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Synthesis, functionalization, and applications of morphology-controllable silica-based nanostructures: A review

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ABSTRACT

Morphology-controllable silica-based nanostructures (MC SiO_2Ns) have been comprehensively studied because of their potential practical applications in various fields, such as biological chemistry. The superior properties of these nanostructures, including low density, biocompatibility, thermal stability, and high mechanical strength, have been the focus of research to improve their current performance. In this review, experimental parameters, morphology, and formation mechanism of MC SiO_2Ns (including vesicle-like mesoporous silica, rod-like mesoporous silica, and silica mesoporous nanospheres) are discussed. Moreover, current progress in functionalization and performance improvement of MC SiO_2Ns is presented. Applications of MC SiO_2Ns in immobilization techniques, biological catalysis, and drug delivery are also provided.

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1. Introduction

Since the discovery of ordered mesoporous silica (e.g., MCM-41 and SBA-15) in the 1990s, mesoporous materials have attracted increased research attention [1–3]. The synthesis of morphology-controllable silica-based nanostructures (MC SiO_2Ns) has rapidly developed; in particular, various templates and swelling agents, as well as different approaches, can be employed to fabricate MC SiO_2Ns with high specific surface areas, large pore volumes, and diverse morphologies, such as rod-like [4–6], fiber [7,8], cage-like [9], silica nanosphere [10–12], films [13], and vesicle-like structures [14–16]. MC SiO_2Ns are extensively applied in different techniques, such as immobilization [17], catalysis [18], drug delivery [19], sensor fabrication [20], and separation [21]. Therefore, the design and synthesis of MC SiO_2Ns with controllable mesopores and structures are important in terms of fundamental and technological perspectives.

Throughout the development of MC SiO_2Ns, studies have focused on the synthesis of SiO_2Ns because of their unique advantages [22–24]. Supramolecular templating, with surfactant as template to obtain a porous framework, has been employed to fabricate MC SiO_2Ns with controllable structural properties under experimental conditions. As such, the synthesis of MC SiO_2Ns with different structures is important. Surfactant templating is commonly used to synthesize SiO_2Ns with narrow size distribution and controlled pore structure through hydrolysis and cross-linking of inorganic precursors on the surface of the supramolecular surfactant assemblies. Furthermore, synthesis by template fabrication has enabled the production of SiO_2Ns with distinct morphological features for applications in variable structure systems. For example, Sayari et al. [25] prepared monodispersed rod-like mesoporous SBA-15 silica, with 0.4–0.5 μm diameter and 1–1.5 μm length, by using triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) as structure-directing agent. Wang et al. [26] synthesized hollow mesoporous silica nanospheres with radially oriented mesochannels in uniform shells (35–40 nm thick) by using anionic surfactants as template; the product contains intact and dispersed hollow nanospheres, with diameters ranging between 100 and 500 nm, a specific surface area of 502 $m^2\ g^{-1}$, and an average pore diameter of 3.1 nm. In our recently published paper, vesicle-like mesoporous silica with well-defined multilamellar structures was prepared with didodecyldimethylammonium bromide (DDAB)/cetyltrimethylammonium bromide (CTAB) as structure-directing agent. The number of vesicular silica layers was decreased from 7 to 2 by changing the molar ratio of DDAB to CTAB [16]. Currently, to the best of our knowledge, different types of SiO_2Ns can be achieved using single surfactants, mixtures of cationic and anionic surfactants, or combination of nonionic and ionic surfactants as templates [27,28]. In addition to types of surfactants, several parameters, such as silicon source, additives, pH, stirring speed, and temperature, are crucial to the formation of SiO_2Ns.

Researchers have recently explored different approaches to functionalize SiO_2Ns. As a result, the structural and compositional architectures of functionalized SiO_2Ns have received significant attention [29]. A previous study showed that mesoporous silica can be readily functionalized using appropriate functional groups because its surface contains abundant Si–OH groups [3,19]. Functionalized SiO_2Ns present numerous existing and potential applications in the industry and are continuously improve to meet the requirements for this composite [30]. Xu et al. [31] immobilized lipase on amino-functionalized SBA-15; they reported that porcine pancreatic lipase (PPL) immobilized on functionalized SBA-15 has higher loading amount and catalytic activity than PPL immobilized on unfunctionalized SBA-15. To date, SiO_2Ns coated with well-defined polymeric chains can be prepared using several polymerization techniques. Specifically, controlled radical polymerization [32], nitroxide-mediated polymerization [33], atom transfer radical polymerization (ATRP) [34,35], and reversible addition–fragmentation chain transfer polymerization [36] have been applied to graft polymeric chains onto solid supports. These methods can be used to produce well-defined polymers with controlled molecular weight, low polydispersity, and variable functionality. Among these methods, ATRP is the commonly applied to functionalize SiO_2Ns because of its wide range of architectures and compatibility with various monomers and reaction conditions [37]. Moreover, SiO_2Ns functionalized by tethering block copolymers exhibit controllable properties, such as hydrophilicity, hydrophobicity, biocompatibility, adhesiveness, adsorptibility, and corrosion resistance [38,39]. Yin and Zhou [40] successfully prepared poly (2-(dimethylamino) ethylmethacrylate-co-3-dimethyl (methacryloyloxyethyl) ammoniumpropanesulfonate)-grafted (PDMAEMA-*co*-PDMAPS) silica nanoparticles by grafting PDMAEMA brushes onto the SiO_2 surface with the use of activators regenerated through electron transfer (ARGET) ATRP. Our group previously synthesized an amphiphilic polymer graft of polymethyl methacrylate (PMMA)–poly(oligo(ethylene glycol)methyl ether methacrylate) (POEOMA or $PO(EO)_n$MA; $n = 2, 5, 8$) on the silica nanosphere surface by using activators regenerated through ARGET ATRP [39]. Moreover, our group fabricated hydrophobic PMMA–polystyrene diblock (PSt) copolymer brushes on the surface of silica nanospheres with tunable shell thickness by using activators generated through electron transfer (AGET) for ATRP [41].

This paper highlights the synthesis and functionalization of MC SiO_2Ns (vesicle-like mesoporous silica, rod-like mesoporous silica, and silica mesoporous nanosphere) with physical and chemical attributes tailored for different applications. In this regard, factors influencing the synthesis and functionalization of MC SiO_2Ns must be elucidated. This study provides an overview of the synthesis and functionalization of MC SiO_2Ns, particularly on the effects of various factors on these processes, to obtain a theoretical basis and technical guidance for future applications. Experimental conditions and synthesis mechanisms for fabricating MC SiO_2Ns are presented. Moreover, functionalization of MC SiO_2Ns to obtain specific physical excellent properties is discussed and applied.