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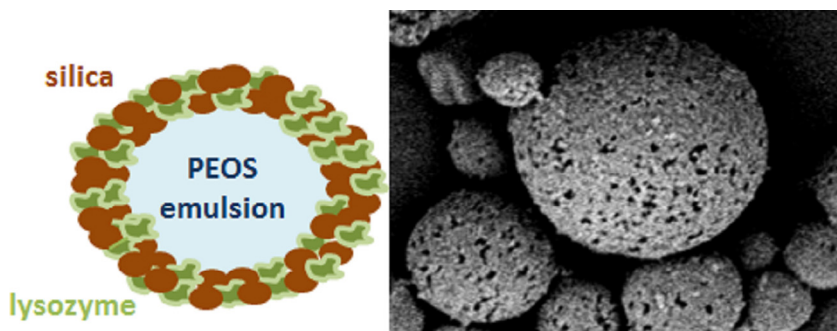
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Regular Article

Controlling the bio-inspired synthesis of silica

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GRAPHICAL ABSTRACT



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ABSTRACT

The influence of different parameters on the silicification procedure using lysozyme is reported. When polyethoxysiloxane (PEOS), an internally crosslinked silica reservoir, is used, regular structures with a narrow size distribution could be obtained only via introducing the silica precursor in two steps including initial dropping and subsequent addition of residual oil phase in one portion. We found that mixing sequence of mineralizing agents in the presence of a positively charged surfactant plays a key role in terms of silica precipitation when tetraethoxyorthosilicate (TEOS) is the oil phase. In contrast, well-mineralized crumpled features with high specific surface area could be synthesized in the presence of PEOS as a silica precursor polymer, regardless of mixing sequence. Moreover, introducing sodium dodecyl sulfate (SDS) as a negatively charged surfactant resulted in regular silica sphere formation only in combination with hexylene glycol (MPD) as a specific co-solvent. Finally, it is demonstrated that by inclusion of different nanoparticles even more sophisticated hybrid materials can be generated.

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1. Introduction

The ability to manufacture inorganic, organic and biological components in a single composite material owing to their hybrid

character and the possibility of further controlling their structure and functionalities [1], represents an interesting direction for developing multifunctional materials with a wide range of novel properties [2]. Among these hybrid materials, protein-SiO₂ composite structures possess unique and distinct properties such as chemical inertness, mechanical stability, biocompatibility, easy functionalization as well as optical transparency [3] and with potential applications ranging from immobilization of sensitive catalysts or enzymes [4] to novel implant substances in the field

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of tissue engineering [5]. Protein-induced SiO₂ formation promoted by various hydrolases, e.g. silicatein, trypsin and lysozyme has been of particular recent interest [6–8]. The physiological importance and the economic advantages of lysozyme, as well as the compatibility of obtained hybrid structures and the controllable morphologies of such composite particles are main factors making this enzyme a good alternative for silica biomineralization [9]. Additionally, the development of synthetic strategies and analytical tools for controlling structures with well-designed shapes and patterns at specific structural level is fundamental to materials science. Moreover it is difficult to build structures which are monodisperse in size.

In particular, the preparation of hollow capsules with a defined structure has attracted significant attention because of their potential applications for encapsulation of various substances and as controlled release systems for drug delivery as well as their use in coating technology, catalysis, micro-reactors and manufacturing of advanced composite materials [10–15].

Moreover, many commercial products based on emulsions include both surfactants and particles; hence, the characterization and mechanisms of stabilization of emulsions with mixed interfacial layers are of great importance [16,17]. Surfactants are able to modulate protein adsorption and induce surface structural alteration by forming protein-surfactant aggregates. The specific role of surfactant, protein, and the surfactant-protein complex in modulating interfacial behaviour is still not well understood. A number of experimental investigations on the interfacial behaviour of surfactant and protein mixtures have already been carried out [18–27], and these have pointed out three possible adsorption scenarios: complete hindrance, reduced amounts, or increased amounts of protein adsorption. Adsorbed surfactant layer sterically prevents protein adsorption as surfactant molecules, because of their smaller size, diffuse faster than protein species resulting in complete hindrance. The other two cases usually occur as a result of formation of surfactant-protein complexes with reduced or increased surface affinity, respectively, which in both cases gives rise to different adsorption behaviours from that of pure protein or pure surfactant in solution.

