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The development of hollow multishelled structure: from the innovation of synthetic method to the discovery of new characteristics

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Hollow multishelled structure (HoMS) is one of the most promising multifunctional structures. The high complexity of its structure makes the general and controllable synthesis of HoMS rather challenging. By integration of multidisciplinary knowledge, a great achievement in HoMSs has been obtained in the past decade. Especially, the developed sequential templating approach has significantly boomed the progress of HoMS in composition and structure diversity and application area. The implementation of the temporal-spatial ordering in HoMS makes it indispensable in solving the key scientific problems in energy conversion, catalysis and drug delivery areas. Further development in HoMSs with novel intricate structures will bring new understandings. In this review, we systematically introduce the development history of HoMSs, summarize the inspiration inherited from the previous research on hollow structures, and discuss the milestones in the development of HoMSs, with a focus on the sequential templating approach for HoMS fabrication, attractive temporal-spatial ordering property and dynamic smart behavior for advanced applications. We hope to reveal the inherent relationship between the precise synthesis of HoMS and its highly tunable compositional and structural characteristics, and point out its future direction to boost HoMS area further.

hollow multishelled structure, sequential templating approach, temporal-spatial ordering, smart dynamic behavior

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1 Introduction

Hollow structures have many attractive properties such as high specific surface area, low density and high loading capacity. They have attracted worldwide attention and have been tremendously fabricated and applied for diverse areas. The Chinese scholars have contributed greatly to the development of hollow structures [1–4]. The template-assisted strategy, which is facilitated to control the shape and size of the void space, has been the mainstream for fabricating the hollow structure. Xia *et al*. [5] developed the adoption of polystyrene sphere template to synthesize TiO_2 hollow spheres, while Li *et al*. [6] developed a carbon microsphere template that could absorb metal salt precursors without surface modification and could be applied to fabricate series of metal oxides, including Ga_2O_3 hollow spheres. In addition to hard templates, the Chinese scholars also developed various soft templates to synthesize hollow structures. For example, Shi *et al*. [7] developed a soft emulsion templating approach to synthesize aluminosilicate hollow spheres, while Zhao *et al*. [8] developed a reverse emulsion templating strategy to fabricate siliceous hollow spheres. Besides, Xie *et al*. [9] demonstrated a CS_2 oil templating approach to prepare CdS hollow sphere, and Wan *et al*. [10] synthesized V_2O_5 hollow microspheres *via* poly(vinylpyrrolidone) templating

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approach. The development of diverse templates significantly enriches the hollow structure family.

Apart from the template-assisted method, there comes in template-free method with the hollowing mechanism deeply investigated. Yin *et al*. [11] developed the formation of chalcogenides hollow nanocrystals through the Kirkendall effect; Zeng *et al*. [12] revealed the hollowing process of oxides rooted from Ostwald Ripening process; Yan *et al*. [13] investigated the solid-to-hollow transition of $NaYF_4$:Yb,Er nanocrystals *via* electron-beam lithography. Benefiting from the flourish of synthetic methods, hollow structures with various shapes and compositions have been fabricated for energy, environmental and biomedical area applications [14–19].

Single-shelled hollow structures have been proved to possess many attractive physiochemical properties. The hollow multishelled structure (HoMS) featured two or more shells that are separated by internal void and expected to bring more fascinating properties [20–25]. In addition, the unique temporal-spatial ordering character makes HoMS stand out as a promising candidate for complex and important applications like cascade reaction, sequential wave absorption, sustained drug release and hybrid energy storage [4]. However, the increased complexity in structure makes the fabrication of HoMS highly challenging. As far as we know, a single-shelled hollow structure was reported as early in the 1970s [26], while HoMS was not reported until 2004 [27]. As another fact, about 36,871 papers related to the hollow structure had been published during 2004 and 2008 (search “hollow structure” in the “web of science” database), while only 15 papers were about HoMS due to the lack of a general and controllable method for the synthesis of HoMS.

