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ARTICLES

"Host—Guest" Chemistry in the Synthesis of Ordered Nonsiliceous Mesoporous Materials

YING WAN, HAIFENG YANG, AND
DONGYUAN ZHAO**Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China*

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ABSTRACT

On the basis of the consideration of "host—guest" chemistry, the interactions between guest molecules are highlighted in the synthesis of nonsiliceous mesoporous materials by the "soft-template" and "hard-template" approaches. A generalized "acid—base pair" concept is utilized in selecting appropriate guest molecules to prepare highly ordered mesoporous metal oxides, phosphates, and borates with diversified structures. Mesoscopically ordered polymer and carbon frameworks with uniformly large pore sizes are derived from the self-assembly of an organic surfactant with an organic guest. Properly building the guest unit and decorating the host are important in replicating ordered nonsiliceous single-crystal nanoarrays. Outlooks on the potential possibilities for synthesizing ordered mesoporous nonsiliceous materials are presented as well.

1. Introduction

The invention of a surfactant self-assembly approach for the fabrication of highly ordered mesoporous silicates by Mobil's scientists¹ has led to a series of interesting research

Ying Wan completed each of her academic degrees in industrial catalysis from the East China University of Science and Technology, receiving her Ph.D. in 2002 with Professor Jianxin Ma. Then, she joined Shanghai Normal University as an Associate Professor. She is currently a postdoctoral member in Fudan University working with Professor Dongyuan Zhao on mesoporous carbon molecular sieves in catalysis and electrodes.

projects that have stimulated the growth of a large international community focused on mesostructured materials.^{2–4} With attractive properties, such as large surface areas, uniform pore sizes, and tunable periodic structures, mesoporous silicates are, without a doubt, one of the most promising candidates for the nanoreactors of large molecules,⁵ which are becoming a commercial necessity and will continue to grow in significance as the demand for oil outpaces production and bio-application.^{6,7} From the viewpoint of application, it is natural to find possible mesoporous materials composed of other components. These include important design features and manufacturing processes that are vital to a long-term success in the mesoporous solids technology. The intrinsic chemical and physical properties of nonsiliceous solids, in particular crystallites, together with the confined-space effects of their nanopores open up inestimable potential applications in optics, magnetics, electronics, mechanics, microdevices, and quantum dots.^{8,9}

With respect to the assembly technologies used in the preparation of mesoporous silicates,¹⁰ there are two challenging questions for material scientists: (1) Are the regeneralized assembly approaches for producing ordered

* To whom correspondence should be addressed. E-mail: dyzhao@fudan.edu.cn. Telephone: 86-21-6564-2036. Fax: 86-21-6564-1740.

Haifeng Yang received his B.S. and M.S. in chemistry from Northwest University in Xi'an, Shanxi, China. He obtained his Ph.D. in 2004 from Fudan University under the supervision of Professor Dongyuan Zhao. He is currently a postdoctoral member in Ecole Nationale Supérieure de Chimie de Mulhouse. His research includes the synthesis of periodic meso-/nanostructured materials and quantum computational chemistry.

Dongyuan Zhao received his B.S. and M.S. in chemistry from Jilin University. He obtained his Ph.D. in 1990 from Jilin University and Dalian Institute Chemical Physics. In 1992–1993, he was a visiting scholar at the Department of Chemistry, University of Regina and later carried out his postdoctoral research at the Weizmann Institute of Science (1993–1994), University of Houston (1995–1996), and University of California at Santa Barbara (1996–1998). He is now a Professor (Cheung Kong Professorship) in the Department of Chemistry at Fudan University. His current research interests include synthesis and property studies on ordered porous materials, such as mesoporous materials, zeolites, and coordination polymers.

nonsiliceous mesoporous materials, especially in the case of multicomponent and three-dimensional (3D) channels? (2) Are there versatile methodologies to generate crystalline mesostructures?

Today, there are many types of assembly technologies, but surfactant self-assembly and confined-space growth have been generally used to solve the above problems.⁸ Mesoscopic self-assembly is a construction of atoms, ions, molecules, and/or nanoclusters into ordered arrays and patterns by weak noncovalent bonds such as hydrogen bonds, van der Waals forces, and electrovalent bonds. Instead of a simple superposition of the weak interaction, an integrated and complicated synergistic reaction facilitates the process. An organic surfactant template here serves as a host, and a cooperative assembly between the host and guest is involved. In a process of confined-space growth, a host material possesses a mesoscopically topological structure and an assembly of the guest is restricted to the confined space in the host. A true replication of the guest from the host depends upon either the interactions between them or the outside forces (e.g., capillary force, electrical force, etc.). A generalized template concept includes not only the confined-space growth but also the surfactant self-assembly. Mesoscopic surfactant self-assembly and growth in the pore channels of molecular sieves can therefore be reckoned as “soft-template” and “hard-template” approaches, respectively.⁸ Both of them have been applied into fabricating nonsiliceous mesoporous materials. The interaction between the host and guest is certainly fundamental, but the interaction between the guests themselves should also be taken into account. Herein, we summarize the recent developments based on “host–guest” chemistry in the synthesis of ordered nonsiliceous mesoporous materials mainly by our group. Mesoporous metal oxides, metal phosphates, metal borates, and mixed metal oxides, which are obtained from an “acid–base pair” route, as well as polymer and carbon frameworks from an organic–organic assembly, are the instances of the “soft-template” approach. Moreover, several methodologies are addressed to replicate highly ordered nonsiliceous single-crystal nanoarrays by using the “hard-template” approach.

2. The “Soft-Template” Approach

The classical products from a surfactant assembly, which is based on the cooperative organization of an organic surfactant host and an inorganic guest, are mesoporous silicates.¹⁰ Numerous studies have been explored at least on the following three aspects: (1) rationally synthesizing mesoporous materials with desired components and structures, (2) investigating morphology, pore structures, and surface chemistry, and (3) implementing the physical and chemical properties into applications.

