Review

New families of mesoporous materials

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Received 14 August 2006; received in revised form 6 October 2006; accepted 25 October 2006
Available online 22 December 2006

Abstract

Mesoporous materials have been paid much attention in both scientific researches and practical applications. In this review, we focus on recent developments on preparation and functionalization of new families of mesoporous materials, especially non-siliceous mesoporous materials invented in our research group. Replica synthesis is known as the method to synthesize mesoporous materials composed of various elements using originally prepared mesoporous replica. This strategy has been applied for the syntheses of novel mesoporous materials such as carbon nanocage and mesoporous carbon nitride. Carbon nanocage has a cage-type structure with huge surface area and pore volume, which exhibits superior capabilities for biomolecular adsorption. Mesoporous carbon nitride was synthesized, for first time, by using mixed material source of carbon and nitrogen simultaneously. As a totally new strategy for synthesis of mesoporous materials, the elemental substitution method has been recently proposed by us. Direct substitution of component elements in original mesoporous materials, with maintaining structural regularity, provided novel mesoporous materials. According to this synthetic strategy, mesoporous boron nitride and mesoporous boron carbon nitride have been successfully prepared, for first time. In addition to these material inventions, hybridization of high functional materials, such as biomaterials, to mesoporous structure has been also developed. Especially, immobilization of proteins in mesopores was systematically researched, and preparation of peptide-hybridized mesoporous silica was demonstrated. These new families of mesoporous materials introduced in this review would have high potentials in future practical applications in wide ranges from electronics and photonics to environmental and medical uses.

Keywords: Mesoporous material; Template synthesis; Replica synthesis; Elemental substitution; Biomaterial

Contents

1. Introduction ......................................................... 753
2. Carbon nanocage and mesoporous carbon nitride via replica synthesis ............................................. 756
3. Mesoporous boron nitride and mesoporous boron carbon nitride via elemental substitution method ............................................. 760
4. Biomaterial-hybridized mesoporous materials .......................................................... 762
5. Summary ........................................................... 768
Acknowledgment .................................................................. 769
References ........................................................................ 769

1. Introduction

Mesoporous materials with regular geometries have been recently paid much attention owing to their great potentials in practical applications such as catalysis, adsorption, separation, sensing, medical usage, ecology,
and nanotechnology [1–15]. According to IUPAC classification, they are defined as porous materials with diameter in the size range of 0.2–2.0 nm. In 1990, Kuroda and coworkers first reported the preparation of mesoporous silica with uniform pore size distribution from the layered polysilicate kanemite (FSM-16, Folded Sheet Materials) [16,17]. A significant breakthrough in the mesoporous materials research has come when Mobil scientists disclosed the M41S family of materials, which have large uniform pore structures, high specific surface areas and specific pore volumes, including hexagonal-MCM-41 [18,19], cubic-MCM-48 [20], and lamellar-MCM-50 [21]. As illustrated in Fig. 1, the mesoporous materials were basically prepared through silica formation around template micelle assemblies followed by template removal by appropriate methods such as calcination.

These pioneering findings were followed by various kinds of mesoporous materials. For example, hexagonal mesoporous silica (HMS) prepared using neutral amine as template possesses slightly disordered hexagonal structure and thicker walls, superior thermal stability upon calcination in air, and a smaller crystallite size, which affords complementary textural mesoporosity for improved access to the framework-confined mesopores [22]. Michigan State University (MSU-1) synthesized by using polyethylene oxide (PEO) as a structure directing agent also has a disordered channel structure [23]. This material possesses large wall thickness and small particle size with considerable textural mesoporosity due to pores formed between the relatively small particles. As widely used materials, highly ordered large pore mesoporous silica Santa Barbara Amorphous-15 (SBA-15) with thicker pore walls and two-dimensional hexagonal structure, by using amphiphilic triblock-copolymer of poly(ethylene oxide) and poly(propylene oxide) (Pluronic P123) as the structure directing reagent in highly acidic media [24,25]. The pore diameters of the SBA materials are well tunable in the range of 5–30 nm, and these materials exhibit higher hydrothermal stability as compared to that of other mesoporous materials. Meso cellular form (MCF) materials can be prepared by using triblock-copolymers stabilized oil in water to result in aerogel-like structure, which offers the benefits as catalyst supports and separation media [26]. In addition to preparation of various mesoporous silica structures, incorporation of heteroatoms such as Cu, Zn, Al, B, Ga, Fe, Cr, Ti, V and Sn into mesoporous silica framework has been widely investigated [27–45]. Furthermore, it is possible to synthesize mesoporous structures of the materials other than silica. Methodology to prepare mesoporous silica via the template synthesis is extended to preparation of a various mesoporous metal oxides [46–59] such as TiO2, Ta2O5, Nb2O5, ZrO2, Al2O3, and V2O5 as well as synthesis of mesoporous aluminophosphate [60–63].

