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Review

Interfacial engineering of magnetic particles with porous shells: Towards magnetic core – Porous shell microparticles

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ABSTRACT

The surface engineering on various functional nanomaterials has enabled the creation of diverse nanocomposites that possess pre-designed architectures with improved and complementary properties. Magnetic porous materials with core-shell structures have recently received great attentions due to the combination of the respective properties of cores and shells that achieves cooperatively boosted performance. Core-shell magnetic nanoparticles are well-known for their outstanding properties of enhanced stability, being able to protect the active species from harsh environments, improved physical, chemical and photoelectric properties, and easiness of surface functionalization, *etc.* All of their exciting synergistic properties are heavily depending on the controllable and ingenious design towards cores and shells, and precise regulation of the interaction between them. In this paper, different surface engineering strategies, based on sol-gel chemistry and confined interfacial coating, for the construction of iron oxide-mesoporous core-shell materials have been reviewed. Attentions are paid not only on the selection of promising candidates for cores or porous shells and the creation of different shapes, but also more importantly on the synthetic principles and mechanisms for interfacial control in achieving perfectly adjustment of porous shells with various compositions, different pore sizes, pore structures and functionalities. Following the methods and principles presented in the review, it is very easy even for new beginners to synthesize various magnetic porous materials with well-defined core-shell structure and integrated functionalities for various applications.

Contents

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Introduction

The rational design and controllable synthesis of multifunctional hybrid nanostructured materials is a favorable driving force for advancing the development of nanomaterials. Precise design and preparation of optimal structures with desired functions including catalytic activity, magnetic, electronic and optical properties and high stability should be one of the most challenging aspects in the development of multifunctional nanocomposites [1]. An effective approach for the organization of different building blocks with tunable functions, sizes and morphologies is to directly integrate these functional components into core-shell nanostructures [2]. Core-shell nanocomposite materials are a new type of functional materials in which different components with various functionalities respectively derived from cores and shells are spatially distributed at nanoscale and integrated into one entity showing broadened potentials for a variety of applications [3]. Benefiting from the well combination of various functions through the core-shell concept, such as high porosity [4,5], catalytic properties [6], magnetic features [2] and so on, a large number of hybrid core-shell nanomaterials have been established with a high degree of control over the compositions, morphologies and physical/chemical properties.

Recently, many attempts have been made to enhance the performance of magnetic microspheres for improving their magnetic-field responsiveness, achieving effective manipulation, and introducing additional functionalities with tailored physicochemical properties. Core-shell structured nanocomposites with magnetic components have attracted great attention [7–9] due to their unique magnetic responsivity, low cytotoxicity, and modifiable functional surface, showing great potentials in theranostics [10], thermotherapy of cancer [11], Lithium Storage [12–14], and even separation and catalysis [15–17]. Among these integrated nanosystems, magnetic core-shell materials together with porous nanostructures are of particular interest since they exhibit high porosities, excellent chemical stability and easily modifiable internal/external chemical surfaces [18]. The high surface area and pore volume derived from the porous component ensure facile adsorption as well as high loading of various guest materials. The obtained composites can serve as excellent supports for catalysis, ideal absorbents for bioseparation or immobilization, and unique functional agents or carriers for diagnosis and therapy. Moreover, such nanocomposites can be easily manipulated, delivered or separated through an intangible space at a distance simply by using an external magnetic force due to the existence of magnetic constituents [19]. Furthermore, during catalytic process, such core-shell porous materials also allow the fine control over the catalyst particle growth according to the pore size and the enhancement of the dispersion and concentration of the active sites in the host matrix [20]. In addition, the directed functionalization of the surfaces of such type magnetic core-shell materials is an elegant way to bridge the gap between heterogeneous and homogeneous catalysis [21].

Until now, a number of methods have been established for the construction of magnetic nanoparticles with porous and core-shell structures. In 1996, Liz-Marzán et al. have reported the synthesis of core-shell colloids particles with homogeneously coated silica shells using the silane coupling agent (3-aminopropyl)-trimethoxysilane as a primer to render the particle surface vitreophilic [22]. The thickness of the silica layer could be precisely controlled, and the particles could be transferred into practically any solvent after surface modification. When this coating procedure of silica was modified with the addition of surfactants (cetyltrimethylammonium chloride CTAC, cetyltrimethylammonium bromide CTAB, *n*-octadecyltrimethoxysilane C_{18}TMS, *etc.*), core-shell particles with nanoporous silica shells were generated. A series of microspheres with magnetic cores and porous shells were successfully synthesized [23–25]. This is the well-known strategy of "Stöber"-based coating process. Besides, the post-etching method is also a widely employed strategy to create nanopores by etching on nonporous silica shells coating onto the magnetic particles [26,27]. Surfactants were not necessary during etching process; however disordered nanopores were normally generated. By using a surfactant-containing solution system, either hydrophobic or hydrophilic magnetic nanoparticles could be easily coated by nanoporous shells through a reverse microemulsion method without any surface modification [28]. Another straightforward approach was the spray-drying-process in which magnetic species were first introduced into the precursor solution, and porous core-shell structured nanocomposites with embedded magnetic nanoparticles could be obtained [29,30].

Summarily, all strategies mentioned above are mainly based on the fine control and precise tailor at different interfaces by using various species and building-units. However, for practical applications, design and controllable fabrication of novel functional magnetic core-shell nanomaterials with unique porous structures are still great challenges. There are also a series of urgent issues should be addressed, which can be classified into the following several categories:

1. General and more feasible pathways should be established for the organization of different nano-objects with various functions into magnetic core-shell porous structures in order to open new possibilities for their applications.
2. More effective and easier methods should be found to finely tune the pore characters, such as pore size and structure, of desired magnetic core-shell porous materials since their functions and applications largely depend on the properties of mesopores or even micropores.
3. Functionalizing magnetic materials by a uniform and continuous shell with crystallized structure is always a difficult but important issue which should be well considered and examined.
4. Finding more suitable and fantastic magnetic materials for the synthesis of core-shell porous materials is also highly desirable, which must provide novel properties for new applications

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