Research on nonsiliceous mesoporous materials, however, lags behind that of the mesoporous silicates, which were first attempted in 1994.¹⁰ The important success did not appear until the versatile evaporation-induced self-assembly (EISA) strategy, initially used in the preparation

of mesoporous silica thin films,¹¹ was introduced to synthesize ordered mesoporous metal oxides.¹² Semicrystalline frameworks were obtained where nanocrystallites nucleated within the amorphous inorganic matrices. Nevertheless, the compositions of ordered mesoporous oxides directly obtained from the EISA approach are still limited. Most oxides are disordered or hybrid-mesostructured, that is, more distinct for multicomponent mesoporous solids.¹² The reasons for this may arise from the complexity of reactive properties and chemical stability intrinsic in the desired constituents, as well as the difficult control of hydrolysis, polymerization, cross-linkage, and inorganic–organic assembly. Unlike the silicate precursors, few inorganic precursors can survive mesostructured inorganic–organic interactions. It is not general although several methods have been applied into controlling the hydrolysis of inorganic precursors, for example, relying on metal chlorides and coordination.^{12,13}

Organic precursors are even more complicated.¹⁴ Periodic organic mesostructures have been derived from organic–organic phases, such as phase separation^{14,15} and cross-linking lyotropic liquid crystal procedure.¹⁶ In the phase separation, the pore structure can be formed by etching or dissolving one block (A) from the assembled diblock copolymer (A–B).¹⁵ However, large porosities have rarely been reported. Moreover, template removal is also a hard task because the unstable frameworks may collapse during the calcination, owing to crystallization of the metal oxides or volume contractions and structural defects of the organics, resulting in disordered mesostructures.^{8,17} Previously, elaborate investigations on mesoporous materials were focused on understanding and utilizing the organic–inorganic (OI) interactions.¹⁰ A series of ordered nonsiliceous mesostructured solids (e.g., tungstate and molybdate) were prepared. However, the inorganic–inorganic (II) interaction and organic–organic (OO) self-assembly in the synthesis of highly ordered mesoporous materials are somewhat ignored. They are also issues of undeniable importance and crucial impact. A better understanding of the interaction between guest molecules is far more beneficial for careful regulation of the assembly. On the basis of the compatibility of acid and base precursors, an “acid–base pair” concept was set forth to accomplish the “self-modulation” of acidity in fabricating mesoporous metal oxides with various components under the nonaqueous systems.^{18,19} Very recently, an amphiphilic surfactant templating route for the preparation of ordered mesoporous polymers and homologous carbon was also presented following a similar strategy.^{20–22}

2.1. “Acid–Base Pair” Concept in Guest Constitution.

Titanium oxides are one of the largest research areas in semiconductor photocatalysts, which offer the advantages of cleaner and quieter power generation while utilizing solar energy. This kind of material has already been prepared via various methods by using different templates and/or TiCl_4 as the precursor.^{12,23} However, the main limitations are the long synthetic period (>1 week) and the less ordered structural regularity compared to their

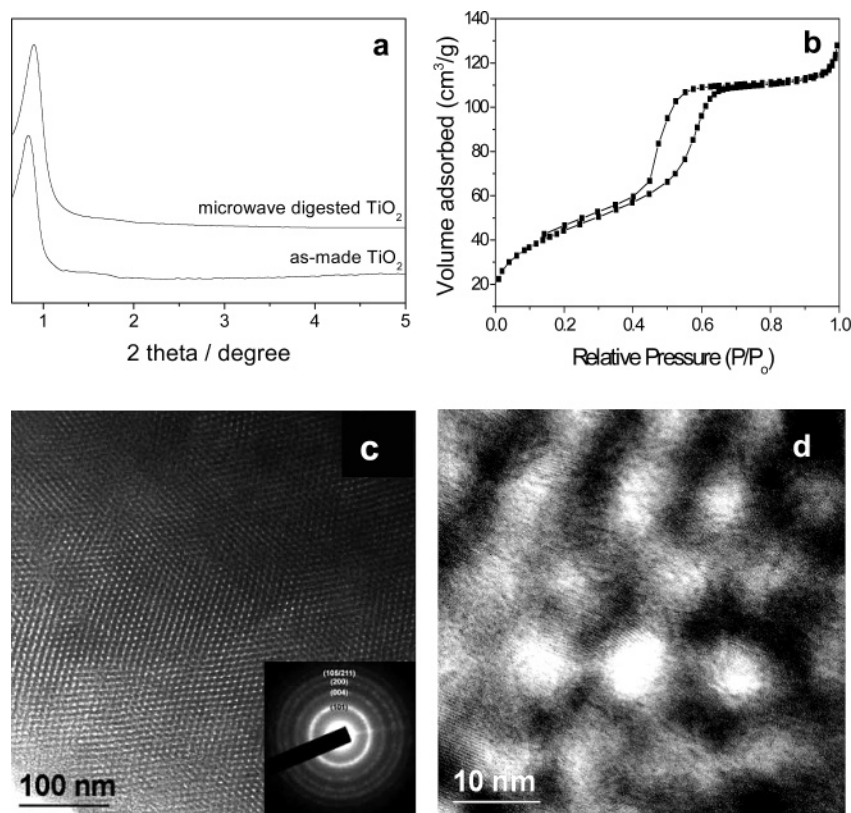


FIGURE 1. (a) XRD patterns of as-made and MWD mesoporous titania. (b) N₂ adsorption isotherms. (c) TEM image and (d) HRTEM image of calcined mesoporous titania templated by triblock copolymer P123. The inset in c shows the electron diffraction pattern of the same hexagonal area. The data were reproduced with permission from ref 19. Copyright 2002, Royal Society of Chemistry.

silica counterparts, which are related to the destructive cross-linkage of the titania framework by the large amount of HCl generated from the hydrolysis of TiCl₄. In combination with the detailed and complete studies on EISA-based synthesis of titania thin films¹³ and sol-gel chemistry, the acidity of the precursor solution is believed to be one of the essential factors in the entire process of preparing mesoporous titania under the nonaqueous system.¹⁹

