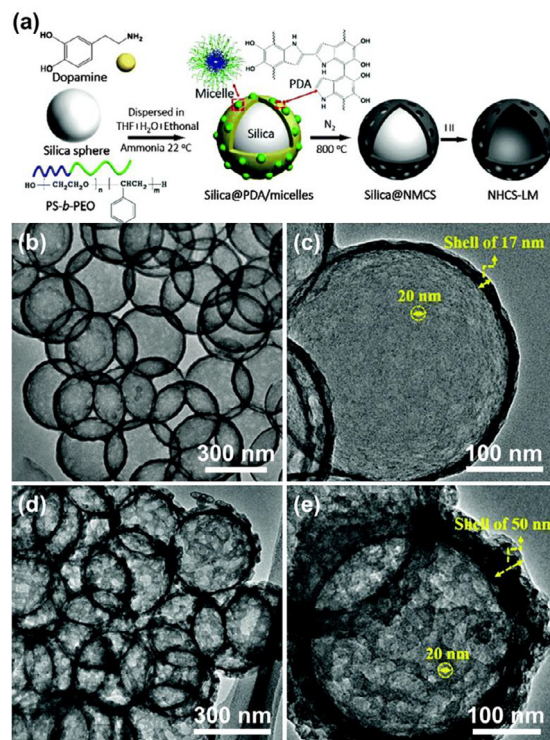
F127 with polyurethane (PU) foam and KOH as the activating agent. The OMCs possessed high surface area (1410 m<sup>2</sup> g<sup>-1</sup>), suitable microporosity, and large pores (0.73 cm<sup>3</sup> g<sup>-1</sup>), and displayed excellent supercapacitor performance, good cycling stability and high gravimetric capacitance (200 F g<sup>-1</sup>) [76]. Su et al. developed another route toward OMCs by using P123 (as the template), resorcinol, and HMTA (as the crosslinking monomer) in a strongly acidic aqueous solution and these materials exhibited excellent capacitor efficiency which was

attributed to their ordered pores and hierarchical fiber structure [77]. Yamauchi et al. hydrothermally processed PS-*b*-P2VP-*b*-PEO (as a soft template and directing agent) and phenolic resol resin (as the carbon source) at various temperatures (800, 900, and 1000°C) under an N<sub>2</sub> atmosphere for 2 h to produce hollow carbon nanospheres (HCNs). Transmission electron microscopy (TEM) revealed that the HCNs had an outer diameter of 43 nm and a hollow core of 19 nm. The specific capacitance of the HCN-1000 sample (206.4 F g<sup>-1</sup>) was greater than



**Figure 5.** (a) Synthesis of hierarchically mesoporous carbons co-templated by F127 and TEOS and (b–e) corresponding SEM and TEM images. Reprinted with permission from Ref [80] Copyright 2014 Royal Society of Chemistry.

