Soft Vesicles in the Synthesis of Hard Materials

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CONSPECTUS

Vesicles of surfactants in aqueous solution have received considerable attention because of their use as simple model systems for biological membranes and their applications in various fields including colloids, pharmaceuticals, and materials. Because of their architecture, vesicles could prove useful as "soft" templates for the synthesis of "hard materials". The vesicle phase, however, has been challenging and difficult to work with in the construction of hard materials.

In the solution-phase synthesis of various inorganic or macromolecular materials, templating methods provide a powerful strategy to control the size, morphology, and composition of the resulting micro- and nanostructures. In comparison with hard templates, soft templates are generally constructed using amphiphilic molecules, especially surfactants and amphiphilic polymers. These types of compounds offer advantages including the wide variety of available templates, simple fabrication processes under mild conditions, and easy removal of the templates with less damage to the final structures. Researchers have used many ordered molecular aggregates such as vesicles, micelles, liquid crystals, emulsion droplets, and lipid nanotubes as templates or structure-directing agents to control the synthesis or assembly hard micro- and nanomaterials composed from inorganic compounds or polymers. In addition to their range of sizes and morphologies, vesicles present unique structures that can simultaneously supply different microenvironments for the growth and assembly of hard materials: the inner chamber of vesicles, the outer surface of the vesicles, and the space between bilayers. Two main approaches for applying vesicles in the field of hard materials have been explored: (i) in situ synthesis of micro- or nanomaterials within a specific microenvironment by vesicle templating and (ii) the assembly or incorporation of guest materials during the formation of vesicles.

This Account provides an in-depth look at the research concerning the association of soft vesicles with hard materials by our laboratory and others. We summarize three main principles of soft vesicle usage in the synthesis of hard materials and detailed procedures for vesicle templating and the characterization of the synthetic mechanisms. By use of these guiding principles, a variety of inorganic materials have been prepared, such as quantum dots, noble metal nanoparticles, mesoporous structures, and hollow capsules. Polymerization within the vesicle bilayers enhances vesicle stability, and this strategy has been developed to synthesize hollow polymer materials. Since 2004, our group has pursued a completely different strategy in the synthesis of micro- and nanomaterials using vesicles as reactive templates. In this method, the vesicles act not only as templates but also as reactive precursors. Because of the location of metal ions on the bilayer membranes, such reactions are restricted to the interface of the vesicle membrane and solution. Finally, using the perspective of soft matter chemistry, we stress some basic criteria for vesicle templating.

Introduction

Vesicles, usually spherical, are enclosed and hollow lamellar aggregates with a curved bilayer membrane comprised of amphiphilic molecules.¹ Not only can they be stably dispersed in and filled with water¹ or organic solvents,² vesicles can also be obtained as nearly perfect hollow capsules on solid surfaces.³ Depending on the fabrication method, vesicles generally exhibit three morphologies: oligovesicular, multilamellar, and unilamellar,⁴ the dimensions of vesicles generally vary from 10 nm to 50 μm. On the basis of the unique architectures available, current functional applications of vesicles have focused on
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Unlike the reverse micelle method, the vesicle method allows the synthesis of particles with excellent dispersity in aqueous solution under mild conditions. Second, with transcriptive templating and polymerization, the vesicle method provides an extremely convenient route to prepare hollow materials. Third, vesicles, especially multilamellar onions, provide different stable microenvironments that can support parallel reactions for the formation of surprisingly complex and multifunctional products.

However, vesicle methods indeed have shortcomings in material synthesis, including the weak reproducibility and stability of the templates. This limits the production of functional materials on a large scale. If new research does not focus on a real technological impact, this field may end without fulfilling its original promise. Hence, the future direction of vesicle methods in the field of materials synthesis is a concern. For example, specific amphiphilic molecules for the formation of novel vesicles are needed for particular chemical reactions or crystal growth processes. To scale up vesicle templating, different models have to be proposed to explain the formation of particles in vesicle microreactors. In addition, taking vesicles as a matrix, smart and multifunctional vesicle hybrids are required to develop effective carriers in biotechnological and catalytic applications. In terms of potential pharmaceutical applications, these hybrids must be biocompatible, load hydrophobic or hydrophilic drugs, respond to pH or temperature, and be easily tracked in vivo.

Conclusions and Perspectives

This Account relates recent developments in the use of soft vesicles for hard materials fabrication and characterization. The control and understanding of vesicle templating is an important route to study the physical chemistry of hard materials/soft matter organization. Vesicles have provided various means to synthesize different functional materials. However, success in this templating area hinges largely on the stability of the vesicles employed. Therefore, the study of the factors that influence the phase behavior of amphiphilic molecules is another important issue; these factors include solvent selection, composition, temperature, pH, the presence of salts, and pressure. In fact, using amphiphilic molecular aggregates as templates for material synthesis is also a study of the phase behavior of amphiphilic molecules. No matter how materials are prepared using different templating strategies, stable vesicles with expected structures should be preferentially fabricated. As stated succinctly by Kaler et al., “Template synthesis is not only a powerful means for materials synthesis, but it can also contribute to the determination and analysis of self-organized morphologies.”

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Biographical Information

Renhao Dong received his B.S. in Chemistry from Shandong University, Jinan, China, in 2008. He is currently working on his Ph. D. with Professor Hao investigating the self-aggregation of surfactants in solution.

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Footnotes

10 Korgel, B. A.; Mombourquette, H. G. Controlled synthesis of mixed core and layered (Zn, Cd)S and (Hg, Cd)S nanocrystals within phospholipid/n-hexane vesicles. Langmuir 2000, 16, 3589–3594.