A mixture of titanium alkoxide and TiCl₄ serves as precursors, with the former being the main titanium source and the latter being the pH “adjustor” and hydrolysis–condensation “controller”. In comparison with the synthesis from a single titanium source, namely, TiCl₄, the acidity of the precursor solution is significantly and controllably reduced by the addition of titanium alkoxide, which decreases the amount of TiCl₄ and neutralizes the acid. The added metal alkoxide is also an extra oxygen donor. Therefore, the cross-linkage and gelation of inorganic guest molecules may be easier and better. It shortens the synthetic period, improves the thermal stability, hence, maintains the mesostructure, and facilitates the crystallization. Ordered hexagonal mesoporous titania with a large uniformed pore size of about 4.0 nm and a high surface area of 240 m²/g was obtained from triblock copolymer P123 (EO₂₀PO₇₀EO₂₀) (Figure 1). TEM images show that the mesoporous titania have a large domain regularity with a semicrystalline wall. Significantly, the simple neutralization concept in the “acid–base”

chemistry principle and the appropriate acidity self-adjusted by the guest pairs are introduced. On the basis of lots of experimental observations, this versatile and valid approach can be used as an “acid–base pair” concept for guiding the selection of precursors.¹⁸ The “acid–base” synthesis route can also be used for the synthesis of microporous zeolites, for example, microporous aluminophosphates.²⁴ This concept, together with the increased understanding on the EISA strategy, sol-gel chemistry, and host–guest interaction, which are interdependent of each other, will pave the way for preparing ordered mesoporous nonsiliceous materials.

As depicted in Figure 2, an “acid” mineral precursor is designed to couple with a “base” counterpart, forming the “acid–base” pair. The pair not only generates a proper acidic medium by tuning the ratio of “acid” to “base” precursors for both the “host–guest” assembly and the gelation of inorganic precursors but also is crucial for the homogeneous mineral compositions within the whole framework. For assembling ordered mesostructures, normally the “acid–base” pairs formed from strong “acid” and strong “base” or strong “acid (base)” and medium “base (acid)” in nonaqueous media are required, which can be applied in the formation of homogeneous multi-component inorganic guest precursors. Routes A, B, and E are reminiscent of the well-known nonhydrolytic sol-gel process, which produces molecular homogeneous oxides, and routes C and D are similar to the synthesis of mesoporous silicates or mesostructured metal chalc-

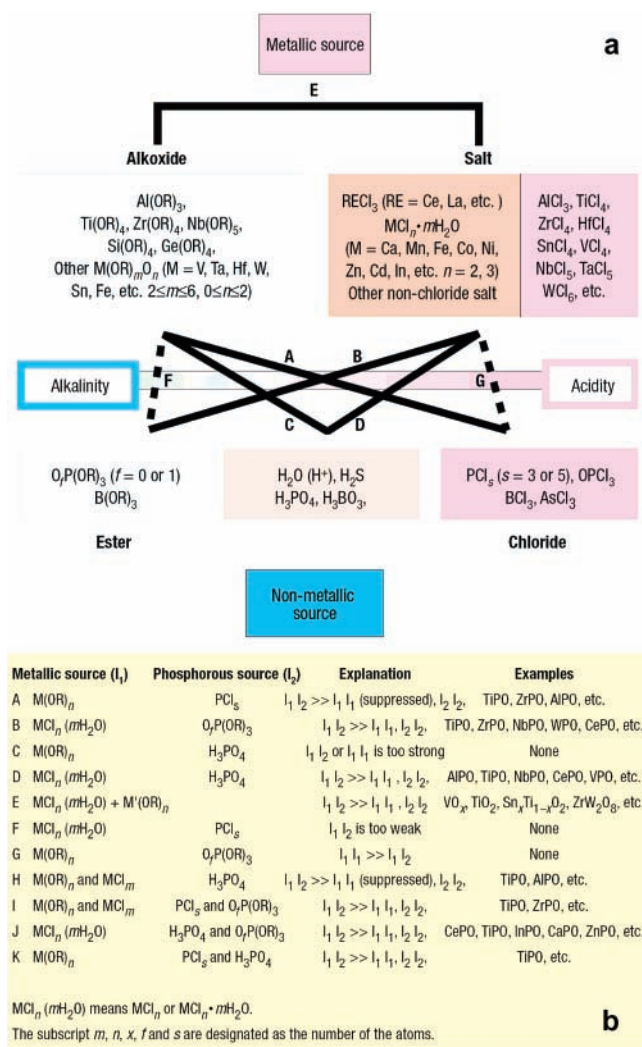


FIGURE 2. (a) General scheme of the “acid–base pair” concept and guided synthetic routes for mesoporous minerals. Five fundamental (A–E) acid–base pair connections between metallic and/or nonmetallic sources. For convenience, nonmetallic alkoxides such as $Si(OR)_4$ and $Ge(OR)_4$ (where R is a short-chain alkyl such as CH_3 , C_2H_5 , C_3H_7 , and C_4H_9) are listed in the metallic alkoxides column. Routes F and G (dashed lines) are forbidden. (b) Syntheses of various mesoporous metal phosphates through fundamental routes A–E and their derivatives. This figure was adapted from Tian et al.¹⁸ Copyright 2003, Nature.

genides and microporous aluminophosphates, while routes F and G are experimentally proven to be less effective with poor function.

To assemble a multicomponent ($I_1 I_2$) composite, it is necessary to match acid–base interactions of the various species presented during nucleation of the mesostructured phases in the order of the interaction $I_1 I_2 \gg I_1 I_1, I_2 I_2$ and $O(I_1 I_2) \gg OI_1, OI_2$ (Figure 2b). For example, in the synthesis of TiPO, the starting precursors can be $TiCl_4$, $Ti(OC_3H_7)_4$ and $P(OC_2H_5)_3$, PCl_3 and the acidity can be well-managed by changing the $TiCl_4/P(OC_2H_5)_3$ or $PCl_3/Ti(OC_3H_7)_4$ ratio. Beginning with a $PCl_3-Ti(OC_3H_7)_4$ pair as the guest and triblock copolymer P123 as a host, the interactions between Ti and P oxide species are stronger than those between Ti–Ti and P–P species, resulting in a 2D hex-

agonal mesostructure (Figure 3). N_2 -sorption measurements show that the ordered mesoporous TiPO displays a narrow pore size distribution with 5.4 nm and a BET surface area of around $220 \text{ m}^2/\text{g}$. When the P123/(Ti + P) (host/guest) molar ratio is tuned, bicontinuous cubic $Ia\bar{3}d$ and unstable lamellar mesostructures can be modulated. Body-centered cubic mesoporous TiPO ($Im\bar{3}m$) can also be obtained by switching the template to F108 ($EO_{132}PO_{50}-EO_{132}$). Narrow pore size distributions are observed at the mean values of 5.4–9.8 nm.