Recent researches have revealed that use of silica sources and templates designed by organic syntheses results in mesoporous materials with unique structural features. Two examples are shown in Fig. 2. One of the most unique approaches upon modification of silica source is synthesis of periodic mesoporous organosilicates (PMO) (Fig. 2A). The PMO materials were invented independently by three groups, Inagaki group [64], Ozin group [65], and Stein group [66] in 1999. This method uses organic molecules having multiple alkoxysilane groups as silica source and introduces various organic components in frame-work.
As the one of the unique finding, Inagaki et al. successfully prepared crystal-like pore-wall structure in PMO material from benzene-bridged organosilane, 1,4-bis(triethoxysilyl)benzene, where hydrophilic silicate layers and hydrophobic benzene layers array alternately [67]. Unlike use of conventional surfactants like cetyltrimethylammonium salt and triblock-copolymers, several examples of syntheses of the mesoporous materials with synthetically designed surfactant have been recently reported [68–76]. For example, chirality was first introduced in mesoporous materials by using chirally defined surfactant template (Fig. 2B) [77–79]. A newly synthesized surfactant, N-acyl-type alanine-based surfactant, was used as structure-directing reagent, resulting in mesoporous silica materials with regularly twisted rod-like structures with diameter of 130–180 nm and length of 1–6 mm. In the obtained structure, hexagonally aligned mesoscopic channels with diameter of 2.2 nm wound together in particular direction.
As briefly summarized above, various approaches have been extensively proposed for development of technologies based on mesoporous materials mainly with mesoporous silica and the related mesoporous metal oxide. However, preparation of non-oxide materials with mesoporous structures has also played important roles especially in 21st century, which is virtually initiated from invention of mesoporous carbon materials. Such trends in researches of mesoporous materials have successfully created new families of mesoporous materials. In this review, we introduce recent development of preparation of mesoporous materials of non-oxide materials, including mesoporous carbon, mesoporous carbon nitride, mesoporous boron nitride, and mesoporous boron carbon nitride. In addition, hybrid materials with mesoporous materials and bio-related structures are also described as a new direction of researches on mesoporous materials.

2. Carbon nanocage and mesoporous carbon nitride via replica synthesis

From the later periods in 1990s, regular carbon materials have been synthesized using regularly structured template such as zeolite and mesoporous silica [80–84]. Such carbon materials with nanoscale pore sizes prepared from periodic inorganic silica templates have been receiving much attention because of their versatility, and shape-selectivity. These characteristics are expected to be useful for chromatographic separation systems, catalysts, nanoreactors, battery electrodes, capacitors, energy-storage devices, and biomedical devices. The porous carbon materials with regular structures are usually obtained by the replica synthesis (or nano-casting), which is preparation method by replication of nano-structures to the other materials. For example, Kyotani and coworkers successfully synthesized highly regular microporous carbon [85,86]. Mesoporous carbon materials structures (CMK-x) were first reported by Ryoo using sucrose as carbon source and mesoporous silicates template such as MCM-48, SBA-1 and SBA-15 as templates and named as CMK-x [87–91]. Hyeon et al. reported, independently and somewhat later, the similar approach for the well-ordered mesoporous carbon materials designated SNU-x [92–94].

Fig. 3A schematically illustrated the synthetic process of mesoporous carbon materials. In this method, appropriate carbon sources, such as sucrose, are first impregnated into template structures, followed by solidification and template removal, resulting in nano-structured porous carbon materials. Structure of template silica has crucial role in successful preparation of mesoporous carbon, because replicated carbon must have continuous phase to keep their structures. For example, mesoporous silica MCM-48 in cubic phase is the one of the most appropriate template, because it has bicontinuous pore geometry, to result in representative mesoporous carbon, CMK-1 (Fig. 3A(a)). In contrast, MCM-41 is not appropriate for the replica synthesis, owing to independent nature of hexagonally aligned meso-channel in MCM-41. Although SBA-15 has hexagonal array of cylindrical pores as similar to MCM-41, its interconnectivity of the silica channel with micropores leads to preservation of regular carbon structures (CMK-3) even after silica removal (Fig. 3A(b)). Recently, Vinu et al. reported successful tuning of SBA-15 structure upon control of synthetic temperature [95] and applied the pore-tuned SBA-15 replica to synthesize CMK-3 mesoporous carbon materials with pore diameter ranging from 3 to 6.5 nm [96].