In 2009, Wang’s group [28] developed the sequential templating approach (STA) for the general fabrication of HoMS, as inspired by the programmed temperature strategy proposed by Xie’s group [29] and the carbonaceous microsphere (CMS) templated method reported by Li’s group [6]. Since then, both the fabrication and application of HoMS have enjoyed a flourishing development. By precisely manipulating the kinetic and thermodynamic process during the fabrication of HoMS through STA, various HoMSs have been accurately fabricated to meet the requirements of diverse application areas, such as Fe_2O_3 [30] and $ZnFe_2O_4$ [28] for sensors, Co_3O_4 [31] and TiO_2 [32] as anode materials for lithium-ion batteries (LIBs), V_2O_5 [33] and $LiMn_2O_4$ [34] as LIB cathode materials, $Fe_2(MoO_4)_3$ as cathode material for sodium-ion batteries (SIBs) [35], Mn_2O_3 [36] for supercapacitors (SCs), ZnO [37] and SnO_2 [38] for sunlight absorption, TiO_2/Fe_2TiO_5 [39] and $SrTiO_3$-TiO_2 [40] for photocatalysis. Through decades of continuous efforts worldwide, a unique and relatively complete system of synthetic methodology and specific application has taken shape. Recently, Wang’s group [4] revealed the temporal-spatial ordering nature of HoMS and highlighted its dynamic smart evolution in abundant application areas, which will decidedly guide novel HoMSs design and further enrich HoMSs family. To date, scientists from 258 universities or institutions of 26 countries and regions have already published over 600 articles about HoMS [41]. Thus, it is time to retrospect the development of HoMS historically, summarize recent advances and provide future perspectives for this field.

In this review, we aim to look back at the development history of HoMS, especially the milestones (Figure 1) and look forward to its future development. We first revisit the rise of HoMS, starting from the brief history of hollow structures to the function call for multishelled ones. Subsequently, we discuss the development in the synthetic methodology of HoMS inherited from the synthesis of hollow structures. Then the flourish in the fabrication and application of HoMS family benefiting from STA is highlighted. Furthermore, the concepts of “temporal-spatial ordering” and “dynamic smart behavior” are showcased by enabling complex multifunctional applications. Finally, future research directions are suggested to boost this area further.

2 The rise of HoMS

2.1 Brief introduction to the synthetic development of hollow structures

A hollow structure is defined as a solid entity with a relatively large fraction of void space inside a distinct shell. Along with the emergence of nanoscience and nanotechnology in the early 1980s, hollow nanomaterials have immediately attracted general attention from multidisciplinarity [42]. Benefiting from the worldwide efforts, the morphology of hollow structures can be spherical [43,44], cubic [45], tubular [46], fusiform [47], ellipsoidal [48] or urchin-like [49,50], while the composition could be metal oxide [51,52], silica [53,54], alloy [55], metal nitride [6], selenide [56], sulfide [57], fluoride [58,59], lanthanides compounds [60], carbon materials [61–64], polymer [65], covalent organic framework [66].

The synthetic methodologies for hollow nanostructures can be classified into two types: templating method and template-free method. The templating method could be classified into the hard-templating method and soft-templating method. Hard templating method using rigid templates such as nickel [67], anodic aluminum oxide (AAO) [46], SiO_2 [68], polystyrene sphere [69], is the most common and effective method to prepare hollow nanostructures. In addition to hard templates, some soft templates such as supramolecular micelles [70], polymer vesicles [71] can also be applied to fabricate hollow nanostructures. Targeted shells grow along the interfacial region and hollow