On the basis of the “acid–base” route, aluminum organophosphonates (AOPs) were synthesized by using $(HO)_2OPCH_2PO(OH)_2$ and $AlCl_3$ with the initial molar Al/2P ratio of 1:0.75 in the presence of oligomeric surfactants and triblock copolymers. Two-dimensional hexagonal mesoporous AOPs can be obtained. The pore diameters can be varied from 3.3 to 9.2 nm.²⁵ Using the phosphorus trichloride–zirconium propoxide pair as inorganic precursors and triblock copolymers or alkyltrimethylammonium bromide as organic templates, mesoporous zirconium phosphates were prepared with surface areas between 78 and $177 \text{ m}^2/\text{g}$ and controlled pore sizes between 2 and 4 nm.²⁶

Thus far, a wide variety of mesoscopically ordered, large-pore, homogeneous and stable mesoporous metal oxides, mixed metal oxides, metal phosphates, metal borates, etc. have been successfully synthesized.¹⁸ Most of these mesoporous products possess semicrystalline pore walls and relatively high thermal stability. These materials show high surface areas, uniform pore sizes, and tunable periodic structures that may create fascinating chemical and physical properties.

2.2. Self-Assembly of the Organic Host and Guest. The “acid–base pair” concept has been successfully demonstrated in selecting precursors to design and control the inorganic–inorganic interplays on the fabrication of mesoporous materials. It stimulates the understanding of organic guests to develop organic–organic self-assembly for preparing stable mesoporous organic frameworks.²¹ It is noted that disordered porous carbon networks can be transferred by pyrolysis of organic aerogels.²⁷ The open framework and tunable porosity impart carbon aerogel accessibility to metal ions and good contact with reactants, which are extremely important in the fields of catalysis, electronic devices, gas separation, etc. Can the ordered mesoporous organic framework directly transfer to its carbon counterpart? In fact, lots of research is currently ongoing to develop ordered mesoporous carbons.²⁸ However, only mesoporous carbon replicas were obtained by a mesoporous silica hard-templating method.²⁹ A unique amphiphilic surfactant-templating organic assembly approach was therefore applied to create organic mesoporous materials and homologous carbon with zeolite-like open frameworks via a well-controlled polymerization of the proper precursor.^{20–22}

Highly ordered mesoporous phenolic resin polymers can be fabricated by using the low-molecular-weight and soluble polymers of phenolic and formaldehyde as organic precursors and amphiphilic triblock copolymers as tem-

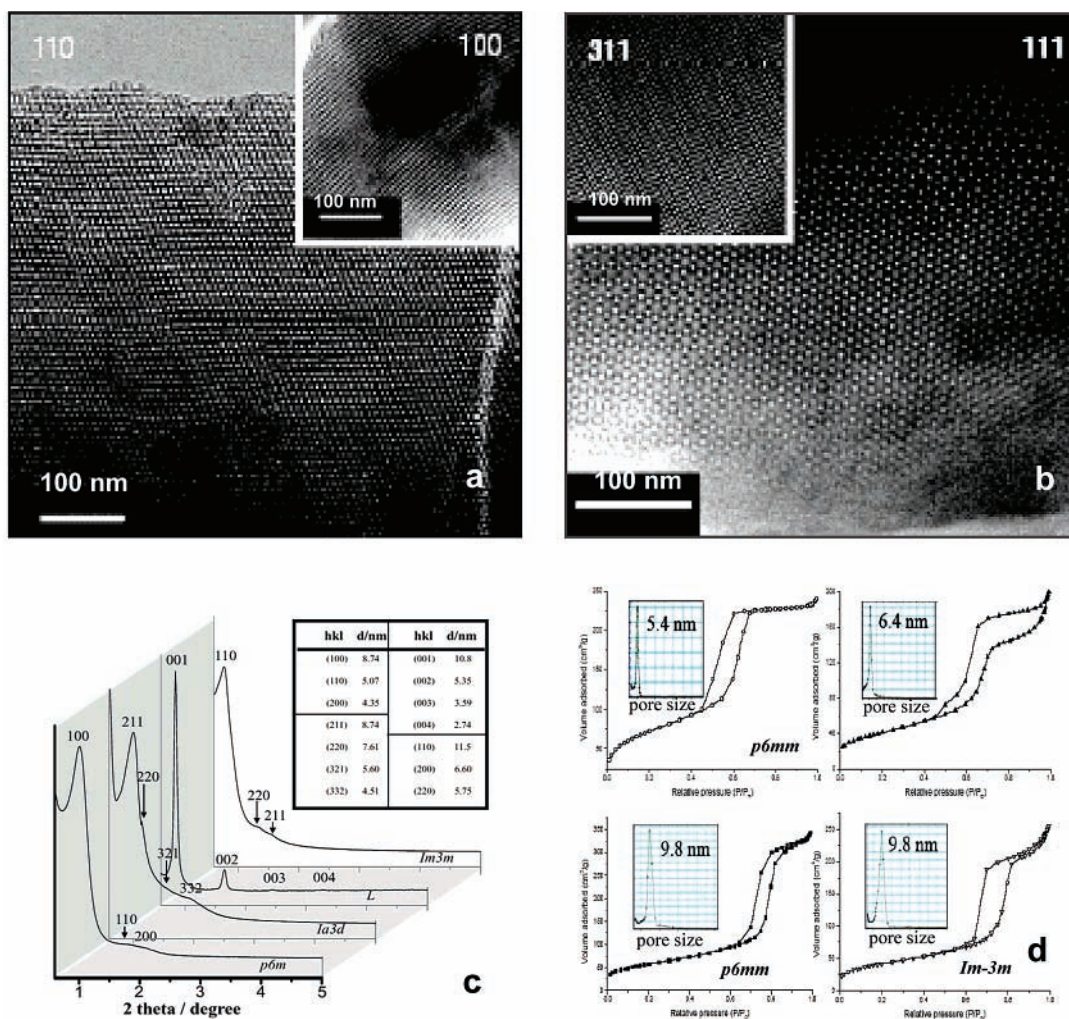


FIGURE 3. (a) TEM images of calcined hexagonal ($p6mm$) TiPO recorded along [110] and [100] directions. (b) Cubic bicontinuous ($Ia\bar{3}d$) TiPO along [111] and [311] directions. (c) XRD patterns and (d) N₂ adsorption isotherms of mesoporous TiPO with diverse structures. The insets in d are the pore-size-distribution curves. Data and images are reproduced with permission from ref 18. Copyright 2003, Nature.