Wisely selection of mesoporous silica template provides regular carbon materials with superior textural characteristics. Vinu and coworkers very recently have reported synthesis of novel nanocarbon, “carbon nanocage” [97–99], through replica synthesis using three-dimensional large cage-type face centered cubic mesoporous silica materials (KIT-5) [100] as inorganic templates. Image of the synthesis of carbon nanocage was illustrated in Fig. 3B that, however, shows just rough idea of the obtained materials. The standard synthetic procedure for the mesoporous carbon, CMK-3 is not suitable in the case to make a highly ordered carbon nanocage due to the higher bulk density and lower pore volume of the KIT-5 as compared to the other mesoporous silicates such as MCM-48 and SBA-15. Appropriate water to silica template weight ratio (ca. 2.5) in the syntheses was found to be a crucial factor by systematic investigation on synthetic conditions. Upon these initial knowledge, carbon nanocage materials with different pore diameter were prepared by using different KIT-5 mesoporous silica synthesized at different temperature (from 100 to 150 °C) as templates and sucrose as the carbon source. Independently, the samples were prepared at different sucrose to silica weight ratio from 0.45 to 2.0. These experiments revealed that tunability of the pore structures and textural parameters in carbon nanocage materials. The powder XRD pattern of all the samples show an intense (1 1 1) reflection and a broader (2 0 0) reflection, demonstrating that the mesoporous structure was preserved even after the removal of the mesoporous. Thermogravimetric analysis under an oxygen confirmed that the maximum silica residue is only in the 1–1.5 wt% range. High-resolution transmission electron microscopy (HRTEM) images of the selected carbon nanocage material are shown in Fig. 4. The images were recorded along two different crystallographic directions, and both of them confirm that the carbon nanocage possesses highly ordered structure with uniform pore size distribution. A regular arrangement of bright spots suggests that the mesoporous material is of the three-dimensional-cage type.

Textural characteristics of the prepared carbon nanocage materials were more deeply investigated by nitrogen adsorption–desorption measurement. Fig. 5A shows examples of the nitrogen-adsorption isotherms. The analyzed parameters are summarized in the other three graphs in Fig. 5B. Pore diameters (Fig. 5B(a)) change little depending on sucrose to silica weight ratio, but specific surface area
(Fig. 5B(b)) and specific pore volume (Fig. 5B(c)) are significantly increased with decreasing the sucrose to silica weight ratio. The specific surface area and specific pore volume reached to 1600 m² g⁻¹ and 2.1 cm³ g⁻¹, respectively, in the case of carbon nanocage at the lowest sucrose to silica ratio. These values are apparently larger than those reported for conventional mesoporous carbon, CMK-3 (surface area, 1260 m² g⁻¹; pore volume, 1.1 cm³ g⁻¹). A further analysis with the method proposed Ravikovich et al. [101] provided the cage diameter of 15 nm for the corresponding carbon nanocage, which has pore diameter of 5.2 nm. Integrated structures with large difference between pore size and cage size would result in huge values of the surface area and pore volume. The carbon nanocage materials with excellent surface texture would be highly useful for material adsorption. Extensive researches on adsorption of toxic, valuable, and especially bio-related materials are now carried out in our research group. Parts
of the results (protein immobilization) are described in later section of this review.

The replica synthesis is not limited to synthesis of carbon materials with mesoporous structure. It can be utilized for synthesis of novel mesoporous materials with elements other than carbon. Instead of using single carbon source, use of sources with other elements and/or their mixtures would provide mesoporous structures with different materials as framework components. As one of the successful examples along this strategy, synthesis of mesoporous carbon nitride is here described, which was very recently reported by Vinu and coworkers [102].

For synthesis of mesoporous carbon nitride material (Fig. 6), co-material source, mixture of carbon source and nitrogen source, was impregnated into appropriate silica template. Mesoporous silica SBA-15 template was added to a mixture of ethylenediamine and carbon tetrachloride and the obtained composite was then heat-treated in a nitrogen flow. The mesoporous carbon nitride was recovered after dissolution of the silica framework in hydrofluoric acid. Thermogravimetric analysis under an oxygen atmosphere revealed that the maximum silica residue was confirmed to be less than 1 wt%. The structure of mesoporous carbon nitride was investigated.
by powder XRD, giving three clear peaks assignable to the (1 0 0), (1 1 0), and (2 0 0) diffractions of a two-dimensional hexagonal lattice with a lattice constant of $a_{100} = 9.52$ nm. This powder diffraction pattern of mesoporous carbon nitride showed a single broad diffraction peak near 25.8°, corresponding to interlayer d spacing of 0.342 nm, which is similar to the d spacing obtained in the non-porous carbon nitride spheres. The latter characteristic indicates turbostratic ordering of the carbon and nitrogen atoms in the graphene layers of the mesoporous carbon nitride.