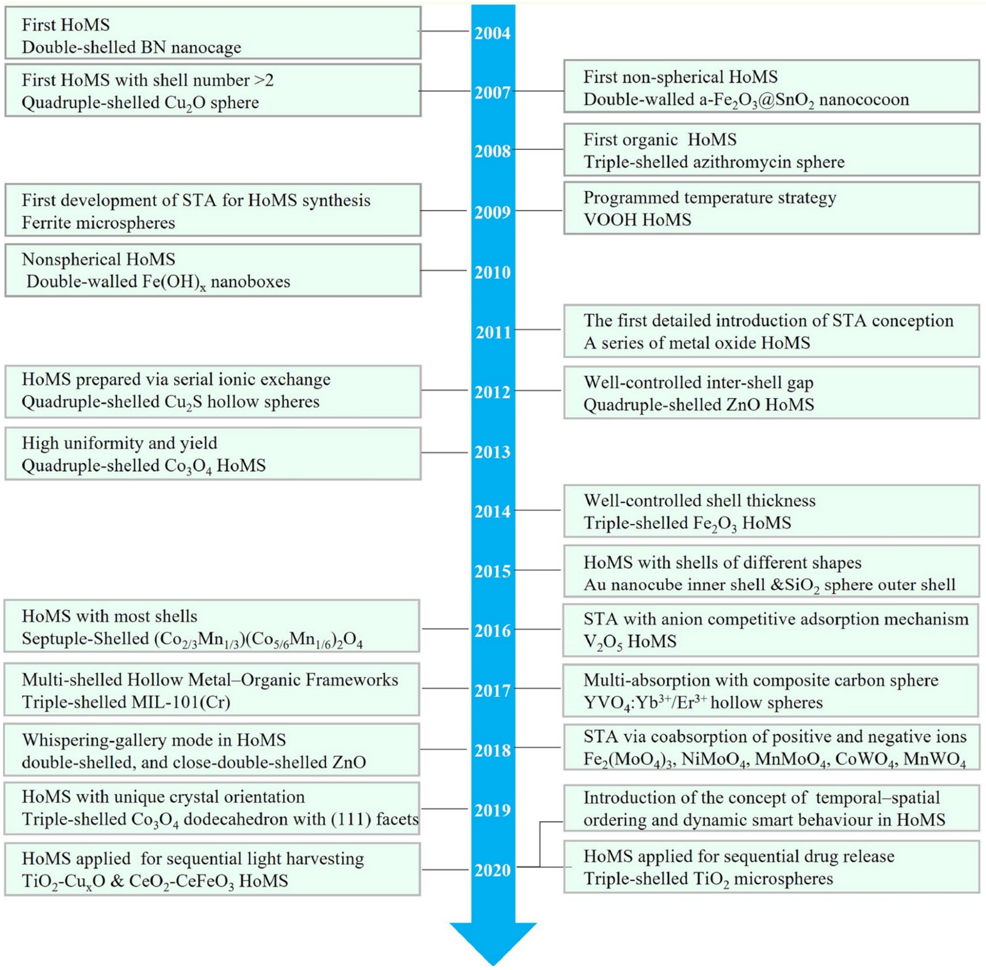

Figure 1 Timeline showing the milestones in the development of HoMSs (color online).

nanostructure could be obtained after the removal of the template. The shape and the void space are usually inherited from that of the template despite that the template may be rigid or soft and the technique could vary greatly. Besides, by adjusting the surfactant or structure-directing agent, highly ordered mesopores/micropores [8], even with 3D network structure [7] could be built up within the shell.

In addition, the template-free method wherein the hollowing is based on the Kirkendall effect [11], Ostwald ripening [72], ion exchange or selective etching is also intensely investigated for fabrication of hollow structures. During the Kirkendall process, small voids are generated at the interface, enlarged through the surface diffusion of atoms, and finally evolve into a hollow cavity inside the shell. Representatively, Chen *et al*. [73] reported the synthesis of Pt_3Ni hollow nanoframes using solid $PtNi_3$ polyhedra as the starting materials through the Kirkendall effect. To minimize the total surface energy, smaller particles tend to dissolve and regrow on larger particles, which would induce void space formation, demonstrating hollowing process based on Ostwald ripening. Typically, Zeng *et al*. [74] demonstrated the formation of a variety of Cu_2O hollow nanostructures through the tailored Ostwald ripening process. Ion exchange indicates ions between a solution and a solid particle, which has also been widely adopted for fabricating hollow nanostructures. As a successful example, Shen *et al*. [75] reported the synthesis of $NiCo_2S_4$ hollow structure through a controlled ion exchange process. Selective etching means selectively removing part of the material to create a cavity by chemical treatment or calcination, which could also be investigated for the formation of hollow structures. For example, Chen and co-workers [76] reported the synthesis of AuNP@SiO_2 yolk-shell structures by a repeated SiO_2 deposition-incubation-etching method.

2.2 Functional requirements promote the emergence of HoMS

The flourishing in the synthesis of hollow structures during the early 2000s has benefited various application areas [77–80]. A HoMS with multiple adjustable shell compositions and structures could provide a relatively complex micro-environment, thus potentially endowing it more fascinating properties and benefiting its application performance [4,81,82], as listed below (Figure 2) [83]. (1) A HoMS has multiple shells with the composition and thickness of each shell highly adjustable. These shells could possess a distinct functionality working together synergistically and collaboratively, making a HoMS an integrated device. What's more exciting, a HoMS can amplify the performance of each shell rather than the simple sum up of every shell. As a typical example, instead of weakened light absorption due to severe reflection of incident light on bulk materials or single-shelled hollow ones, the multiple scattering/reflection within HoMS could enhance the light absorption [38,39]. (2) HoMS has multiple spaces as separated by multiple shells, which could provide separated micro-environments to host different guests or reactions. For example, HoMS, which consists of an upconversion-material-based shell and magnetic shell, can function multimodal bioimaging (in this case, fluorescence imaging and magnetic resonance imaging). Meanwhile, the different cavities within HoMS can be loaded with different biomedicines, which enables HoMS to work as cargo for multiple drugs delivery, and afford advanced diagnose and therapy [84]. (3) HoMS with multiple shells arranged in order from outside to inside, possesses unique temporal-spatial ordering nature, by which the matter passes through each shell in a sequence based on the exact spatial distribution, making HoMS indispensable choice for complex and important applications like cascade reaction, sequential wave absorption and sequential drug release, *etc*. [4].