plates via an EISA approach.²¹ Subsequent carbonization directly transforms the polymers to carbon counterparts. A schematic representation used in preparing the mesoporous polymers and homologous carbons is shown in Figure 4. The key issue for the successful organization of organic–organic mesostructures is the preformed polymer guest, which has plenty of hydroxyl groups and strongly interacts with the amphiphilic triblock copolymer host via hydrogen bonds. Furthermore, three- and four-connected benzene rings can be generated via covalent bonds, the same as the silicate in zeolites or/and mesoporous silicate molecular sieves. Upon solvent evaporation at room temperature and following thermopolymerization, the phenolic–formaldehyde resols further polymerize and condense to yield a rigid hydrocarbon network with long-range continuity, gradually forming a mesostructure. The amphiphilic surfactant can be easily removed by solvent extraction or calcination at 300–500 °C in N₂ (Figure 5). Consecutive cross-linking and polymerization during the calcination retain high carbon contents in the mesostructures. Similar to their inorganic counterparts, the mesoporous polymers have large uniform mesopores (>6.8

nm), high surface areas (~1100 m²/g), large pore volumes (~0.6 cm³/g), and tunable assembled organic mesostructures from the 2D hexagonal ($p6mm$) (FDU-15), the 3D caged cubic ($Im\bar{3}m$) (FDU-16), to the unstable lamellar structure (Figure 5).

The continuous hydrocarbon frameworks of mesoporous resins impart highly stable characteristics for the direct transformation to mesoporous homologous carbon frameworks by heating to 600–1400 °C under nitrogen (Figure 5). Both the structural and textural features such as mesostructures with various space groups, high surface areas (~1150 m²/g), narrow pore size distributions (>3.0 nm), and large pore volumes (~0.5 cm³/g) are inherited. The derived carbons with very thick walls (~7.0 nm) are the first example of molecular sieves that have extremely high thermal stability in the nitrogen atmosphere.

After we recall the manufacture of ordered mesoporous silicates, the assembly of organic surfactant host and inorganic guest in a dilute aqueous solution is now considered to be a facile, low-cost, and versatile approach, which has been demonstrated to be feasible in the industrial production. Bicontinuous cubic mesoporous

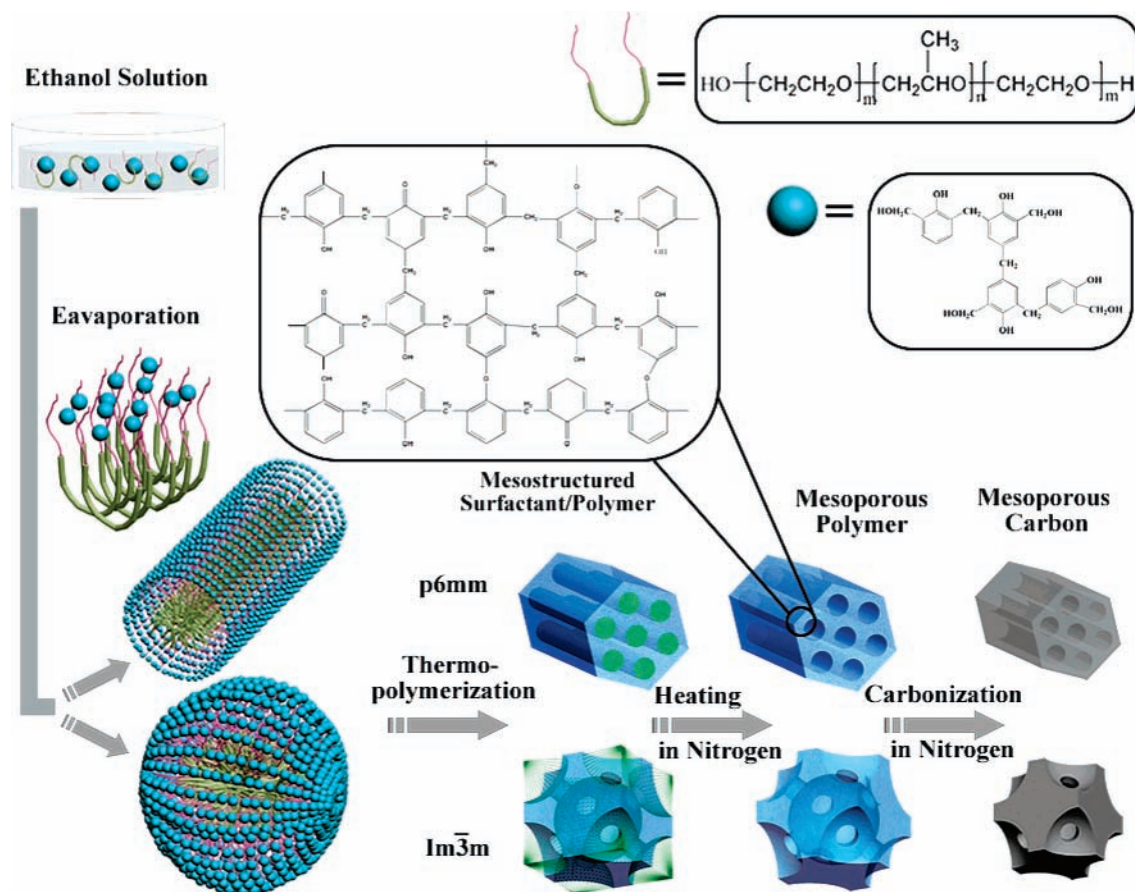


FIGURE 4. Schematic diagram of the synthetic procedure for mesoporous polymer and homologous carbon frameworks. This figure was adapted from Meng et al.²¹ Copyright 2005, Wiley.

polymer (FDU-14) and carbon (C-FDU-14) with $Ia\bar{3}d$ symmetry can also be prepared in an aqueous medium.²² The preformed resols first cooperatively assemble with the triblock copolymer P123, leading to a block-copolymer-resin (host-guest) mesophase in the dilute solution at a pH value of about 8.5. Further polymerization and carbonization direct the mesoporous polymer and homologous carbon molecular sieve to a desired mesostructure (Figure 6).

