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Previews

Revealing the Role of Concentration Waves in Synthesizing Hollow Multi-Shelled Structures

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Recently in *Angewandte Chemie International Edition*, Wang and co-workers presented a comprehensive study that combines a mathematical model with experiments to reveal the key role of concentration waves in the formation of hollow multi-shelled structures (HoMS), and provides a theoretical guideline for the precise engineering of HoMS for targeted applications.

Hollow particles, also known as capsules, have attracted widespread interest over the last two decades and have found diverse applications, including agriculture, environmental science, and biomedicine.¹⁻³ To achieve the desired functions and performance of hollow particles, several parameters need to be controlled during particle preparation and characterization.^{4,5} These include shell composition, which plays a pivotal role in dictating the physicochemical properties of the hollow particles. For instance, metallic hollow particles, such as gold and silver, are widely used for their optical, electronic, and catalytic properties, whereas organic hollow particles are mainly explored for biomedical applications owing to their high biocompatibility and facile loading of various cargos such as drugs. In templating synthesis approaches, the size of hollow particles is largely controlled by the size of the sacrificial template used and can be tailored from nanometers to millimeters in diameter. The thickness of the shell can be adjusted by using different precursor concentrations and reaction times. Generally, thicker shells offer higher mechanical and chemical stability than thinner shells. Conversely, thinner shells provide higher permeability, which can potentially increase the catalytic or reaction activity. Hollow particles can have single, double, or multiple shells (i.e., hollow multi-shelled structures; HoMS), with each shell having the same or different compositions. HoMS have recently attracted increasing attention owing to their high surface areas and their capacity for sequential transfer and storage of matter, which are rarely achieved by other nano/micro-structured materials, and are useful for various applications including cascade catalysis, drug delivery, and as biosensors.⁶

Several strategies have been developed to synthesize HoMS, among which the sequential templating approach (STA) is the most widely explored.^{7,8} This approach involves distributing the precursors within templates, regulating the balance between template removal and shell formation, and using precursor-enriched templates as "sequential templates" to facilitate the formation of HoMS in one step (Figure 1A, B). Despite recent advances, the theoretical mechanism of formation HoMS using STA remains unclear.