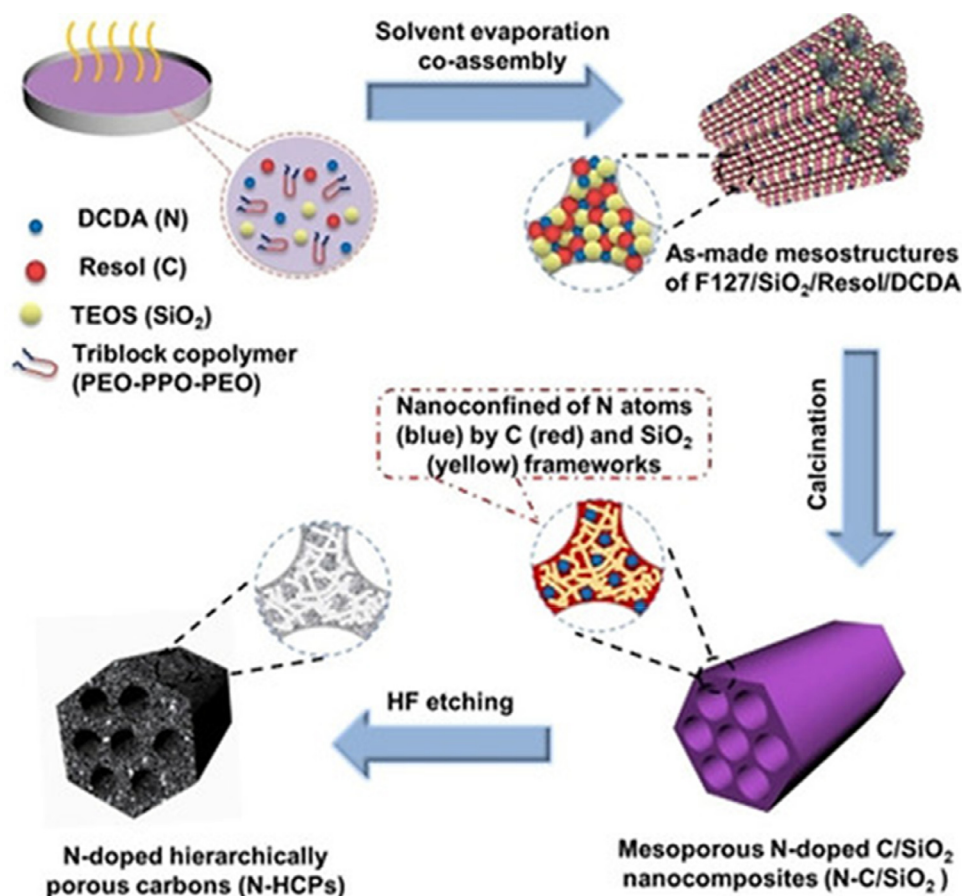
those of the HCN-800 ( $162.3 \text{ F g}^{-1}$ ) and HCN-9000 ( $177.0 \text{ F g}^{-1}$ ) samples, based on electrochemical measurements [78]. Guo et al. fabricated hierarchical OMC/graphene composites rapidly in a simple way through EISA, thermopolymerization, and carbonization of the triblock copolymer F127, phenolic resin, and graphene oxide. The resulting OMC/graphene composites exhibited high specific capacitance ( $329.5 \text{ F g}^{-1}$ ) in 6 M KOH [79]. The Liu group synthesized hierarchically interconnected ordered micro- and mesoporous carbons (OMMCs) through a triconstituent co-assembly approach using F127, TEOS, and phloroglucinol/tetraphthalaldehyde. EISA and thermal treatment gave 3D polymeric arrays and with subsequent carbonization and HF-mediated removal of silica, afforded the OMMC [Figure 5(a)]. SEM and TEM images revealed that OMMC<sub>0.37</sub> possessed an ordered porous surface and an interconnected micro-mesoporous structure [Figures 5(b)–(e)] [80]. Furthermore, Sevilla et al. used a one-pot method to prepare highly hierarchical micro- and mesoporous carbon nanosheets having high surface areas ( $1390 \text{ cm}^2 \text{ g}^{-1}$ ) and thicknesses in the range of 40–200 nm through direct carbonization of sodium gluconate at elevated temperatures (700–900°C). These highly hierarchical micro- and mesoporous carbon nanosheets possessed high specific capacitances of 140 and  $100 \text{ F g}^{-1}$  in 1 M H<sub>2</sub>SO<sub>4</sub> and TEABF<sub>4</sub>/MeCN, respectively [81].



**Figure 6.** (a) Preparation of hollow NHCS-LM co-templated by PS-*b*-PEO and silica spheres and (b–e) corresponding TEM images. Reprinted with permission from Ref [86]. Copyright 2016 Royal Society of Chemistry.

#### 4. Hierarchical Nitrogen-Doped Mesoporous Carbon

The introduction heteroatom such as nitrogen into the ordered mesoporous carbons can enhance the electron donor character, surface polarity, electrical, field emission, semiconducting and mechanical properties of the carbon materials. N-doped mesoporous carbons (NMCs) have recently used in different potential applications such as catalysis, fuel cells, CO<sub>2</sub> capture and electric double-layer capacitors [82, 83]. Zhao et al. obtained N-doped and uniform mesoporous carbon materials through in-situ polymerization of urea-formaldehyde resin when they used poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) as the template. After pyrolysis of the bulk urea-formaldehyde resin blends with PS<sub>138</sub>-*b*-PAA<sub>171</sub> and PS<sub>230</sub>-*b*-PAA<sub>150</sub> as templates at 600°C under N<sub>2</sub> gas, TEM images revealed the pore sizes of the N-doped and uniform mesoporous carbons to be approximately 10 and 20 nm, respectively. Furthermore, these materials exhibited high surface areas, excellent CO<sub>2</sub> uptake, and high specific capacitances ( $239\text{--}252 \text{ F g}^{-1}$ ) [84]. Yamauchi et al. prepared highly ordered 2D hexagonal N-doped carbons in two steps: (i) self-assembly of triblock copolymer micelles of P123 with melamine/formaldehyde resins as nitrogen and carbon precursors and (ii) activation with KOH at high temperature. The ordered OMNCs possessed ultrahigh surface areas of up to  $2400 \text{ m}^2 \text{ g}^{-1}$  while maintaining mesoporous structures. The pore sizes of the OMNCs prepared at 700, 800, and 900°C were measured to be 2.7, 3.6, and 4.0 nm, respectively [85]. They also formed large tunable mesoporous (20 nm) nitrogen-doped hollow carbon spheres (NHCS-LM) from dopamine as the precursor and the diblock copolymer PS-*b*-PEO and colloidal silica as templates [Figure 6(a)]. TEM images [(Figure 6(b–e))] revealed that the average diameter of the central hollow cores and the average thickness of the porous shells of the NHCS-LM structures were 350 and 17 nm, respectively [86]. In addition, the Zhao group prepared N-doped OMCs having high surface areas ( $1741 \text{ m}^2 \text{ g}^{-1}$ ), large pore sizes (3.6–4.1 nm), large pore