Nitrogen adsorption–desorption measurement provided the detailed data on pore structures of the mesoporous carbon nitride materials. Fig. 7A displays the nitrogen-adsorption isotherms of the mesoporous carbon nitride (curve a) and of the parent mesoporous silica template SBA-15 (curve b). The isotherm of the mesoporous carbon nitride is of type IV with a H1 hysteresis loop. The adsorption pore size distributions of mesoporous carbon nitride are centered at 4.0 nm, the corresponding pore size distribution of SBA-15 is centered at 7.1 nm (Fig. 7B). As compared with SBA-15, the pore size distribution of the mesoporous carbon nitride materials is somewhat broadened but still exhibits narrow pore size distribution. Further analyses provided its specific surface area and specific pore volume as $505 \text{m}^2 \text{g}^{-1}$ and $0.55 \text{cm}^3 \text{g}^{-1}$, respectively. Pore structures of the mesoporous carbon nitride were directly investigated by HRTEM as shown in Figs. 7C and D. Only a stripe pattern could be detected when viewed down the [1 0 0] direction (Fig. 7C). Bright contrast strips on the under-focused image represent images of the pore walls and empty channels appear as dark contrast cores. Inserted figure displays the corresponding Fourier-transform optical diffraction pattern derived from the image, which only shows a one-dimensional array of spots along the [1 0 0] direction. It can be indicated that there is no crystallographic ordering along the axis of the empty mesopores. The cross-sectional HRTEM image shown in Fig. 7D clearly exhibits a hexagonal arrangement of the mesopores.

In addition to the pore size analyses, elemental composition of the mesoporous carbon nitride materials was investigated by several methods. Figs. 8A and B show nano-scopic distribution of carbon and nitrogen, respectively, which clearly confirm that the both of the elements homogeneously dispersed over the whole of the mesoporous structures. The traces of other elements were not detected during these mapping processes. An electron energy loss (EEL) spectrum of mesoporous carbon nitride material shows that carbon and nitrogen K-edges are located at 284 and 401 eV, respectively. The fine structure of the edges could be a fingerprint of sp² hybridization, in particular their left-hand shoulders revealing 1s–π* electronic transition. The X-ray photoelectron spectroscopy (XPS) survey spectrum of mesoporous carbon nitride did not show any peaks for elements other than carbon, nitrogen, and oxygen: the oxygen peak may originate from unavoidable contaminants such moisture, ethanol, atmospheric O₂, or CO₂ adsorbed on the surface. As shown in Fig. 8C, the XPS C 1s spectrum was deconvoluted into four peaks with binding energies of 289.3, 287.5, 285.7, and 284.1 eV. The lowest energy contribution fitted for C 1s is assigned to pure graphitic sites in the amorphous CN matrix, and the peak at 285.7 eV is attributed to the sp² carbon bonded to nitrogen inside the aromatic structure. The energy contributions at 287.5 and 289.3 eV are assigned to the sp² carbon and the sp² carbon in the aromatic ring attached to NH₂ groups, respectively. The XPS N 1s spectrum was similarly deconvoluted into two peaks centered at 397.8 and 400.2 eV as shown Fig. 8D. The peak at higher binding energy (400.2 eV) corresponds to nitrogen atoms trigonally bonded to all sp² carbons, or to two sp² carbon atoms and one sp³ carbon atom in an amorphous CN network, while another peak at 397.8 eV is attributed to nitrogen sp²-bonded to carbon. Furthermore, structure of the mesoporous carbon nitride materials was investigated by the other spectral techniques. Fourier-transform infrared (FTIR) spectrum of the mesoporous carbon nitride material contains the bands at 1257.3 and 1570.7 cm⁻¹.
assignable to aromatic CN stretching bonds and aromatic ring modes, respectively. The broad peak centered at 3412 cm\(^{-1}\) in higher-energy region attributed to the stretching mode of NH groups in the aromatic ring. The absence of the peak around 2200 cm\(^{-1}\) in turn confirms that there are no C≡N components in the mesoporous carbon nitride material. From these IR characteristics, the presence of a 1,3,5-triazine ring is highly suggested. The band with maxima at 255 and 275 nm in UV–Vis spectrum of the mesoporous carbon nitride material can be unambiguously assigned to \(\pi-\pi^*\) electronic transition in the aromatic 1,3,5-triazine compounds.

As described above, successful preparation of mesoporous carbon nitride was confirmed by both from structural and elemental analyses. This example demonstrates the wide possibility to synthesize non-oxide materials with mesoporous structures. They are not limited to carbon and carbon nitride. Upon wise selection of material sources and design of template structures, various kinds of materials with regular mesoporous structures would be created via the replica synthesis.