As a result, there is a growing desire to construct HoMSs. The first successful trial on the fabrication of HoMS came in 2004 with a peanut-like double-shelled hollow boron nitride (BN) nanocages [27]. Unfortunately, afterward, HoMS suffered from a bottleneck development due to the limited synthetic methodology. In 2009, Wang's group [28] developed STA for the fabrication of HoMS, and since then, the HoMS field has boomed greatly, with numerous scientists from different disciplines across the world flowing over into this field.

3 Innovation of synthetic method for HoMS

During the past decade, various approaches have been explored to synthesize HoMSs. Typical HoMSs synthesized through different methods are compared in Table 1 [85–115].

3.1 Synthesis of HoMSs through inherited synthetic methods of hollow structures

The templating method is the most straightforward for the preparation of hollow structures. During the early attempt, the shell-by-shell assembly is usually combined with templating for constructing HoMS, which involves the sequential coating of precursors for targeted shell onto the surface of a template and another material as an interlayer. After repeating the coating procedure several times and subsequently removing the interlayers and the template, HoMS is finally obtained (Figure 3). For example, through this approach, Li *et al*. [115] prepared silica HoMS.

In 2009, Xie's group [29] proposed a programmed temperature strategy to synthesize VOOH HoMSs from the solid templates. They revealed that the solid templates could experience different hollowing rates by controlling the temperature during the Kirkendall effect process following the Arrhenius activation-energy equation (Figure 4). By initiating a second shell on the surface of the inner core and ensuring the core particles to evolve into hollow ones inside the outer shells, double-shelled hollow spheres are formed. This programmed temperature strategy provides essential and general access to more complex hollow nanostructures.

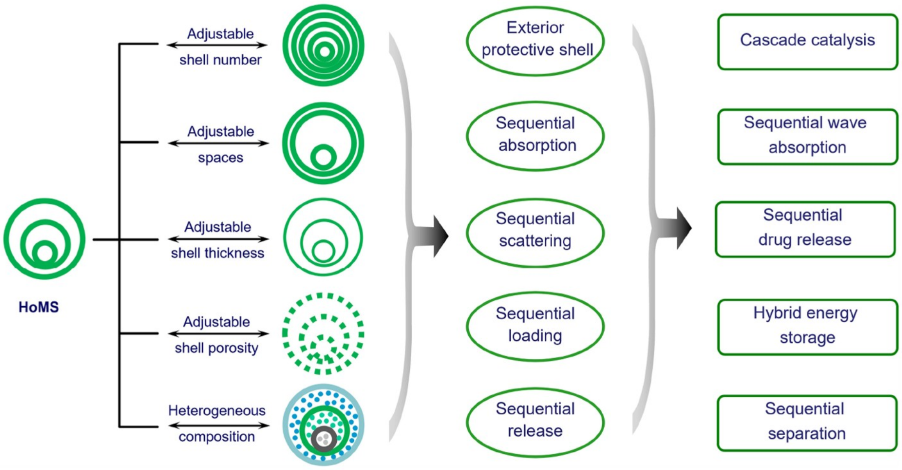

Figure 2 Illustration of the superior characteristics and applications of HoMSs. Adapted with permission from Ref. [83], copyright by Wiley (2019) (color online).