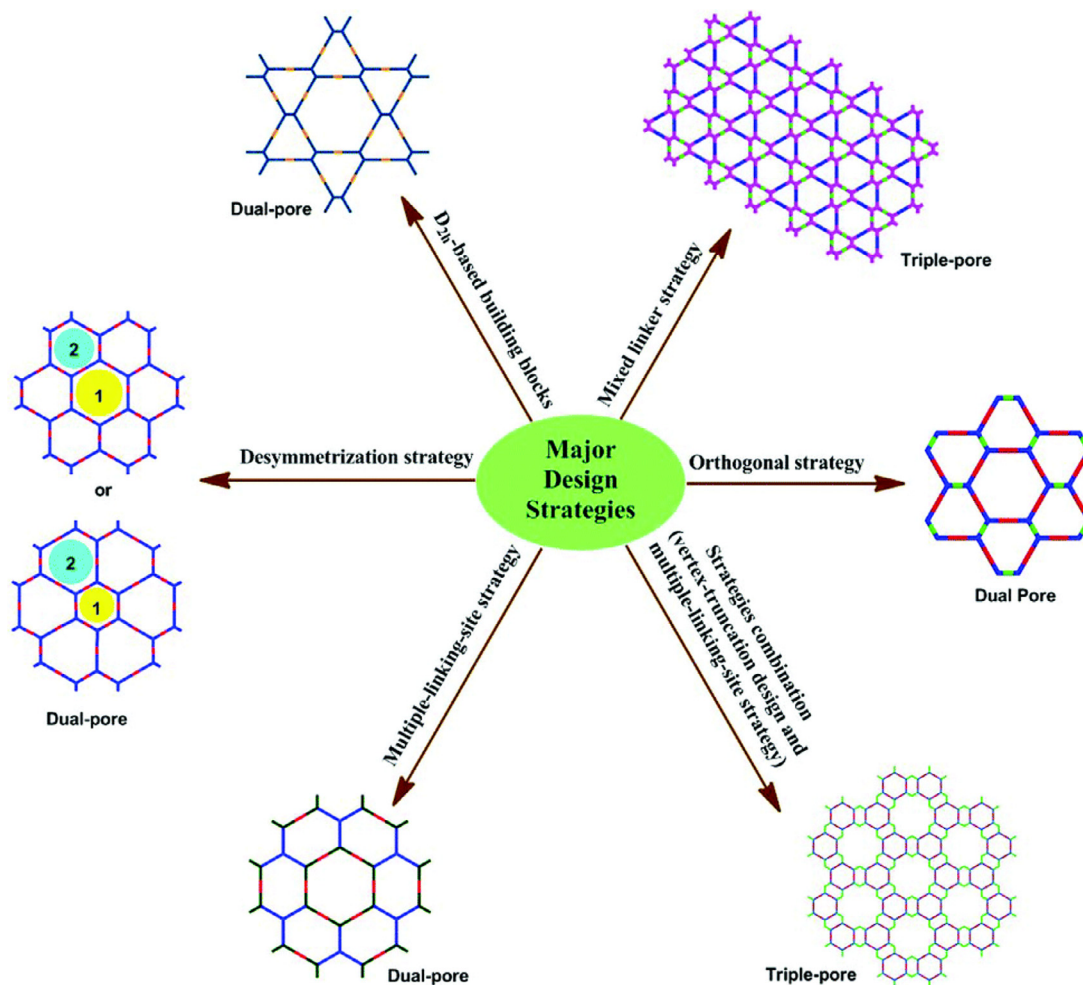


**Figure 7.** Preparation of N-doped hierarchically mesoporous carbons through multicomponent co-assembly of DCDA, resol, TEOS, and the triblock copolymer F127. Reprinted with permission from Ref [91]. Copyright 2019 John Wiley and Sons.