3. Mesoporous boron nitride and mesoporous boron carbon nitride via elemental substitution method

Mesoporous materials have been so far prepared by two major routes, soft template synthesis using micelle assemblies and replica synthesis using hard mesostructured template. Very recently, Vinu and coworkers has proposed the third method for synthesis of mesoporous materials [103]. This method can be called “elemental substitution method”, where component elements are substituted by the other elements with retaining mesoporous structure. The similar concept was realized in syntheses of the other types

![Fig. 7. Characterization of pore structure of mesoporous carbon nitride: (A) nitrogen adsorption (closed symbol) and desorption (open symbol) isotherms of parent SBA-15 (a) and mesoporous carbon nitride (b); (B) BJH pore size distribution of parent SBA-15 (a) and mesoporous carbon nitride (b); (C) HRTEM image of mesoporous carbon nitride, longitudinal projection; (D) HRTEM image of mesoporous carbon nitride, cross-sectional projection.](image)
of nanostructures such as nanotubes. For example, nanotubes composed of boron nitride and boron carbon nitride can be easily prepared via substitution reaction from carbon nanotubes [104–106]. However, this concept was not applied to fields of mesoporous materials before Vinu and coworkers first reported the synthesis of mesoporous boron nitride and mesoporous boron carbon nitride [103,107]. In this section, syntheses and characterizations of mesoporous boron nitride and mesoporous boron carbon nitride are introduced as pioneering work for the third-generation method for synthesis of mesoporous materials. Hexagonal boron nitride is structurally resembles graphite, and can be an insulator exhibiting a band gap of ca. 5.5 eV, chemically inert, and thermally stable up to 1600 °C. These natures cannot be easily obtained from the other mesoporous materials. Therefore, boron nitride and boron carbon nitride in ordered arrays of channels would lead to novel applications through combining characteristics of high surface area nature of mesoporous structure and unique electronic and thermal properties of boron nitride and boron carbon nitride.

According to Vinu’s procedure, mesoporous boron nitride and mesoporous boron carbon nitride with a very high surface area and pore volume can be fabricated via substitution reactions at high temperatures, using a well-ordered hexagonal mesoporous carbon (CMK-3) as a template and boron trioxide as a boron source and nitrogen gas as a nitrogen source. Selective preparation of these materials can be done by careful tuning of synthetic temperature. As illustrated in Fig. 9, the mesoporous boron nitride is usually synthesized at higher temperature such as 1750 °C, while the mesoporous boron carbon nitride is obtained via the substitution reaction at lower temperature condition (1450–1550 °C) with rather short reaction time. The textural parameters of these mesoporous materials were obtained through nitrogen adsorption–desorption isotherms measurement. Nitrogen adsorption–desorption isotherms of the mesoporous boron nitride and mesoporous boron carbon nitride.
nitride and the mesoporous boron carbon nitride are shown in Fig. 10A, where both the isotherms are classified as a type IV with a H1-type broad hysteresis loop, which is typical of mesoporous materials. These characteristics confirm the mesoporous nature of the obtained materials. Fig. 10B displays pore size distribution of mesoporous boron nitride and mesoporous boron carbon nitride. Although both the curves are somewhat broad as compared with those of the parent mesoporous carbon, they are still sharp enough to ensure narrow pore size distribution. These materials contain an appreciable amount of mesopores of irregular shapes. The Brunauer, Emmett and Teller (BET) surface area and mesopore volume decreased as the carbon content in the mesoporous materials lowered. The mesoporous boron carbon nitride synthesized at 1450 and 1550 °C possess relatively high surface areas of 740 and 650 m² g⁻¹ and large pore volumes of 0.69 and 0.60 cm³ g⁻¹, respectively. The specific surface area and the specific pore volume are decreased to 565 m² g⁻¹ and 0.53 cm³ g⁻¹, respectively, for mesoporous boron nitride synthesized at 1750 °C.

