

Review

New families of mesoporous materials

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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.

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

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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,

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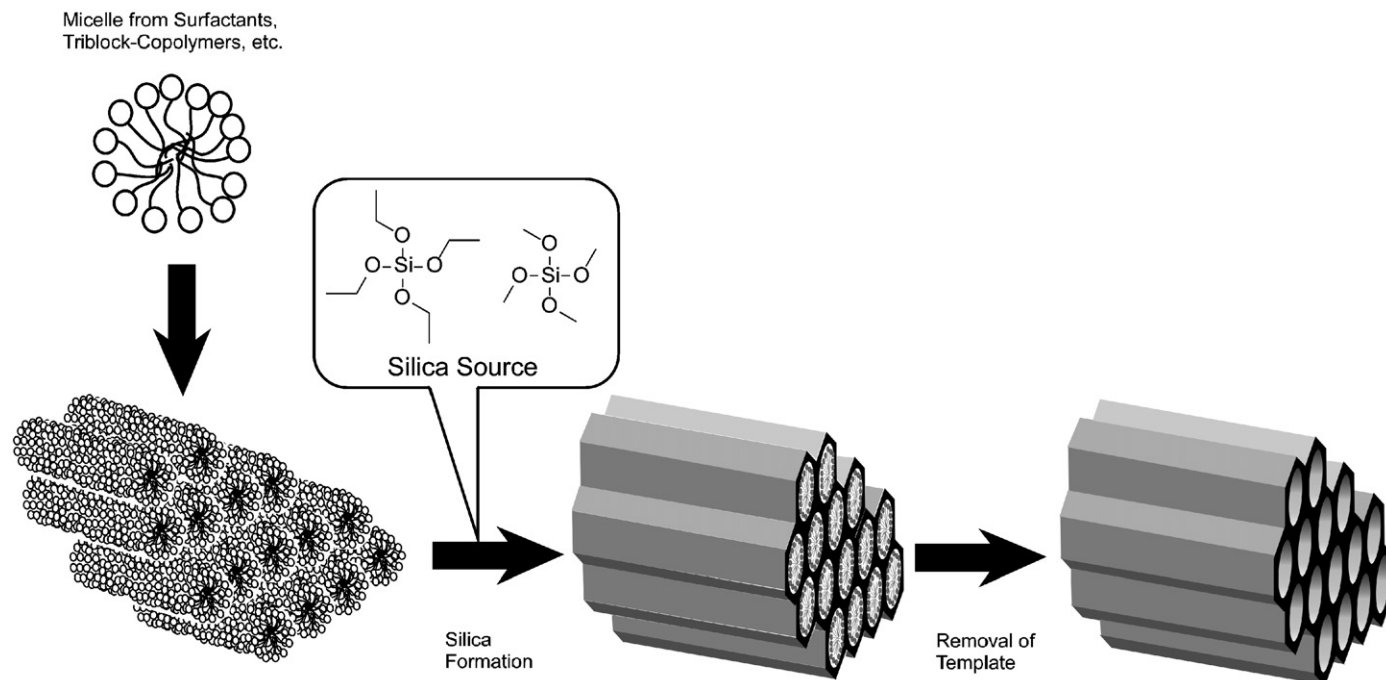


Fig. 1. General concept for synthesis of mesoporous silica from micelle template.

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 TiO_2 , Ta_2O_5 , Nb_2O_5 , ZrO_2 , Al_2O_3 , and V_2O_5 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 alkoxy silane groups as silica source and introduces various organic components in frame-work.

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