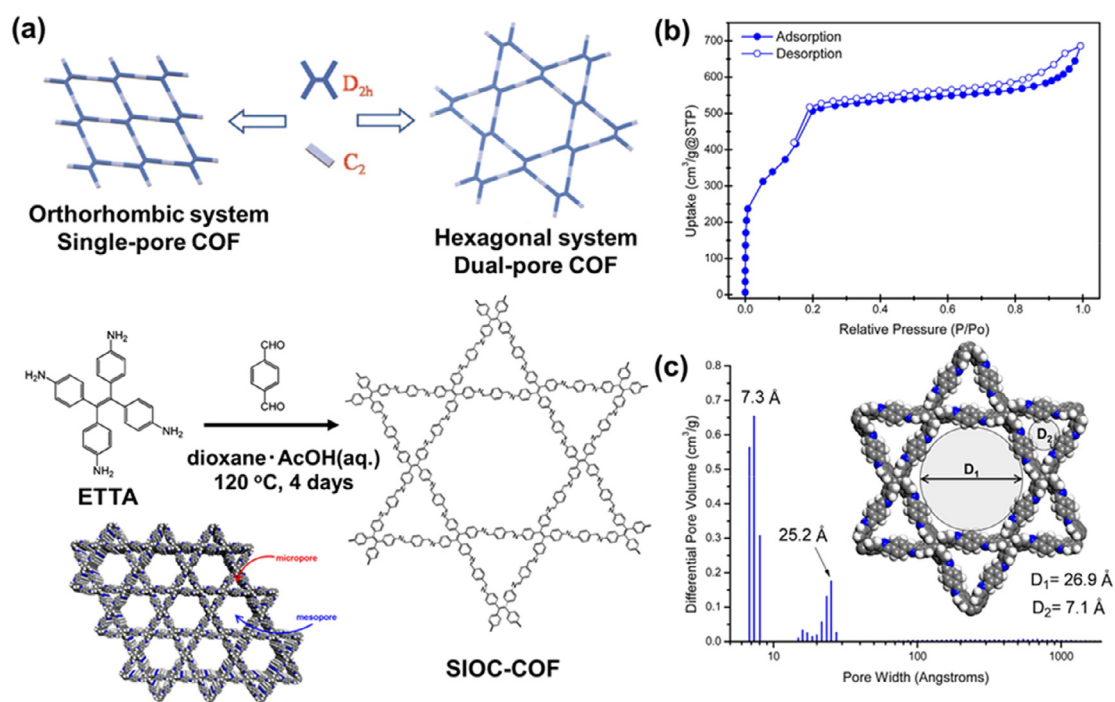
volumes ( $1.2\text{--}1.81\text{ cm}^3\text{ g}^{-1}$ ), and high nitrogen compositions (up to 15 wt %) when using SBA-15, resol, and cyanamide as the nitrogen dopant [87]. The group also fabricated hierarchical nanoporous nitrogen-doped carbon flakes (NNCFs) having a sheet morphology through a two-step process: (i) hydrothermal organic reaction assembly of P123 triblock copolymers and phenol-melamine/HMT resin (as nitrogen/carbon precursors) to afford the layered PMF-P123 precursors and (ii) subsequent carbonization. These materials possessed a bimodal mesopore size distribution and high surface areas, maintained the sheet morphology, and exhibited high specific capacitance ( $543.3\text{ F g}^{-1}$ ) [88]. Yamauchi and co-workers synthesized highly N-doped mesoporous carbon spheres (NMCSs) through a multistep process: (i) the self-assembly of PS-*b*-PEO and self-polymerization of DA, (ii) the reaction of the DA/PS-*b*-PEO composite micelles with NH<sub>3</sub> at 220°C to obtain PDA/PS-*b*-PEO composite spheres, and (iii) the activation at 800°C to afford NMCSs with large mesopores (16 nm) and particle sizes (200 nm) [89]. We have prepared ordered gyroid mesoporous and N-doped mesoporous carbon materials by using PEO-*b*-PCL (as a soft template) and resol resins to afford self-assembled resol/PEO-*b*-PCL mixtures which were subjected to calcination at 800°C to produce the OMCs and OMNCs, respectively. This N-doped gyroid mesoporous carbon exhibited a high CO<sub>2</sub> uptake of  $6.72\text{ mmol g}^{-1}$  at 0°C [90]. Zhao et al. synthesized rich N-doped hierarchically mesoporous carbons with ultrahigh specific surface areas through a facile multicomponent co-assembly method [Figure 7]. These N-HPC materials possessed uniform pore inter-penetrating micropores (1.3 nm), large mesopores (7.6 nm), and high surface areas ( $1960\text{ m}^2\text{ g}^{-1}$ ), which functioned as supercapacitor electrodes with high specific capacitance ( $356\text{ F g}^{-1}$  at  $0.5\text{ A g}^{-1}$ ) in KOH solution [91].

