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Historical perspective

Interfacial engineering for silica nanocapsules

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ABSTRACT

Silica nanocapsules have attracted significant interest due to their core–shell hierarchical structure. The core domain allows the encapsulation of various functional components such as drugs, fluorescent and magnetic nanoparticles for applications in drug delivery, imaging and sensing, and the silica shell with its unique properties including biocompatibility, chemical and physical stability, and surface-chemistry tailorability provides a protection layer for the encapsulated cargo. Therefore, significant effort has been directed to synthesize silica nanocapsules with engineered properties, including size, composition and surface functionality, for various applications. This review provides a comprehensive overview of emerging methods for the manufacture of silica nanocapsules, with a special emphasis on different interfacial engineering strategies. The review starts with an introduction of various manufacturing approaches of silica nanocapsules highlighting surface engineering of the core template nanomaterials (solid nanoparticles, liquid droplets, and gas bubbles) using chemicals or biomolecules which are able to direct nucleation and growth of silica at the boundary of two-phase interfaces (solid–liquid, liquid–liquid, and gas–liquid). Next, surface functionalization of silica nanocapsules is presented. Furthermore, strategies and challenges of encapsulating active molecules (pre-loading and post-loading approaches) in these capsular systems are critically discussed. Finally, applications of silica nanocapsules in controlled release, imaging, and theranostics are reviewed.

Contents

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1. Introduction

In the past decades, considerable progress has been made in the design, synthesis and application of core/shell nanostructured materials [1–6]. Nanocapsules represent a class of core/shell structure composed of a solid shell that surrounds a core-forming space available to entrap active molecules [7]. The tailorable functionalities of both core and shell endow nanocapsules with new properties, thus rendering it attractive as a superior nanocarrier platform for loading and delivery of functional cargoes. Various types of cargoes have been loaded into the core domain of nanocapsules, including drugs, genes, proteins, imaging agents, pesticides, and catalysts, since the hollow core allows high loading-capacity of active molecules as compared to their solid- and porous-nanoparticle counterparts. The nanocapsules shell, on the other hand, serves to: (i) protect the cargo against premature decomposition (e.g., by photolysis, hydrolysis, microbial, or oxidation/reduction); (ii) protect the environment where the nanocapsules are dispersed against toxicity of the cargo; (iii) provide accessible and stimuli-sensitive pathways for cargo release; and (iv) enhance dispersibility and stability of the nanocapsules in a given medium. While the core composition determines whether the nanocapsules are intended to be applied in biomedical, agricultural, or chemical fields, the shell material also plays an important roles in nanocapsular performance.

Inorganic silica has received a great deal of attention as a shell material encapsulating a core [8–11] because of its unique features, including: (i) optical transparency; (ii) stable and dispersible in aqueous medium; (iii) diffusional barrier; (iv) biocompatible (as the U.S. Food and Drug Administration (FDA) considered silica, in an amorphous form, as Generally Recognized As Safe (GRAS) material [12]); and (v) tunable physical (e.g., thickness, porosity, and mechanical strength) and chemical (e.g., charge, functionality, and reactivity) properties. To enhance the performance of silica nanocapsules, much effort has been directed toward the interfacial engineering of the silica shell, both at the silica framework (siloxane bonds, ≡Si—O—Si≡) and/or the silica surface (silanol groups, ≡Si—OH) level. For example, engineering silica nanocapsules with a 'stealthy' polymer such as poly(ethylene glycol) (PEG) can allow the nanocapsules to be dispersed in biological fluids and also enhance their bioavailability hence circulation times in vivo [13]. Further conjugation of silica nanocapsules with stimuli-responsive, targeting, optical, and contrast agents enhances their performance for controlled release, targeted delivery, and imaging/diagnosis. Functionalization of the silica shell is facile through well-established silane chemistry, and thus a plethora of conjugation strategies have been developed. These features of silica combined with the merits of core/shell structure to load active molecules with high-capacity have been driving the development of a cargo loaded, multifunctional and stimuli-sensitive silica nanocapsule (Fig. 1).