Table 1 Summary of typical HoMSs

Type	Materials	Method	Surface area ($m^2 g^{-1}$)	Application	Ref.
Oxide	Cu_2O quadruple-shelled hollow sphere	Soft templating	–	–	[71]
	$ZnFe_2O_4$ double-shelled hollow spheres	STA	109.8	Gas sensor	[28]
	CeO_2 double-shelled hollow sphere	STA	47.3	Bio-sensing	[85]
	SnO_2 quadruple-shelled hollow sphere	STA	–	Photodetector	[86]
	WO_3 triple-shelled hollow sphere	STA	124	Photocatalysis	[87]
	$LaCo_{1-x}Ni_xO_{3-\delta}$ triple-shelled hollow sphere	STA	11.2	Electrocatalysis	[36]
	Mn_2O_3 quadruple-shelled hollow sphere	STA	36.5	Supercapacitor	[88]
	α-Fe_2O_3 triple-shelled hollow sphere	STA	29.2	Lithium-ion battery	[89]
	TiO_2 triple-shelled hollow spheres	STA	20.56	Lithium-Sulfur Battery	[90]
	SiO_2 triple-shelled hollow sphere	Shell-by-shell assembly	329.2	*In vitro* and *in vivo* imaging, and drug delivery	[116]
Sulfide	Cu_2S quadruple-shelled hollow sphere	Hard templating	–	–	[91]
	NiS_2 quadruple-shelled hollow spheres	STA & sulfidation	36.3	Rechargeable alkaline battery	[92]
	SnS-MoS_2 double yolk-shell sphere	STA & sulfidation	–	Na-ion storage	[93]
	$NiCo_2S_4$ onion-like holow sphere	STA & ion exchange	74	Hybrid supercapacitor	[94]
	Sb_2S_3 triple-shelled hollow truncated octahedron	STA & ion exchange	–	Sodium-ion battery	[95]
Selenide	$CoSe_2$/(NiCo)Se_2 double-shelled box-in-box	Hard templating	16.13	Sodium-ion storage and hydrogen evolution	[96]
	$CoSe_2$/$FeSe_2$ hollow nanocuboid	Hard templating	107	Electrocatalysis	[97]
Phosphide	CoP double-shelled Nanocages	STA and phosphorization	30.8	Photothermal therapy	[98]
	CoP triple-shelled hollow sphere	STA and phosphorization	–	Electrocatalysis	[99]
Fluoride	$Na_3(VOPO_4)_2F$ quadrple-shelled hollow sphere	Soft templating	23	Na-ion storage	[100]
Hydroxide	$Fe(OH)_x$ double-shelled nanobox	Template-engaged redox etching	–	–	[101]
	Ni–Fe LDH double-shelled spindle-like nanocage	Hard templating	–	Electrocatalysis	[102]
Carbonate	$CaCO_3$ triple-shelled hollow sphere	STA	25	CO_2 adsorption	[103]
Metal	Ag@Au double-shelled hollow quasi-sphere	Galvanic replacement		Optical nanodevice	[104]
Carbon based material	Mesoporous carbon onionlike quadruple-shelled hollow sphere	Self-assembly approach	867	–	[105]
	Carbon double-shelled hollow sphere	Shell-by-shell assembly	1124	Lithium-sulfur battery	[106]
	Nitrgon doped carbon quadruple-shelled hollow dodecahedrons	Hard templating	414	Hydrogenation of furfural	[25]
	Quadruple-shell hard carbon hollow sphere	Selective etching	47.6	Na-ion storage	[107]
Polymer	Onion-like dendrimersome HoMSs	Self-assembly approach	–	–	[108]
	Sulfonated microporous organic network triple-shelled hollow sphere	Hard templating	484	Drug delivery	[109]
Zeolite	ZSM-5 double shelled hollow cuboid	Shell-by-shell assembly	403	–	[110]
MOF	Single-crystalline MIL-101(Cr) triple-shelled hollow truncated octahedral	Shell-by-shell assembly	1486	Styrene oxidation	[111]
	ZIF-8 Double shelled hollow cube	Shell-by-shell assembly	1323	Fluorescence	[112]
Hybrid Composite	TiO_2/PMMA-PMA double-shelled hollow sphere	Hard templating	~10	–	[113]
	PS-SO_3H@phenylenesilica double-shelled sphere	Shell-by-shell assembly	422	Friedel-crafts alkylation	[114]

As discussed above, the template-free method has been widely adopted to fabricate hollow structures. Zhao *et al.* [83] prepared azithromycin HoMSs by using a self-assembly approach (Figure 5). Azithromycin vesicles form in an ethanol-water mixture system due to the different solubility of azithromycin in ethanol and water, and the concentration gradient would induce that the azithromycin self-diffuses outward and precipitates to form the first shell. Then, azithromycin molecules continue to diffuse outward to form another shell, and finally result in an azithromycin HoMS