## 5. Hierarchical COFs

COFs are crystalline porous organic materials that possess periodic 2D and 3D network structures. These materials can be fabricated by linking organic building blocks through dynamic covalent chemistry (DCC). COFs have attracted great attention because their unique properties suggest potential applications in drug delivery, optoelectronic devices, energy storage, catalysis, and gas adsorption [92–101]. Many strategies have been developed to construct dual- and triple-pore COFs, including the use of mixed linkers, D<sub>2h</sub>-based building blocks, orthogonal desymmetrization, multiple-linking sites, and combination strategies, as displayed in Figure 8 [102]. Zhao et al. constructed the first heteropore COF (SIOC-COF) possessing dual pore sizes (hexagonal mesopores, trigonal micropores) through Schiff base condensation of 4,4,4,4-(ethene-1,1,2,2-tetrayl)tetraaniline (ETTA, as a D<sub>2h</sub>-symmetric monomer) and *p*-phthalaldehyde (as a C<sub>2v</sub>-symmetric monomer) in 6 M acetic acid in dioxane at 120°C for 4 days [Figure 9(a)]. They confirmed the dual pore sizes of SIOC-COF through (i) the matching of both the experimental and simulated powder XRD profiles for a dual-pore COF with eclipsed stacking (AA) and (ii) the N<sub>2</sub> adsorption/desorption isotherm exhibiting two modes [I and IV types; Figure 9(b)], attributable to the mesoporous and microporous structures having two narrow pore sizes distributions centered at 7.3 and 25.2 Å, respectively [Figure 9(c)] [103]. Bein and co-workers condensed ETTA with benzo[1,2-*b*:4,5-*b'*]-dithiophene-2,6-dicarboxaldehyde (BDT) to prepare Kagome-type heteropores (BDT-ETTA COF) that functioned as good photocathodes for water-splitting [104]. Furthermore, Zhao and co-workers combined 1,4-(bis(4-formylphenyl)amino)-[1,1'-biphenyl]-3,5-dicarboxaldehyde (BABB, as the C<sub>2v</sub>-symmetric monomer) with 1,4-diaminobenzene (DB) and benzidine (BZ) to synthesize high-fluorescence and high-quantum-yield