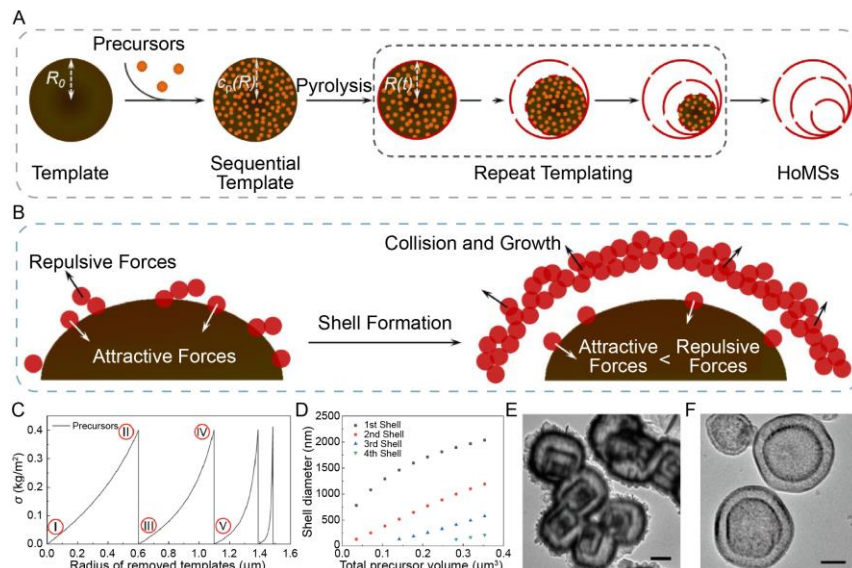


Figure 1. Schematic of the formation mechanism of the hollow multi-shelled structure (HoMS). (A) Schematic of the formation of HoMS via STA. (B) Schematic of the formation of shells, achieved when the repulsive forces between the templates and linked particles (aggregation of precursors on the surface of the template) after collision and growth are larger than the attractive forces between the particles and template. (C) Variation of the concentration of the precursor on the surface of the template (σ) during the template removal process confirms the existence of concentration waves. (D) Simulation result of shell structures engineered using different volumes of precursors. Note that precursors are uniformly distributed across the template. (E, F) TEM image of Cu_2S (E) and CaCO_3 (F) with HoMS. Scale bars are 200 nm. Adapted with permission from Wei et al.⁹ Copyright 2023 Wiley-VCH GmbH.

In a recent paper published in *Angewandte Chemie International Edition*, Wang and co-workers presented a comprehensive study that includes both mathematical and experimental approaches to gain deeper insights in the physical mechanism driving the formation of HoMS and to develop regulation methods for the precise engineering of HoMS, including composition, and shell diameter and number.⁹ The mathematical model was constructed based on simplified experimental conditions in which metal oxides with HoMS were synthesized using carbonaceous microspheres (as templates) during calcination. The dehydration and crystallization reactions of precursors were ignored to simplify the model. The simulation results revealed the appearance of a periodical variation of the concentration of the precursors on the surface of the templates, referred to as “concentration waves” (Figure 1C). Specifically, the precursors gradually accumulated and aggregated (forming nanoparticles) on the surface of the templates as the latter shrank during calcination, and shell formation occurred when the repulsive forces between the templates and linked particles after collision and growth were greater than the attractive forces between the particles and templates (Figure 1B). The separation of the aggregated precursors from the templates (stand-alone shell) led to a significant decrease in the concentration of the precursors. This process (aggregation of precursors on the surface of the templates as the templates shrank and shell formation) is repeated until consumption of the precursors or template removal is complete.

An important achievement of the study is elucidating the underlying formation mechanism of HoMS, which provides a quantitative model for predicting and controlling shell formation. The effects of different experimental parameters on concentration waves and shell formation were investigated, revealing that the shell structure (e.g., number, diameter, and distance between shells) could be regulated by controlling the total amount of the precursors and their distribution across the templates (Figure 1D), which is consistent with the experimental results. Generally, a higher number of shells could be formed by increasing the precursor amount or through deeper adsorption and better distribution of precursors across

the template. Increasing the precursor concentration offers a simpler and more facile route to increase the number of shells on hollow particles.

Furthermore, this study demonstrated that the synthesis method of HoMS could be extended from a high-temperature calcination process in the solid state to processes requiring milder conditions in the solid–liquid phase (Figure 1E, F). For instance, Cu₂S and CaCO₃ with HoMS were synthesized under aqueous conditions by creating concentration waves and employing precursor-enriched templates. These pioneering attempts provide a new synthesis avenue for possibly fabricating HoMS composed of active compositions (e.g., biomolecules).

In summary, this study by Wang and co-workers fills the theoretical gap in the formation of HoMS by STA and provides a mathematical model that can predict and control shell formation. Identifying concentration waves as the physical mechanism driving the formation of HoMS offers insights for an improved understanding of engineering the structure and properties of materials. Furthermore, this study offers a new avenue for the rational design of HoMS under mild conditions, which is essential for further developing HoMS with different compositions and properties for a range of applications.

However, although the mathematical model developed in the study can predict the shell diameter of materials, the difference between the simulation and experimental shell diameters is still significant. Therefore, though challenging, consideration of the dehydration and crystallization reactions in the simulations is an important aspect to be examined. Furthermore, expanding the range of shell composition to include organic or hybrid materials (e.g., metal–organic frameworks) can broaden the library of materials with HoMS and further advance the field.¹⁰ In addition, future directions in HoMS also include optimizing synthesis conditions, developing new characterization methods, investigating the relationship between multi-shelled structure and performance, and identifying new applications.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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