3. The "Hard-Template" Approach

The "hard-template" approach is a confined-space assembly, in which the growth of a "guest" is restricted to the surface, cages, channels, and substrate of a "hard host". Perfectly replicating the topological structure of the host derives the guest replica.²⁹ In particular, the Au-silica mesostructured superlattice thin film is a model of the hard-template approach, which is templated by gold nanoparticles.³⁰

Using ordered mesoporous silica materials as hard templates, a nanocasting process can be carried out to obtain replicated mesostructures constructed by nanorod, nanowire, or nanotube arrays.⁸ The most fascinating success is the replication of mesoporous carbon materials.²⁷ However, other inorganic replicas are not as successful that normally consist of disordered nanowires or nanoparticles without long-range periodicity owing to the

partial loadings of precursors inside the mesopores and the fast growth of guest molecules outside the mesopores. How to promote the filling of guest into the hard host is therefore an urgent task. Accurate control of the interaction between the hard host and guest or the guest molecules themselves will certainly facilitate the "host-guest" assembly process.²⁹

Recently, we summarize the work about the synthesis of the replicated mesostructures prepared by the hard-template approach of mesoporous silica.²⁹ Evidently, molding the hard hosts with designed properties, decorating the hosts to improve "host-guest" interactions, and building the guest units are all essential in the hard-template approach.

3.1. Molding the Host. Frequently, used inorganic hard templates are anode porous alumina,³¹ mesoporous silica, etc.^{8,29} The latter is advantageous because of the flexibly modulated structures, textures, and morphology. A large variety of silicate periodic mesostructures have been synthesized by using various surfactants as the structure-directing agents (SDAs), adding organic swelling substances and inorganic salts, as well as adjusting synthetic parameters.^{1-3,32} Extending research on constructing mesopores and controlling morphologies offers the opportunities in generating the mesotunnels on the pore walls of SBA-15, enlarging the window size of FDU-12 to more than 20 nm and the pore size to 27 nm,

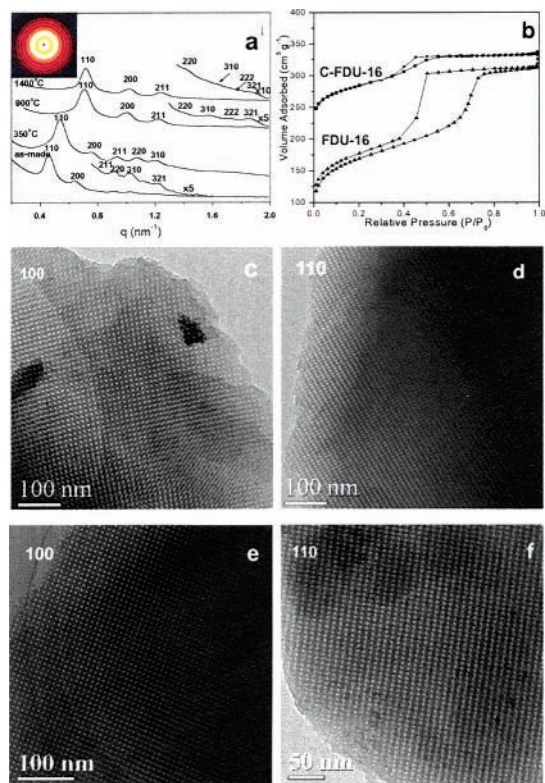


FIGURE 5. (a) SAXS patterns of mesoporous polymer FDU-16 and mesoporous carbon C-FDU-16. The reflection peaks can be indexed as (110), (200), (211), (220), (310), (222), and (321) of the body-centered cubic space group ($Im\bar{3}m$). The inset is the 2D SAXS pattern of FDU-16. (b) N_2 adsorption isotherms of FDU-16 and C-FDU-16. (c and d) TEM images of FDU-16 recorded along [100] and [110] directions. (e and f) TEM images of C-FDU-16 viewed along the same directions. Data and images are reproduced with permission from ref 21. Copyright 2005, Wiley.

respectively, as well as molding the solid shapes, including thin films, spheres, rods, single crystals, monoliths, fibers, etc.^{33,34}

3.2. Decorating the Host. Filling the guest molecules inside the channels of the host is important for nanocasting. The main driving force of a guest entering into a host comes from the capillary force. However, the interaction of the inorganic precursor with the mesopore surface is also a fundamental point. If the contact is too weak, a partial loading is the result, thus producing disordered nanowires or nanoparticles. On the contrary, orifice growth of the guest occurs in the case of extraordinary interplay, which blocks further guest transportation. As reported previously, both the silanols located on hollowed-out mesopore walls and the copolymers in surfactant/silica hybrid materials can coordinate with the guest molecules.^{28,29}

Silanols ($\equiv\text{Si}-\text{OH}$) located on the pore walls of mesoporous silicates are noticeable in attracting guest molecules, which participate in the formation of hydrogen bonds with H atoms and the electron-negative atoms (e.g., oxygen atoms) of the guest precursors, as well as the chelation with metal ions in the guest precursors. When more silanols on the pore walls are retained, the stronger interaction between the host and guest may occur. In

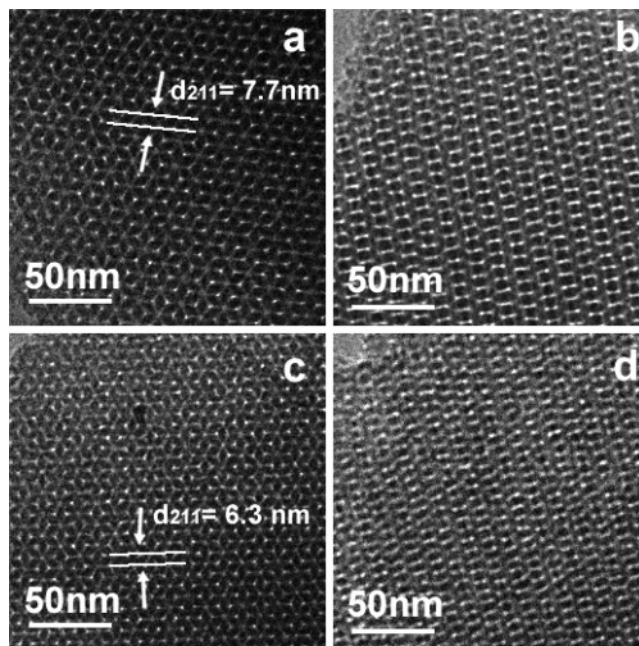


FIGURE 6. TEM images of FDU-14 (a and b) and C-FDU-14 (c and d) viewed along [111] (a and c) and [311] (b and d) directions. This figure was adapted from Zhang et al.²² Copyright 2005, American Chemical Society.

contrast to calcination, the microwave-digested (MWD) technique is facile and effective in removing the surfactant without sacrificing the silanols on pore walls and distinct framework shrinkage.³⁵ The surfactant in the mesopores can be totally oxidized by a mixture of HNO_3 and H_2O_2 . It is reasonable that the MWD silicates with large pore volumes, high surface areas, and, the most important of all, abundant silanols serve as the ideal hosts for nanocasting replicas.

