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FRONTIERS ARTICLE

Magnetically responsive ordered mesoporous materials: A burgeoning family of functional composite nanomaterials

Yonghui Deng, Yue Cai, Zhenkun Sun, Dongyuan Zhao *

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials and Advanced Materials Laboratory, Fudan University, Shanghai 200433, PR China

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ABSTRACT

Magnetic mesoporous materials, as a family of novel functional nanomaterials, have attracted increasing attention due to their unique properties. Much work has been done to synthesize these materials and to explore applications in various fields, such as catalysis, separation, hyperthermia, drug delivery, and MR imaging. This Letter reviews the synthesis approaches, which can be grouped into three categories, *i.e.* sol–gel coating, post-loading, and nanocasting approaches. Emphasis is placed on the elucidation of the design principles, synthesis strategies and the properties–applications relationship of the mesoporous materials.

1. Ordered mesoporous materials

Ordered mesoporous materials are a type of porous molecular sieves with pore size of 2.0–50 nm which are aligned in 2-D or 3-D arrays throughout the materials. In this article, unless otherwise specified, mesoporous materials refer to 'ordered mesoporous materials'. Retrospectively, the research interest in mesoporous materials originated from conventional zeolites and molecular sieves possessing ordered micropores (<2.0 nm) in the early 1990s when scientists were pursuing systems with large pores for heavy petroleum oil conversion. Since their discovery [1,2], mesoporous materials have stimulated a great interest among various fields spanning chemistry, materials science, biomedicine, and bioengineering. The extensive research has been carried out due to their unique features, including tunable pore size, high surface area, large pore volume, and controllable framework composition, which endow them with great application potential in fields such as catalysis, adsorption, separation, fuel cell, sensor, enzyme immobilization, electrode materials [3–9]. Therefore, considerable effort has been devoted to synthesis, structure analysis, as well as applications, which led to an exponential increase in publications within the past decades (Figure 1), and the production of a large number of mesoporous materials with varying chemical compositions and pore structures.

The synthesis approaches for mesoporous materials can be basically categorized into two groups, soft- and hard-templating. The former usually relies on the use of surfactant molecules or amphiphilic block copolymers as templates. The template molecules interact with framework precursors and cooperatively assemble into hybrid composites with ordered mesostructures (Figure 2A). After co-solidification, the template molecules in the mesostructured composites can be removed by calcination or solvent extraction, giving rise to the mesoporous materials. The latter approach is usually realized through casting the pre-synthesized mesoporous materials as hard-templates with various guest precursors, *in situ* conversion of them into the target species in the mesopore channels, and finally removal of the hard templates through either chemical dissolution or combustion (Figure 2B). Using the two synthesis methods, continuous progresses have been achieved in mesoporous materials through various strategies, including solution-phase self-assembly [1,2,10–13], solvent evaporation induced self-assembly (EISA) and nanocasting [14–20]. And with the ever advancing characterization techniques, such as Cryo-TEM, 3-D electron tomography, researchers are now able to precisely elucidate the pore structures, features, and related parameters and understand formation mechanism of mesoporous materials.

2. Magnetic nanomaterials and magnetic mesoporous materials

With the rapid progress in modern nanoscience and nanotechnology, mesoporous materials as a family of unique nanomaterials, have garnered increasing interest in fields, including chemistry,

Abbreviations: APS, γ-aminopropyltriethoxysilane; BET, Brunauer–Emmett–Teller; BTME, 1,2-bis(trimethoxysilyl)ethane; CTAB, cetyltrimethylammonium bromide; CTAC, cetyltrimethylammonium chloride; C_{18}TMS, *n*-octadecyltrimethoxysilane; 2-D, two-dimensional; 3-D, three-dimensional; EG, ethylene glycol; EISA, evaporation induced self-assembly; FESEM, field-emission scanning electron microscopy; FETEM, field-emission transmission electron microscopy; MRI, magnetic resonance imaging; NIR, near infrared; OTAB, octadecyl-trimethylammoniumbromide; PEG, poly(ethylene glycol); PMO, periodic mesoporous organosilica; P123, poly(ethylene oxide)–*b*-poly(propylene oxide)–*b*-poly(ethylene oxide) (EO_{20}–PO_{70}–EO_{20}); SEM, scanning electron microscopy; TEM, transmission electron microscopy; TEOS, tetraethyl orthosilicate; XRD, X-ray diffraction.

* Corresponding author.
E-mail address: dyzhao@fudan.edu.cn (D. Zhao).

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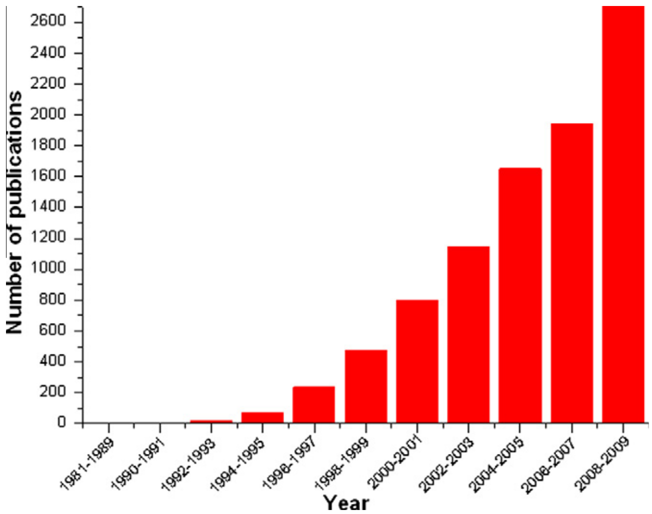

Figure 1. Increase in the number of publications on mesoporous materials from years 1985–2009. Source, ISI; keyword, mesoporous materials.

materials science, and biomedicine. Recently, functionalization of mesoporous materials with novel physical and chemical properties has emerged as one of the new research directions in the community of porous materials. Various approaches have been developed to integrate functional nanomaterials (quantum dots [21], magnetic nanoparticles [22], plasmonic metal nanorods [23]) within mesoporous materials, resulting in a great variety of functional materials that combine their excellent properties.