HRTEM images of the mesoporous boron nitride in low and high magnification are shown in Figs. 10C and D, respectively. Both the images suggest that the mesoporous boron nitride materials possess a less-ordered mesoporous structure with a disordered boron nitride framework with highly crystalline layers. In Fig. 11A, higher magnification of the TEM image of the mesoporous boron carbon nitride material is exhibited. The image may suggest the well-ordered mesoporous structures with local interlinking of crystalline boron carbon nitride layers, but actual phase of boron carbon nitride has not been fully explored yet. Investigations on the state of this material are now under way, using several analytical approaches including NMR study at 21.8 T [107]. In order to confirm distribution of component elements, elemental mapping was carried out in the same scope of the TEM image of mesoporous boron carbon nitride, as shown in Fig. 11B for boron, in Fig. 11C for carbon, and in Fig. 11D for nitrogen. Comparison with these images with the parent image in Fig. 11A clearly revealed that boron, carbon, nitrogen atoms homogeneously distributed in all parts of the sample. In addition, the traces of other elements were not detected using this technique. The elemental composition of mesoporous boron nitride and the mesoporous boron carbon nitride were also analyzed by EEL spectroscopy. The EEL spectrum of the mesoporous boron nitride revealed that the boron-to-nitrogen ratio in the corresponding material was 1.0 and that carbon signal was virtually absent. The EEL spectrum of mesoporous boron carbon nitride showed an increase of the carbon content (8.0% and 20.1% for the corresponding materials synthesized at 1550 and 1450 °C, respectively. The overall boron-to-nitrogen ratio of the mesoporous boron nitride obtained from the XPS analysis is 0.94, which is again well consistent with ideal composition of boron nitride. The XPS measurement provided elemental composition of mesoporous boron carbon nitride synthesized at 1450 °C as 21.1% of boron, 37.7% of carbon, and 23.0% of nitrogen with 18.2% of oxygen as unavoidable contaminant. Thermal stability of the obtained materials would be one of the most important issues as their specific properties, which is now under investigation.

Above-mentioned confirm successful preparation of mesoporous boron nitride and mesoporous boron carbon nitride from regularly structured mesoporous carbon, via elemental substitution method. This preparative concept is new in fields of mesoporous materials and can be regarded as the third-generation method after template synthesis and replica synthesis. With this concept, mesoporous materials with various component elements will be prepared in near future.

4. Biomaterial-hybridized mesoporous materials

Biomaterials have flexible nature with sophisticate function and attractive for many advanced applications such as sensing, medical uses, and selective material conversion. Immobilization of biomaterials into nano-organized structures, including supermolecules [108–113], lipid bilayers [114–126], self-assembled monolayers [127–129], Langmuir–Blodgett films [130–149], and layer-by-layer assemblies [150–163], have been paid much attention. However, most of them have less mechanical stability, and some of them have difficulty in material diffusion and unsuitability to make contact with artificial devices. Unlike these materials, inorganic mesoporous...
materials have several advantages as media for biomaterial immobilization. They are mechanically much stronger than the organic supports. Diffusion of materials should be ensured in mesopore spaces. Mesoporous materials have high flexibility in fabrication including film formation [164–168], which is highly advantageous characteristic for practical applications. Therefore, preparation of biomaterial-hybridized mesoporous materials are highly worthy of being investigated.

One of the simplest approaches to make biomaterial-hybridized mesoporous materials is use of physical adsorption of biomaterials onto mesoporous structures. Adsorption of proteins to mesoporous materials, especially to mesoporous silica, has been rapidly paid attentions [169–185]. As shown below, Vinu et al. provide systematic researches on protein adsorption onto mesoporous materials [96,186–196]. Typical results of adsorption of hen egg white lysozyme and horse heart cytochrome c are shown in Fig. 12. Fig. 12A displays adsorption isotherm of lysozyme onto three mesoporous silica materials (C_{12}-MCM-41, C_{16}-MCM-41, and SBA-15) at pH 10.5 [186]. The use mesoporous materials possess different textural parameters: pore volume (C_{12}-MCM-41, 0.70 cm^{3} g^{-1}; C_{16}-MCM-41, 0.86 cm^{3} g^{-1}; SBA-15, 1.25 cm^{3} g^{-1}) and pore diameter (C_{12}-MCM-41, 3.54 nm; C_{16}-MCM-41, 4.10 nm; SBA-15, 10.98 nm). All the isotherms obeyed Langmuir-type behavior with 13.4, 28.1 and 35.3 mol g^{-1} for C_{12}-MCM-41, C_{16}-MCM-41, and SBA-15, respectively. Fig. 12B compares the adsorption isotherms of cytochrome c on the same silica mesoporous adsorbents at pH 9.6 [187]. Adsorption capability of these materials in the cytochrome c adsorption is in the similar tendency to the lysozyme adsorption (C_{12}-MCM-41 < C_{16}-MCM-41 < SBA-15). Both the results indicate protein adsorption capability increases as pore volume and/or pore diameter increases. In order to determine predominant factor (pore diameter or the specific pore volume) for effective protein adsorption, SBA-15 materials synthesized at different temperatures are used for adsorption experiments of cytochrome c. It was known that increase of synthetic temperature results in an increase of the pore diameter of
SBA-15 at the expense of specific pore volume. The amount of adsorbed cytochrome c is almost similar for SBA-15-100 (¼ SBA-15) and SBA-15-120, and is reduced for SBA-15-130 and SBA-15-150, where X in SBA-15-X indicates the synthesis temperature. This result suggests that pore volume could be more important factor than pore diameter. Change in pore geometry such as pore curvature could also modify the packing density of the cytochrome c molecules.