Normally mesoporous silicates with small sizes of 1D channels, such as MCM-41, are thought to be unsuitable for preparing mesoporous carbon, probably because of the lack of complementary micropores within the silicate walls in contrast to SBA-15.³⁶ However, mesoporous carbon, constructed of ordered hexagonal-packed carbon nanowire arrays with a small diameter around 2.2 nm, can be replicated from a MWD MCM-41 host.³⁷ It can be attributed to the unique microwave radiation in the strongly acidic and oxidative system under a high pressure, where the siliceous framework may undergo local structural evolution, e.g., recondensation and reconstruction. The process causes some disordered meso/micro-tunnels on the pore walls, which are important for the assembly of self-supported ordered carbon nanowires. As evidence, the adjacent carbon nanowires are connected by irregular rods.³⁷ Besides that, the preserved rich silanol groups on the mesopore walls offer better inclusion and contact between the host and guest, which provide strong binding sites for sucrose and facilitate the transcription of the silica structural details, for example, connecting tunnels, to carbon.³⁷

The combination of hollowed-out mesopores and abundant silanol groups enables the general synthesis of mesostructured metal oxides and sulfides within the

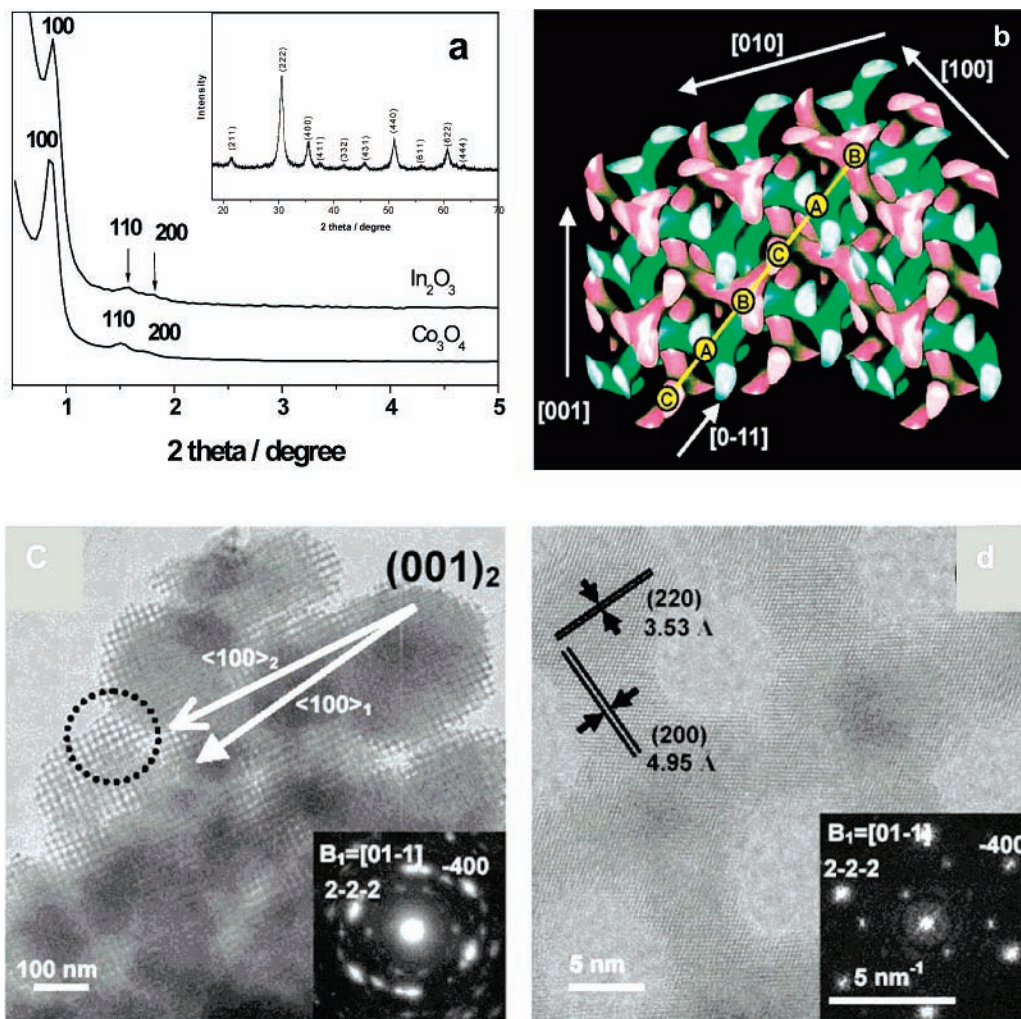


FIGURE 7. (a) Small-angle XRD patterns of In_2O_3 and Co_3O_4 nanowire arrays replicated by MWD SBA-15. The inset is the wide-angle XRD pattern of an In_2O_3 nanowire replica material. (b) Model of the bicontinuous cubic mesostructure model with $Ia\bar{3}d$ symmetry. (c) TEM image of single-crystal In_2O_3 nanowire arrays with $I4_32$ symmetry from a template of FDU-5. (d) HRTEM image of the circled area. The insets in c and d are the corresponding SAED patterns. The arrows in c represent the $\langle 100 \rangle$ plane directions of the micro- and mesostructures, and the arrows in d show the distance of the In_2O_3 single crystal along the (220) and (200) directions. Data and images are reproduced with permission from refs 29 and 38. Copyright 2005, Royal Society of Chemistry, and copyright 2004, American Chemical Society.