Magnetic nanoparticles have received considerable attention in the past several decades due to their unique magnetic properties and potential applications in magnetic fluid, data storage, catalysis, biotechnology/biomedicine, magnetic resonance imaging, and environmental remediation [24–33]. Different methods have been developed for synthesis of magnetic nanoparticles, including chemical co-precipitation, thermal decomposition, solvothermal synthesis and so on [34–39]. Combination of magnetic nanoparticles and mesoporous materials is undoubtedly of a great interest to the development of novel functional materials, because the magnetic nanoparticles can provide unique magnetic properties that are very useful for the applications in catalysis, drug delivery, cell and tissue imaging, hyperthermal therapy and so on. Several excellent review articles have been reported about the synthesis and applications of functionalized mesoporous materials [40–47], including magnetic mesoporous materials [40]. In this review, we mainly focus on the elucidation of the design principles and synthesis strategies of magnetic mesoporous materials.

Generally, the magnetic components in the magnetically responsive mesoporous materials are magnetic metals or alloys (*e.g.* Fe, Co, Ni, or PtFe) or oxides such as MFe_2O_4 (M = Fe, Co, Ni, Zn, *etc.*) and γ-Fe_2O_3. Because of their low toxicity [48], iron oxide nanoparticles have been widely used in the synthesis of magnetic composite materials. From a viewpoint of their practical applications, magnetic mesoporous composites should meet several criteria as follows. Firstly, the magnetic components should be free from being etched in application media, which is important to maintenance of their magnetic property. Secondly, for application in magnetic separation, the magnetic mesoporous materials should possess saturation magnetization (*M*s) enough to ensure a rapid response to the applied magnetic field. Thirdly, the mesopores should be accessible so that the high surface area and large pore volume can be used for the applications. Besides, superparamagnetism is usually highly desired, because it can prevent the magnetic composite particles from irreversible aggregation and ensure an excellent dispersibility once applied magnetic field is removed. While for some biorelated applications, such as MRI contrast-enhancing agent and drug delivery, the materials should have high water dispersibility, uniform size, biocompatible surface and low cytotoxicity. To date, extensive work has been done in pursuit of magnetic mesoporous materials with desired structure, morphology, and surface property for diverse applications.

The synthesis approaches for magnetic mesoporous materials can be grouped into three categories. The first one is the sol–gel coating method that is based on encapsulation of magnetic particles with mesoporous shells using surfactants, amphiphilic block

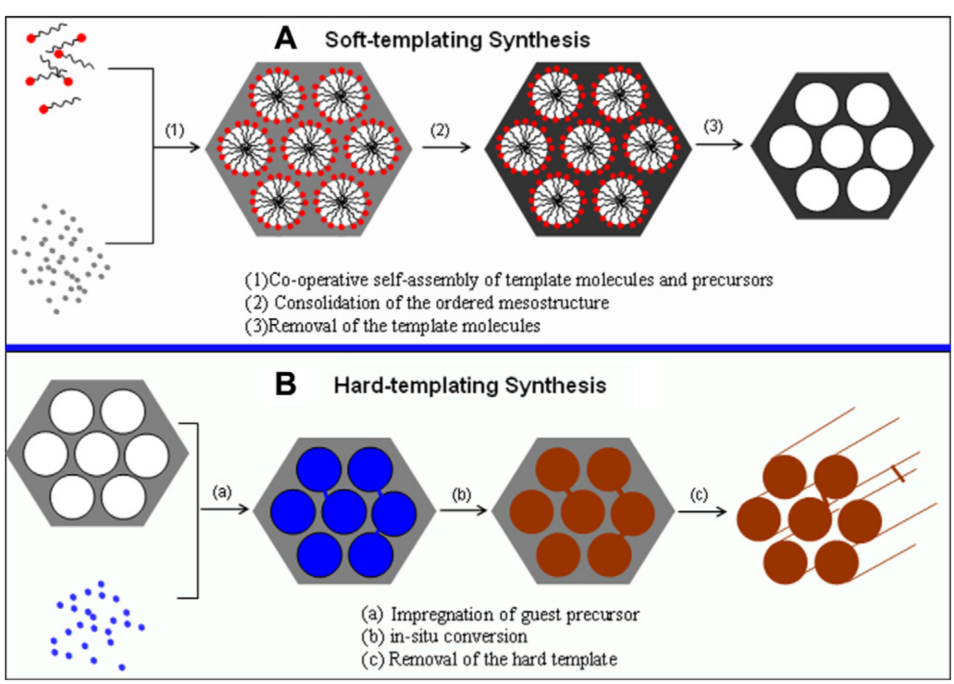

Figure 2. Two approaches to synthesis of mesoporous materials: (A), soft-templating; (B), hard-templating synthesis.