Charged states of both the proteins and silicate significantly depend on surrounding pH and, therefore, pH conditions in adsorption media should have significant effect on the protein adsorption. Figs. 12C and D show adsorption isotherms of lysozyme [186] and cytochrome c [187] onto SBA-15 at various pH conditions, respectively. The maximum adsorption capability of lysozyme to SBA-15 was obtained at pH 10.5 that are very close to the isoelectric point of lysozyme and the most efficient adsorption of cytochrome c similarly occurred at around pH 9.6, close to the isoelectric point of cytochrome c. At near the isoelectric point of the protein, electric repulsion between the protein molecules are significantly suppressed, which may allow proteins to pack densely in confined spaces. Change of the protein size may also explain the peculiar pH tendency of the protein adsorption. Protein molecules tend to be compacted at zero net charge. For example, the area per molecule of lysozyme in solution having a pH near the isoelectric point was reported to be similar to that in its crystallized state (13.5 nm²), whereas it is 26.6 nm² at a solution pH of 4. Smaller occupied area in the former case may result in larger monolayer adsorption capacity.

The above-mentioned knowledge on protein adsorption to mesoporous silica can be generalized to the other mesoporous materials such as mesoporous carbon, as demonstrated in systematic researches by Vinu and coworkers [190]. Fig. 13 compares the adsorption behaviors of the lysozyme molecules adsorbed on various mesoporous carbon materials (CMK-1 and CMK-3-X, X = 100, 130, and 150) at a solution pH of 11. CMK-3-X materials were synthesized from SBA-15-X template. The isotherms of lysozyme adsorption are summarized in Fig. 13A, where adsorption capacity significantly depends on the carbon materials. The monolayer adsorption capacity increases in the following order: CMK-3-150 (22.9 μmol g⁻¹) > CMK-3-130 (15.9 μmol g⁻¹) > CMK-3-100 (9.8 μmol g⁻¹) > CMK-1 (3.8 μmol g⁻¹). The adsorption capabilities are plotted as functions of several textual parameters such as specific surface area (Fig. 13B (a)), specific pore volume (Fig. 13B (b)), and pore diameter (Fig. 13B (c)). Positive correlation

Fig. 11. Characterization of elemental composition of mesoporous carbon nitride. Elemental mapping of mesoporous boron carbon nitride: (A) whole image; (B) boron atom distribution; (C) carbon atom distribution; (D) nitrogen atom distribution. Reprinted with permission from [103], A. Vinu et al., Chem. Mater. 17 (2005) 5887–5890. © 2005, American Chemical Society.
is obviously recognized between the adsorption capacity and the pore volume and pore diameter, while the adsorption capacity does not show clear relevance with the surface area. Interestingly, unavoidable negative deviation from the expected line can be detected for the adsorption capacity to CMK-1. This result would be explained by the size exclusion effect at mesoporous media. A smaller pore diameter (2.3 nm for CMK-1) compared with dimensions of the lysozyme molecule (crystallographic dimension of 4.5 × 3 × 3 nm in ellipsoidal) resulted in very small adsorption capacity.

Similar to mesoporous silica materials, a maximum adsorption of the proteins was observed at near the isoelectric point. In addition to compact packing nature of the proteins at the isoelectric point, effective hydrophobic interaction between carbon surface and neutral proteins may accelerate adsorption process. Vinu and coworkers also extended the adsorption researches of biomaterials to smaller molecules such as vitamins [197,198] and amino acids [199,200], where superiority of the mesoporous carbon in these adsorption processes as compared to mesoporous silica and activated non-structure

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Fig. 12. (A) Adsorption isotherms of lysozyme onto mesoporous silica materials at pH 10.5: (a) C12-MCM-41; (b) C16-MCM-41; (c) SBA-15. (B) Adsorption isotherms of cytochrome c onto mesoporous silica materials at pH 9.6: (a) C12-MCM-41; (b) C16-MCM-41; (c) SBA-15. (C) Adsorption isotherms of lysozyme onto SBA-15 at various pH conditions: (a) pH 6.5; (b) pH 6.5; (c) pH 9.6; (d) pH 10.6. Reprinted with permission from [186], A. Vinu et al., J. Phys. Chem. B 108 (2004) 7323-7330 and [187], A. Vinu et al., Chem. Mater. 16 (2004) 3056-3065. © 2004, American Chemical Society.
carbon is demonstrated. Because of large pore volume of the carbon nanocage, it would show superior capability in the biomaterials adsorption [98]. As a simple demonstration, adsorption behaviors of lysozyme to the carbon nanocage materials were compared with those of conventional mesoporous carbon (Fig. 14). The maximal monolayer adsorption capacity of carbon nanocage was 26.5 μmol g⁻¹, respectively, while that of CMK-3 is assigned to only 9.8 μmol g⁻¹. Not limited to protein adsorption, carbon nanocage would have superior capability in molecular adsorption, extraction, and removal, which are currently investigated in our research group.