channels and cavities of mesoporous silicates. The host-guest incorporation is easily achieved by mixing the silica powders with the alcohol solutions of conventional metal salts. After the solvents were naturally evaporated and the silica hosts were dissolved, highly ordered metal oxide nanowire arrays can be replicated with various components including Cr_2O_3 , Mn_xO_y , Fe_2O_3 , Co_3O_4 , NiO , CuO , WO_2 , CeO_2 , and In_2O_3 (Figure 7). The second-generation mesostructures can also vary from hexagonal-packed nanowire arrays ($p6mm$), 3D bicontinuous nanowire arrays ($Ia\bar{3}d$), to nanosphere arrays ($Im\bar{3}m$) derived from SBA-15, FDU-5 or KIT-6, and SBA-16, respectively.^{38,39}

Considering the chelation between metal ions and $-\text{O}-$ groups in the block copolymer, a one-step nanocasting process is designed to fabricate the ordered mesoporous silica monolith with nanocrystals inside the channels.⁴⁰ The mesophase of the copolymer can be substantially maintained in a certain concentration range

of the metal ions, and the resulting complex can assist in the assembly.

It is interesting that a mutual effect can occur between the host and guest. Their roles during the assembly can be exchanged. A metal complex formed in the micelles of the block copolymer primarily serves as the soft template to direct the mesoporous silicate guest through cooperative assembly and assists in dispersing and transferring the inorganic metal salt precursor. The following pyrolysis of inorganic salts to metal oxide nanocrystals can be assigned to the guest growth in the mesopores of silicate host upon removal of the surfactant by calcination. Assembly in the confined space of the mesoporous silica channels leads to the metal oxide nanocrystals with uniform size. Appropriate cases for this methodology are the low-melting-point metals.⁴⁰ For example, indium metal clusters can be generated by the pyrolysis of indium nitrate and the reduction from copolymer decomposition. The low-melting-point indium clusters (lower than 160

°C) can easily diffuse inside the 1D channels of the mesoporous silicate monolith host and then aggregate to indium nanowires. Once the temperature rises to 400–500 °C, the oxidation occurs, forming a single-crystal In_2O_3 guest. Ordered mesostructure and atomic periodicity of the single crystal exist simultaneously.

3.3. Building the Guest Unit. The greater tendency toward migration inside the mesopore channels is found in the precursors to the van der Waals force or noncovalent bonds such as hydrogen and coordination bonds. The interaction plays a further role in interlinking the stable framework during the annealing stage.

Mesoporous graphitized carbon is the first example of building the guest units. It is well-known that the electrical and adsorption properties of carbon materials are closely related to their graphite nature. However, until now, mesoporous carbons with graphitized structures have remained an attractive topic for researchers, and facile synthetic routes are anticipated. A method of one-step melt-impregnating mesophase pitches (MPs) inside the mesopores of silica host is demonstrated to replicate the mesoporous carbon with a graphitized structure at a low temperature.⁴¹ MPs are derived from polyaromatic systems and generally form polydomain liquid crystals constructed by well-stacking layers of carbon rings. The π - π stacking between the molecular units of MPs keeps the incorporating process in a continuous fashion, leading to a perfect packing of MPs in the pores.^{41–43} Etching the silica host results in a true replica of the 3D bicontinuous cubic mesostructure ($Ia\bar{3}d$) with the complicated graphitized orientation. Hexagonal mesoporous carbon can be replicated from a mesoporous silica SBA-15 template. The guest is composed of graphitized domains with a (002) crystallographic plane perpendicular to the long axis of carbon nanorods.

The active interaction during the annealing process occurs in the nanocasting procedure of mesoporous silicon carbides.⁴⁴ Silicon carbides are a kind of non-oxide ceramic with unique mechanical and functional characteristics. However, because of the high formation temperature, ordered porous SiC solids are very difficult to be obtained.⁴⁵ Recently, highly ordered mesoporous silicon carbides with high surface areas of about 720 m^2/g , large pore volumes of about 0.8 cm^3/g , and extraordinary thermal stability up to 1400 °C under nitrogen atmosphere have been successfully prepared.⁴⁴ After a polycarbosilane solution is impregnated in a mesoporous silica host, the nanocasting process proceeds at 300 °C so that the rough surface of the silica host can be entirely replicated to the polycarbosilane guest. A concretionary amorphous SiC solid is produced during the following pyrolysis of the polymer precursor, fully copying the shape of mesopore channels in a silica host.

4. Summary and Outlook

We illustrate here the “host–guest” chemistry in the fabrication of mesoporous materials, which plays a vital role in designing family members with new structures and,

in particular, with abundant compositions. The “host–host” and “host–guest” interactions have been adequately reflected in mesoporous silicates. However, the preparation of nonsiliceous mesoporous solids also witnesses the important roles of the “guest–guest” interplay. The EISA strategy skillfully eludes the “host–guest” interaction in the cooperative assembly process, which facilitates the soft-template approach. A generalized “acid–base pair” concept and an organic–organic self-assembly strategy are therefore established, which give rise to a large number of highly ordered mesoporous metal oxides, mixed metal oxides, metal phosphates, metal borates, polymers, and carbon molecular sieves. The “guest–guest” interplay in the hard-template approach materializes in building the guest units to a substantial extent. In addition, when we take advantage of molding and decorating the host, the “host–guest” interaction in the hard-template approach can be modified.

The “host–guest” chemistry in the synthesis of nonsiliceous mesoporous materials should not be determined with boundaries. A method for regulating the interaction between guest and/or host has not yet been determined, but such a regulation could produce novel, convenient, economic, and reproducible strategies. Bulk production of nonsiliceous mesoporous materials are also imperative under the situation. The present “host–guest” chemistry is limited to the qualitative description. The quantitative illustration is the future target from the viewpoint of theoretical and configurable computation to develop generalized synthetic pathways and rationally design the structures, compositions, and properties. Once this is achieved, it will be possible to fabricate ordered mesoporous metal oxides and sulfides with crystallite walls, high-melting-point semiconductors, as well as mesoporous Si, SiC, metal carbides, and nitrides with open frameworks, together with achieving direct organic functional walls or channels of the mesoporous materials. The challenges are inevitably great in exploiting their functions in catalysis, sensors, microelectrodes, and dielectric materials.

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