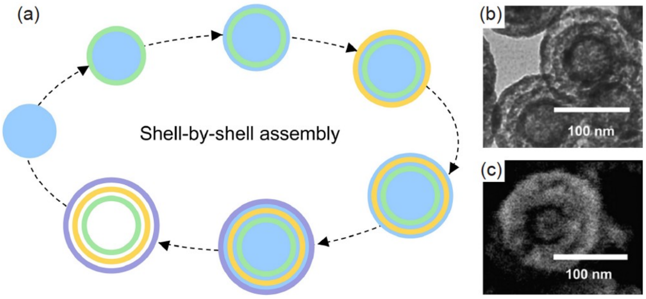

Figure 3 (a) Schematic showing the procedures of fabricating HoMS through the shell-by-shell assembly. Adapted with permission from Ref. [3], copyright by Royal Society of Chemistry (2015). (b) TEM and (c) SEM images of SiO_2 HoMSs prepared through the shell-by-shell assembly approach. Adapted with permission from Ref. [116], copyright by Elsevier Ltd. (2012) (color online).

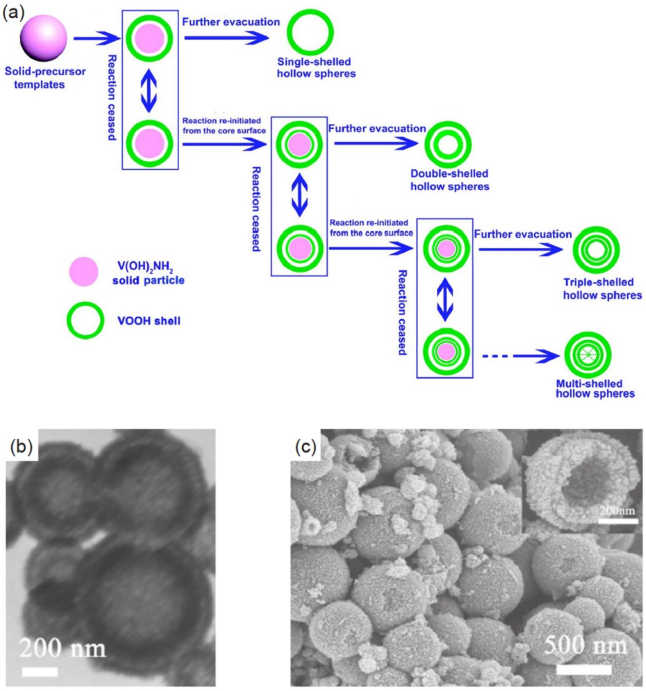

Figure 4 (a) The schematic outline of the transformation of solid templates to VOOH HoMSs. (b) TEM and (c) SEM images of VOOH HoMSs. Adapted with permission from Ref. [29], copyright by American Chemical Society (2009) (color online).

after repeating these processes several times. *Via* a similar self-assembly approach, Zhang *et al*. [116] reported the synthesis of Cu_2O HoMSs.

3.2 Sequential templating approach

Inspired by those pioneering work, in 2009, Wang's group [28] came up with a facile, controllable, universal and scalable method, which was later named as "sequential templating approach" [30] to prepare a wide range of HoMSs with different compositions, sizes and shapes (Figure 6). A typical synthesis process of HoMS through STA starts from the preparation of CMS templates, followed by the enrichment of precursors into CMS templates. Finally, HoMSs are obtained after the calcination of the precursor-rich template to remove the template, during which the CMS acts as a template repeatedly and sequentially. To be more specific, during this calcination process, the precursor near the outside transforms into a rigid shell. Meanwhile, the inner precursor-enriched template core shrinks as the CMS template is calcined to give the combustion products of CO_2 and H_2O. This establishes a gap between the outer shell and the inner core. As calcination proceeds, the precursor in the inner core undergoes a similar templating process and is converted into another shell. This process can be repeated several times, in which case we arrive at the targeted HoMSs.