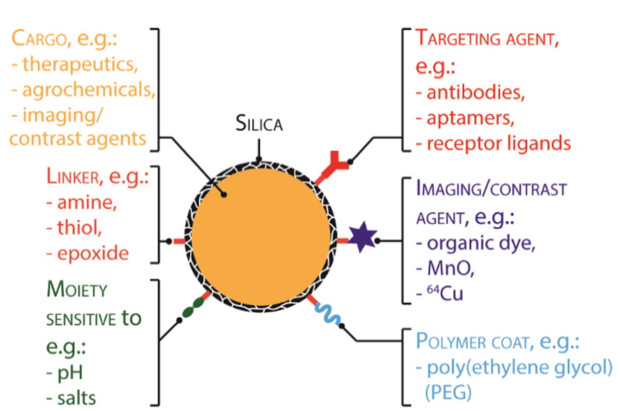

Fig. 1. Schematic of a cargo-loaded, multifunctional, stimuli-sensitive silica nanocapsule as a nanocarrier platform.

Silica nanocapsules in this article refer to hollow core or soft material-filled core that is surrounded with a silica shell. A large number of synthesis approaches are becoming available for the preparation of silica nanocapsules. Template-based methods are often used as they typically result in a well-defined size, shape, and configuration, due to the directing effect of the template. Various molecules have been used to modify the surface of templates, i.e., solid nanoparticles, emulsion droplets, and gas bubbles, as well as to direct silica formation exclusively at the boundary of solid–liquid, liquid–liquid, or gas–liquid interfaces, respectively. In addition, the use of biomolecules has recently emerged as an attractive strategy to develop bioinspired silica nanocapsules as they promote 'green' reaction conditions to form silica. Significant efforts have also been made to tailor the surface chemistry of silica nanocapsules hence evolving nanocapsules as an ideal nanocarrier platform, which has in turn catalyzed fundamental research and new applications of silica nanocapsules.

In this review, the focus is placed on recent research progress in the template-based synthesis of silica nanocapsules and key promising applications. This review article is organized as follows. In Section 2, the manufacturing approaches of silica nanocapsules are overviewed highlighting surface engineering of the core template materials (solid nanoparticles, liquid droplets and gas bubbles) dispersed in aqueous solutions. We intend to restrict the synthesis strategies to the basis of interfacial engineering of the core template using (bio)molecules that are able to both stabilize the template and direct nucleation and growth of silica at the boundary of two-phase interfaces (solid–liquid, liquid–liquid, and gas–liquid). Therefore, macromolecules such as micelles, vesicles, or polymeric aggregates that self-assemble to facilitate silica formation in bulk aqueous solution, instead of at interfaces, will not be discussed in this review. The interface chemistry of silica nanocapsules is further explored for making surface-engineered nanostructures with multiple functionalities. In Section 3, strategies and challenges associated with the encapsulation approaches are critically discussed. In Section 4, the applications of silica nanocapsules are overviewed mainly in the following areas: controlled release, imaging, and theranostics. Finally, we conclude with our opinions on the future direction of the field and important areas for further research.

2. Approaches for making silica nanocapsules

Fig. 2 shows the general procedure to synthesize a cargo-loaded, surface-functionalized silica nanocapsule using a template. A template, either solid nanoparticle, emulsion droplet, or gas bubble, is firstly

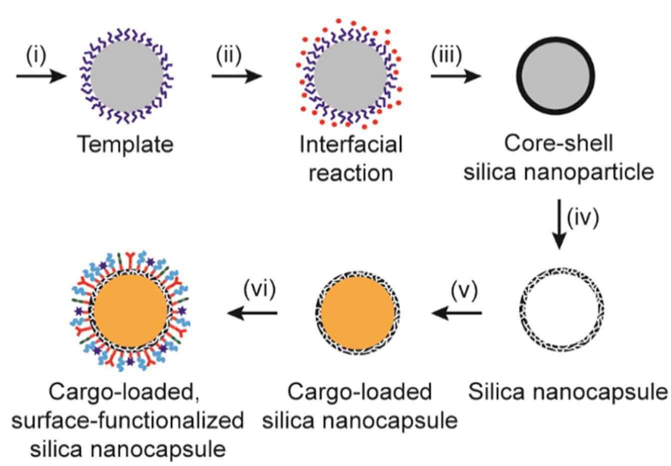

Fig. 2. Schematic procedure for the synthesis of a cargo-loaded, surface-functionalized silica nanocapsule. (i) Preparation of a template i.e., solid nanoparticle, emulsion droplet, or gas bubble which is modified by either molecules or biomolecules adsorbed on the template's surface; (ii) addition of a silica precursor; (iii) formation of silica shell; (iv) removal of the template; (v) loading of cargo molecules; and (vi) surface functionalization.

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