Because mesoporous materials provide well-defined nanostructures, which bare resemblances to the nanospaces found in biological systems in their size and accuracy. Therefore, dense assembling of biological components in mesopores could mimic structures and functions of rather complicated biomaterials. According to this concept, the
mesoporous materials confining the peptide segments in highly organized mesopore nanospace were newly developed by Ariga and coworkers [201–203]. The obtained biomaterial-hybridized mesoporous silica was named as proteosilica (Fig. 15A). Peptide surfactants, which have polar quaternary ammonium salt at the peptide N-terminal and hydrophobic alkyl chain at its C-terminal were used as template for synthesis of proteosilica, which was obtained in both transparent film and powder form. HRTEM image of the films indicate highly ordered regular pore arrays (Fig. 15B). Proteosilica provides optically asymmetric environment for doped molecules. Photoisomerization behaviors of spiropyran doped in the transparent proteosilica films were investigated spectroscopically. Isomerization between the spiropyran form and the merocyanine form can be repeated upon alternate irradiation of the visible light (420 nm) and UV light (280 nm) to the films, respectively. Alternate irradiation with the UV light and the visible light induced repeated changes in the circular dichroism (CD) spectra, and a complete mirror image of the CD spectra was obtained when the chirality of component peptides was reversed. The CD signals from the guest were driven by the chiral environment of the surrounding host. The presented materials are expected to be applied to memory device with non-destructive read-out capability.

Unlike the above-mentioned examples, biomaterial-hybridized mesoporous silica with covalent linkage between silica framework and biological components was proposed by Ariga, Aida, and coworkers (Fig. 16) [204–206]. A surfactant with condensable alkoxy-silane group was used as template in this method. In the presence of this template, sol–gel reactions of tetraethyl orthosilicate resulted in mesoporous silica whose channels are filled with covalently attached biological component (alanine residue). Selective hydrolysis of the ester at the C-terminal of the surfactant caused cleavage and removal of the alkyl tail, leaving open pores with a surface covalently functionalized by the alanine residue. The template behaves like a “lizard,” i.e., the head of the surfactant bites the silica wall and its tail can be cleaved off. Regular mesoporous structures were maintained through the whole process as confirmed by XRD analysis and HRTEM observation. Nitrogen adsorption–desorption measurements before and after the tail removal ensured pore formation upon the hydrolysis. Selective hydrolysis of the template ester was clearly demonstrated by FT-IR measurement. Adsorption of NH₃ gas to the exposed alanine C-terminal in the silicate channel was successfully quantified by temperature-programmed desorption analysis. As demonstrated by these experimental data, this lizard template method copes with both dense functionalization of the pore inside and high accessibility of external guests. The fabrication of mesoporous silica with a variety of organic functional groups by the lizard method is highly expected.
5. Summary

In this review, various methodologies for syntheses of mesoporous materials are described, including recent advances in this field. Traditional template synthesis, which mainly utilizes micelle assembly as a template, is especially useful for preparation of mesoporous metal oxide. The prepared structure such as mesoporous silica can be subjected to a replica synthesis, where structures of mesoporous materials are replicated into mesoporous materials composed of the other components such as carbon. The latter strategy has been recently applied to novel mesoporous materials such as carbon nanocage and mesoporous carbon nitride. As the third-generation technique, the elemental substitution method has been recently proposed by Vinu and coworkers. Direct substitution of component elements in mesoporous materials provided new materials with maintaining structural regularity. According to the synthetic strategy, mesoporous boron nitride and mesoporous boron carbon nitride have been successfully invented. In addition to these material inventions, hybridization of high functional materials, such as

![Diagram](image-url)
biomaterials, to mesoporous structure has been also developed in these days. Especially, immobilization of proteins and peptides in mesopores has been systematically researched and, therefore, their practical applications are now awaited. New families of mesoporous materials introduced in this review would have high potentials in future practical applications in wide ranges from electronics and photonics to environmental and medical uses.

Acknowledgment

The researches described in this chapter were partially supported by Ground-based Research Program for Space Utilization Promoted by Japan Space Forum and Grant-in Aid for Scientific Research on Priority Areas (No. 18033059 “Chemistry of Coordination Space”) from Ministry of Education, Science, Sports, and Culture, Japan.

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