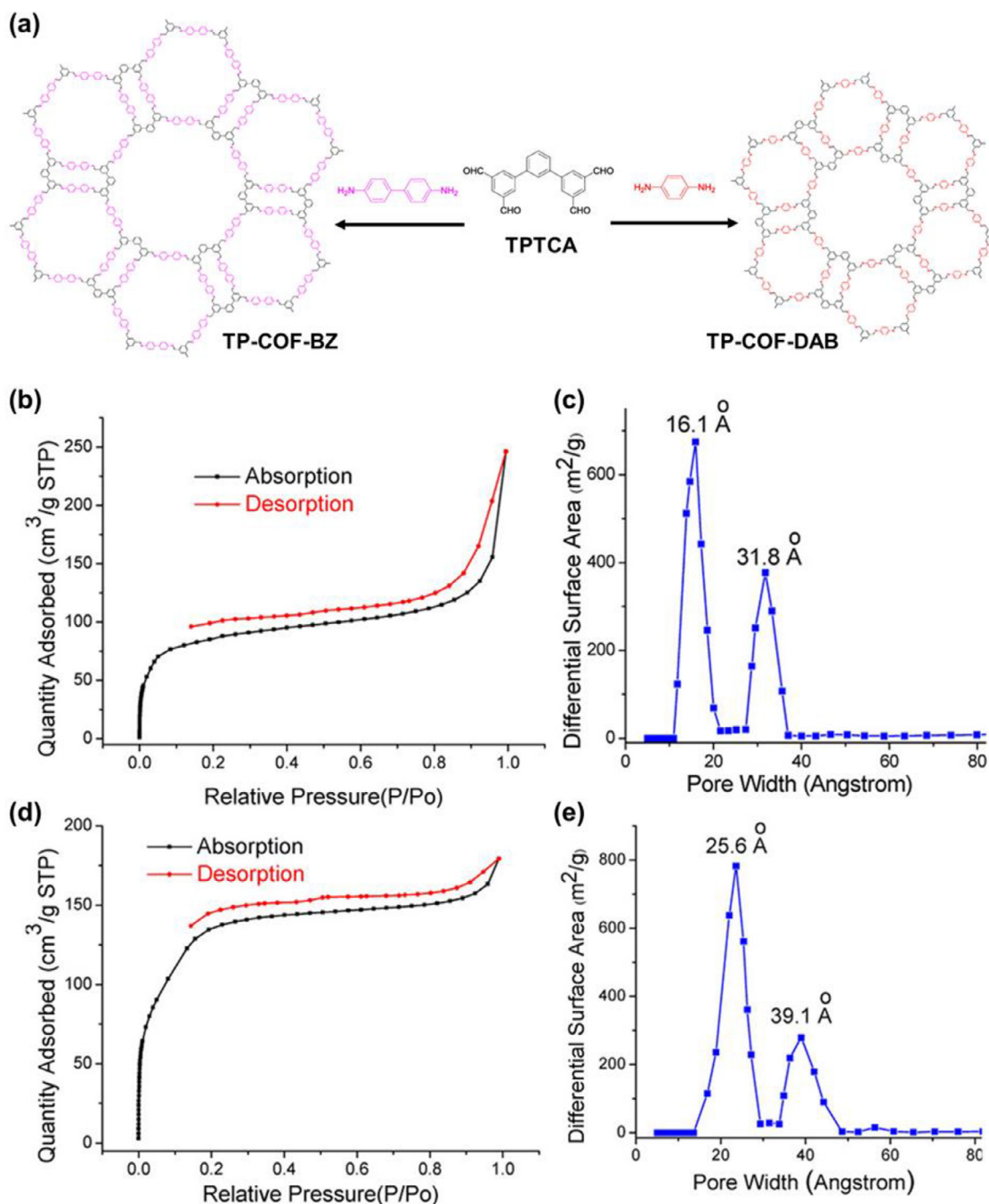


**Figure 8.** Summary the design approaches for the preparation heteropores covalent organic framework. Reprinted with permission from Ref [102]. Copyright 2018 Royal Society of Chemistry.



**Figure 9.** (a) Preparation, (b)  $N_2$  adsorption/desorption isotherms, and (c) pore size distribution curve of the Kagome structure of SIOC-COF. Reprinted with permission from Ref [103]. Copyright 2014 American Chemical Society.





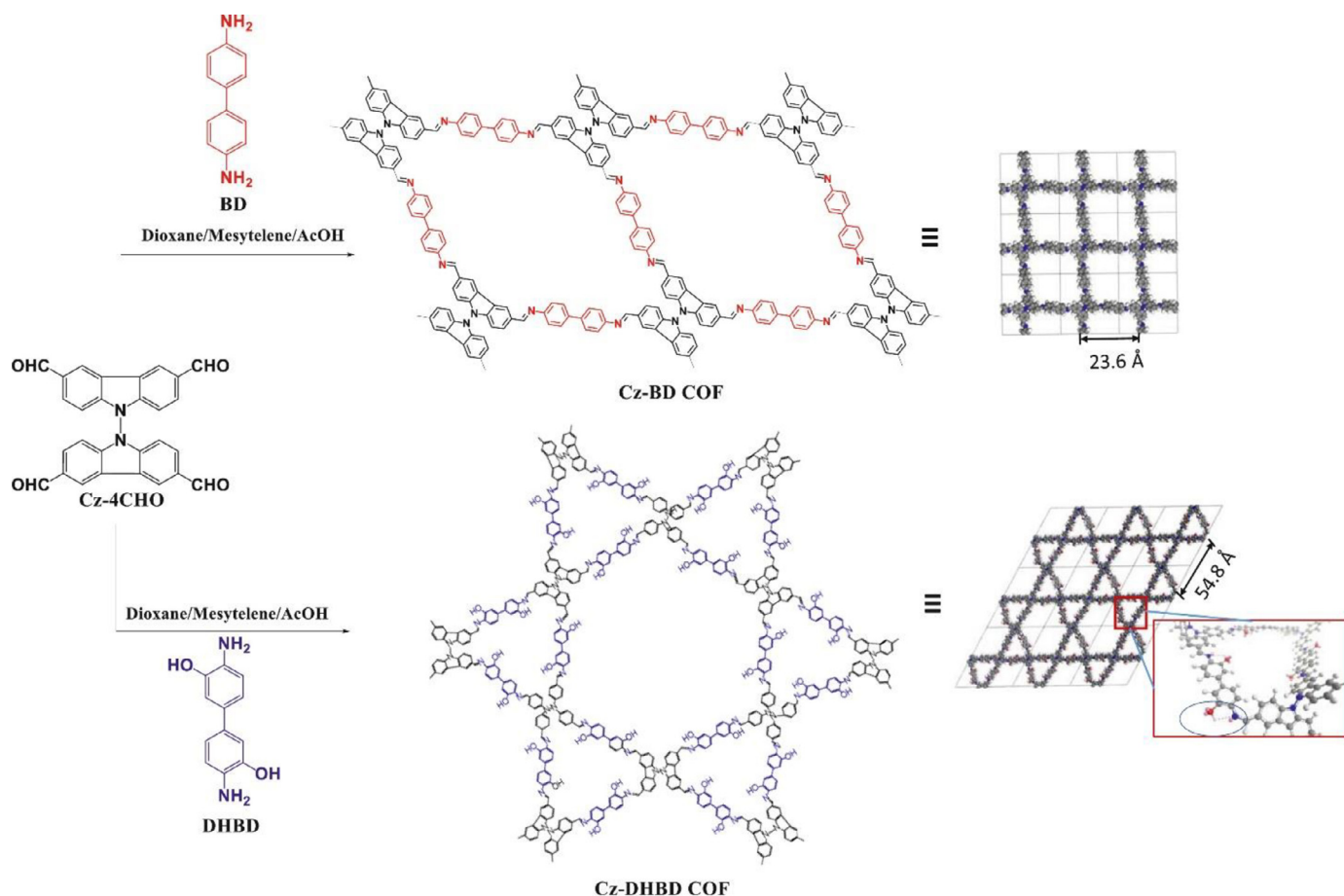
**Figure 10.** (a) Preparation of triple-pore TP-COF-BZ and TP-COF-DAB structures. (b, d) N<sub>2</sub> adsorption/desorption isotherms and (c, e) pore size distributions of (b, d) TP-COF-BZ and (d, e) TP-COF-DAB. Reprinted with permission from Ref [107]. Copyright 2017 American Chemical Society.