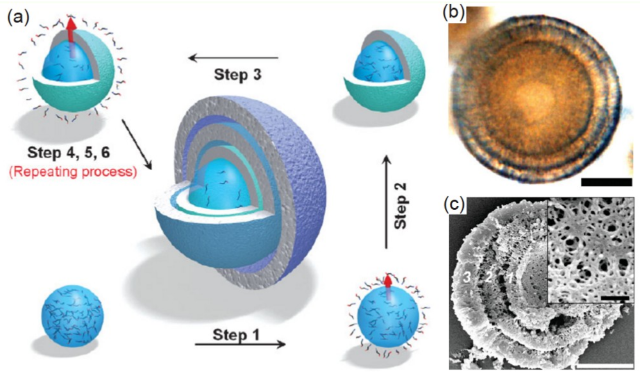

Figure 5 (a) Schematic illustration of azithromycin HoMSs by using a self-assembly approach. (b) Optical microscopy image and (c) SEM image of the triple-shelled hollow microsphere. Scale bar: 10 μm. Adapted with permission from Ref. [83], copyright by Wiley (2008) (color online).

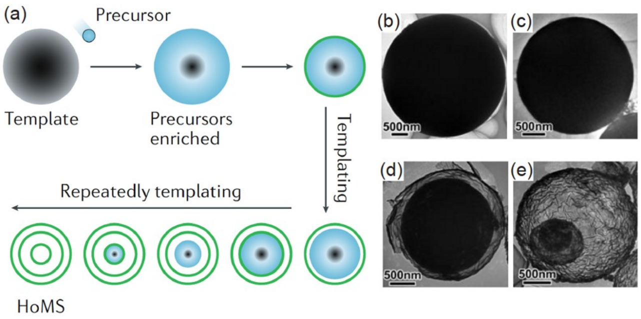

Figure 6 Illustration of the formation of HoMSs through STA. Adapted with permission from Ref. [4], copyright by Nature Publishing Group (2020). (b–e) TEM images of the products obtained at different temperatures during the annealing process for Fe_2O_3 HoMS fabrication. Adapted with permission from Ref. [30], copyright by John Wiley & Sons (2011) (color online).

STA is general for the fabrication of diverse HoMSs and easy to control the compositional and structural parameters of HoMSs by manipulating the precursor enrichment process and the formation of HoMS along with the removal of templates (Figure 7) [117]. During the enrichment process, the content, depth and distribution of precursors within the template can be controlled by adjusting the enrichment conditions like precursor concentration, solvent composi-

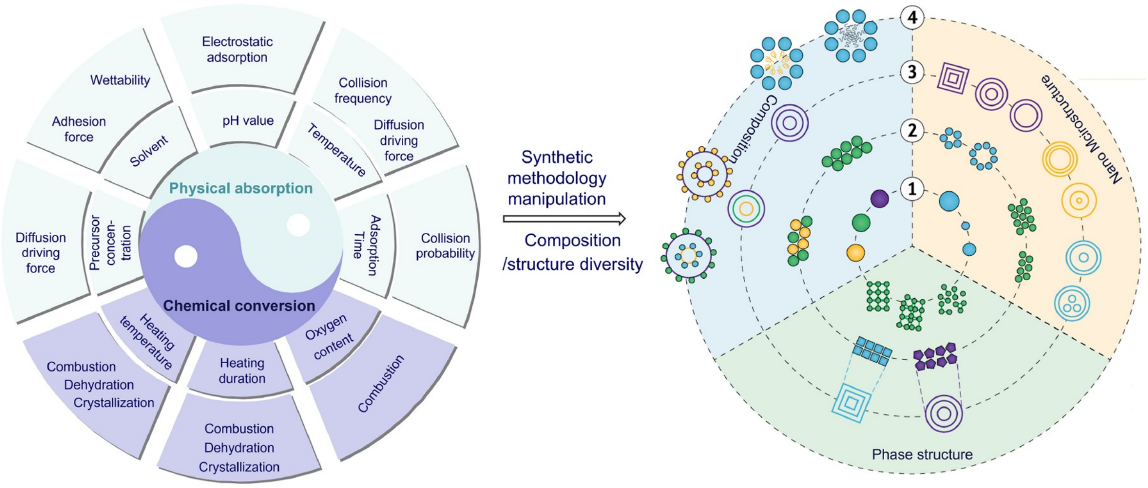

Figure 7 Schematic diagram of relationship between key parameters of STA and compositional and structural parameters of HoMSs. Adapted with permission from Ref. [117], copyright by Wiley (2018) and Ref. [4], copyright by Nature Publishing Group (2020) (color online).

tion, adsorption temperature, and template pretreatment or by tailoring the enrichment capability of CMS template by base or acid pretreatment. Another key process is to convert the precursor into a product and remove the template, normally through calcination. During the calcination process, the shell formation rate and the template removal rate should match with each other to form more shells, both of which could be influenced by the calcination temperature, heating rate, and calcination atmosphere. By adjusting the enrichment and calcination process, the shape, size, shell number, shell thickness, inter-shell gap, crystallization and pore structure of HoMSs could be accurately controlled [118].