Besides, silica-based structures are well suited for the entrapment of dopants such as nanoparticles (NPs) and metal ions within the pores of the silica matrix or inside the silica shell by adding them into the reaction mixtures during sol-gel processes, thereby providing additional properties [28–30]. The presence of metal ions as doping agents has been found critically important to the charge-carrier recombination and interfacial electron transfer, both influencing the photoreactivity of materials [31,32]. More importantly, the NP-doped composites developed so far, present intrinsic drawbacks, that is, possible loss of NPs which leads to a reduction of their anticipated properties and potential harm to biological systems [33]. A strategy to resolve such a shortcoming aiming to prevent the nanoparticle loss via loading them into the interphase region of the merged structures is hence necessary [31].

Shiomi et al. first reported the biomimetic patterning of silica-based spheres catalyzed by lysozyme and ultrasonic treatment [34]. The mechanism through which lysozyme directs the polysiloxane formation from tetraethoxyorthosilicate (TEOS) as silica precursor has been shown. It is demonstrated that when a lysozyme-TEOS mixture was stirred, the sol-gel reaction of TEOS occurs and solid granular particles were mainly observed. By contrast, only when ultrasound was applied to the lysozyme-TEOS mixture, hollow spherical particles in a broad size-range were generated. We previously investigated extending this approach to obtain a wide variety of stable bio-catalyzed SiO₂-hybrid structures by developing straightforward synthesis routes without changing the specific chemical components [35,36].

Via a two-step feeding of TEOS including initial dropping and subsequent addition of residual TEOS in one batch and altering the agitation method (mechanical or ultrasound-assisted mixing), structures ranging from nanoparticles to different sized capsules with various surface morphologies were obtained. These studies clarified the feasibility of the capsule formation assisted by simple self-templating of silica structures even when the sample is not ultrasonicated.

Following this approach, we then investigated the role of buffering solution as well as additive inclusion in the form of salts or surfactants in creating the silica-hybrid materials. Our preliminary studies showed that, even though nanoparticles and crumpled morphologies can be merged depending on the utilized oil phase in the presence of cetyltrimethylammonium bromide (CTAB), as the structure-directing agent, no clear features were generated when sodium dodecyl sulfate (SDS) was introduced into the system. It was also demonstrated that changing the buffer has a drastic influence on the structuring of silica capsules and no regular features could be achieved using hyperbranched polyethoxysiloxane (PEOS) as the only silica supplier. According to these previous studies and considering the precipitation steps of silica particles [37], we assumed that there must be more parameters which have an impact on the mineralization process leading to more advanced control of the resulting structures.

Such parameters could involve reaction time when internally crosslinked silica species are used, mixing sequence of additives/bio-mineralizing agents and feeding a specific co-solvent when SDS is added to the system. The choice of the apolar phase also influences the process to a large extent.

In a first attempt, we test our proposed two-step synthesis procedure based on self-templating of the PEOS during the mineralization process via feeding the silica precursor polymer in two steps. In spite of our previous results which showed that no regular structure could be produced using PEOS, here, namely the subsequently formed PEOS droplets act as both the self-consumptive template and reservoir of the reactant for fabricating the silica particles. Up to now, the reported sol-gel process for capsule formation using PEOS consists only of using this silica precursor polymer as interfacial “glue” to a water-in-oil (water/oil) Pickering emulsion stabilized by silica nanoparticles [3,38,39].

Furthermore, we studied the factors affecting the morphology of the protein-silica materials when additives are introduced into the system. Herein, the concentration of surfactant, as well as the circumstance of surfactant and protein introduction (in sequence or combined), were varied in order to identify the separate roles of protein, surfactant, and the protein-surfactant complex in determining adsorption outcomes.

For lysozyme directed biomimetic silica synthesis, our studies demonstrated that not only the presence of cationic surfactant is influencing the resultant structures but also the mixing sequence of protein and surfactant plays a critical role on the formation of silica structures when TEOS is used. This study addresses the influence of a complex interaction of numerous factors such as electrostatic interactions and steric functions due to the fact that both lysozyme and silica species are charged. Considering this fact, experiments were designed to fabricate high surface area materials that are commonly used for applications where a high volumetric density of structures is critical, such as chromatography and catalysis [40].

In the next effort, we undertook a different approach to focus on the effects of co-solvent, when SDS is an additive of choice in order to understand the function of SDS in assisting the mineralization. The presence of hexylene glycol (MPD) as co-solvent was demonstrated to be essential to guarantee the formation of regular silica structures when SDS is introduced into the reaction mixture. MPD

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