COF-BABD-DB and COF-BABD-BZ structures featuring two different kinds of pores and shapes. They used these two COFs as chemosensors for nitroaromatics [105]. Horike et al. prepared hierarchical structures with controlled domains of imine-linked covalent frameworks (COF-ph-Naph and COF-Naph-ph) through post-synthetic reactions and DCC to construct various domains having core/shell structures and good chemical and thermal stabilities [106]. Zhao et al. prepared heteropore COFs featuring three different types of hierarchical pores through the condensation of [1,1':3,1'-terphenyl]-3,3',5,5'-tetracarbaldehyde (TPTCA, as a C<sub>3</sub>-symmetric monomer) and core building with DB and BZ (as ditopic linear linkers) to afford TP-COF-BZ and TP-COF-DAD [Figure 10(a)]. N<sub>2</sub> adsorption/desorption measurements revealed BET surface areas of 518 m<sup>2</sup> g<sup>-1</sup> and pore size distributions of 25.6 and 39.1 Å for TP-COF-BZ and 302.78 m<sup>2</sup> g<sup>-1</sup> (16.1 and 31.8 Å) for

TP-COF-DAD [Figure 10(b-e)] [107]. Recently, we successfully prepared two new COFs (Cz-BD and Cz-DHBD) through the condensation reaction of 3,3',6,6'-Tetraformyl-9,9'-bicarbazole (Cz-4CHO) as a C<sub>2</sub>-symmetric knot with benzidine (BD) and N,N'-dihydroxybenzidine (DHBD) as C<sub>2</sub>-symmetric linkers [Figure 11]. We found that Cz-BD COF possessed a single type of pore having a tetragonal structure. While, Cz-DHBD COF possessing a Kagome structure featuring two types of pores. [108].

## 6. Future perspectives

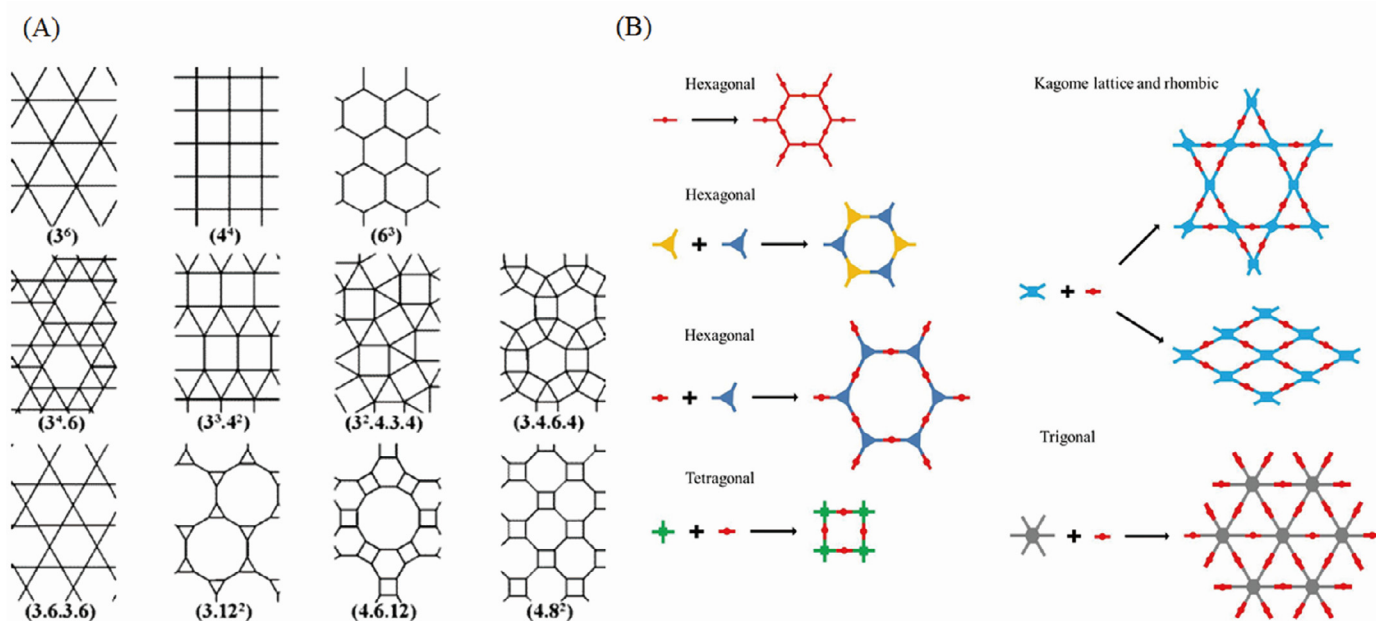
In these four hierarchically porous materials, the connection between these studies could be considered by using the Archimedean tiling patterns concept. We have known that 11 different



**Figure 11.** Preparation of Cz-BD and Cz-DHBD COFs. Reprinted with permission from Ref [108]. Copyright 2020 Elsevier.

Archimedean tiling patterns within the most regular two-dimensional tiling manner as displayed in Figure 12(A) [109], which were generally observed only for ABC star polymers. However, Matsushita et al. have reported that the blending of block copolymers also could

form these hierarchical two-dimensional nanostructures through intermolecular hydrogen bonding interaction. For example, they used PVPh-*b*-PMMA diblock copolymer blending with PI-*b*-PS-*b*-P2VP star polymer displaying the [4.8.8] Archimedean tiling where



**Figure 12.** (A) The common eleven Archimedean tiling patterns from block copolymer [109] and (B) the topology diagrams representing the general basis for COF structure. (Reprinted with permission from 2007 American Chemical Society).

the PVPh/P2VP domain with intermolecular hydrogen bonding interaction [110]. As a result, the block copolymer mixtures [111–115] as templates to form these Archimedean tiling patterns and then form the hierarchically mesoporous materials [116–117] is the next challenge topic.

Furthermore, Figure 12(B) displays several typical approaches to construct COFs with different topologies through mediated the building units. The resulting COF topology could be determined theoretically by the geometry and dimensions of building units, which is unique compared to other porous materials. Based on Figure 12(B), we could observe that these COF topology could be assigned as [36, 44, 63] and [3,6,3,6] Archimedean tiling patterns [118–119] and thus the development of new COF topologies based on the Archimedean tiling patterns as displayed in Figure 12(A) is also the next challenge topic for COF materials [120].

## Conclusions

In this Review, we discuss recent progress made in the preparation, properties, and possible applications of four types of hierarchically ordered meso/microporous materials: mesoporous silica, mesoporous phenolic/carbon, N-doped mesoporous carbon and mesoporous COFs. The construction of these hierarchically meso/microporous materials has received much attention from both academia and industry because, when compared with ordered mesoporous materials, they can exhibit interfacial transport, provide large surface areas for reactions, minimize diffusion barriers, possess tunable pore structures, improve mass transport and provide ready accessibility for guests. As a result, the materials discussed in this review have many diverse potential applications in many fields like energy storage and conversion, photocatalysis, drug delivery, and CO<sub>2</sub> uptake.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests

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## Supplementary materials

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jtice.2020.06.013.

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