During the development of STA, some interesting phenomena were found to make important innovations, which we would like to highlight. Firstly, in 2016, Wang's group [33] found that metal anions can also be adsorbed by negatively charged CMSs, in addition to the conventional metal cation adsorption. Conventionally, nonmetallic anions such as OH^- are first adsorbed by CMSs, and then the metal cations are adsorbed by the resultant negatively charged CMSs. In the anion-adsorption mechanism, both the OH^- and the metal anions are adsorbed by CMSs in a competitive way, and then nonmetallic cations such as NH_4^+ are adsorbed to neutralize CMSs and thus promoting further adsorption of the metal anions. Secondly, in 2018, Wang's group [35] efficiently restrained the hydrolysis and precipitation reactions during the coabsorption of negative and positive metal ions by taking advantage of the chelation effect of citric acid and successfully achieved various binary metal oxide HoMSs, including $Fe_2(MoO_4)_3$, $NiMoO_4$, $MnMoO_4$, $CoWO_4$, and $MnWO_4$. Thirdly, in 2019, Wang's group [119] discovered the "Genetic inheritance" effect when using ZIF-67 template to prepare Co_3O_4 HoMS. It is quite interesting that atoms tended to topologically shift within the crystal lattice to expose facets of similar spatial atom distribution or arrangement preferably. This finding widens our views of manipulating HoMS nanostructures by regulating precursors' atomic arrangement mode in the template.

4 STA flourishes the development of HoMS

Considering the great power of STA in the synthesis of HoMSs, impressive attention and efforts have been devoted to the development of STA. The statistical analysis of the papers about HoMSs in publication years ranging from 2004 to February 2021 is given in Figure 8a. From the data, we can find that the development of HoMSs was very slow before 2009. Since the first example of HoMSs by STA in 2009, the number of papers about HoMSs published each year has enjoyed a rapid growth [117]. It is also worth noting that more and more researchers worldwide are flowing over into this field to contribute to the study of various kinds of HoMSs. As shown in Figure 8b, the number of countries and institutes working on HoMSs has gone through continuous growth and exhibited a faster growth during the last decade after the development of STA. It is also worth mentioning that more than 28 metal elements have been investigated to form HoMSs through STA, and the yield of HoMS has been significantly improved. Given these remarkable achievements, STA has been recognized as a milestone in the design and preparation of HoMSs and developed a new era of HoMSs.

5 Discovery of new characteristics: from proof-of concept to multifunctional materials

5.1 The concept of "temporal-spatial ordering" and "dynamic smart behavior"

In 2020, Wang's group [4] revealed the temporal-spatial ordering nature of HoMS, which is a unique property that only HoMS possesses while its counterparts, like single-shelled or porous ones, do not. As for the concept of temporal-spatial ordering, it means when the matter, which can be a molecule, photon or electron *etc*., passes through a HoMS, it will sequentially cross every shell in a strict inside-out or outside-in order (Figure 9a). Thus, the mass transfer, storage and release must follow a set of sequences from experiencing separate space to queuing up for a step-by-step timeline point of view. This property makes HoMS extraordinarily attractive for cascade reaction, sequential wave absorption, sustained drug release and hybrid energy storage. In the same perspective review, Wang's group highlighted another new characteristic of HoMS, *i.e.*, dynamic smart behavior which describes the target-responsive process that can happen repetitively and/or sequentially within a HoMS (Figure 9b). HoMS may undergo a transformation at a certain point and evolve into other micro/nanostructures for desired functionality. To some point, HoMS resembles a living biological cell, which maintains controlled mass and information exchange with its surroundings. The shells and the separated space between them operate collaboratively in parallel/sequential manners, just as different organelles work together. The dynamic smart HoMSs holds a great promise in drug delivery for targeted and selective therapies.

5.2 Temporal-spatial ordering of HoMSs in advanced applications

5.2.1 Temporal-spatial ordering in cascade catalytic reactions

Cascade or tandem reactions, which involve multiple consecutive catalytic steps in one reactor, are both time- and energy-economic and could save the trouble of the isolation and purification of intermediates [120,121]. Benefiting from

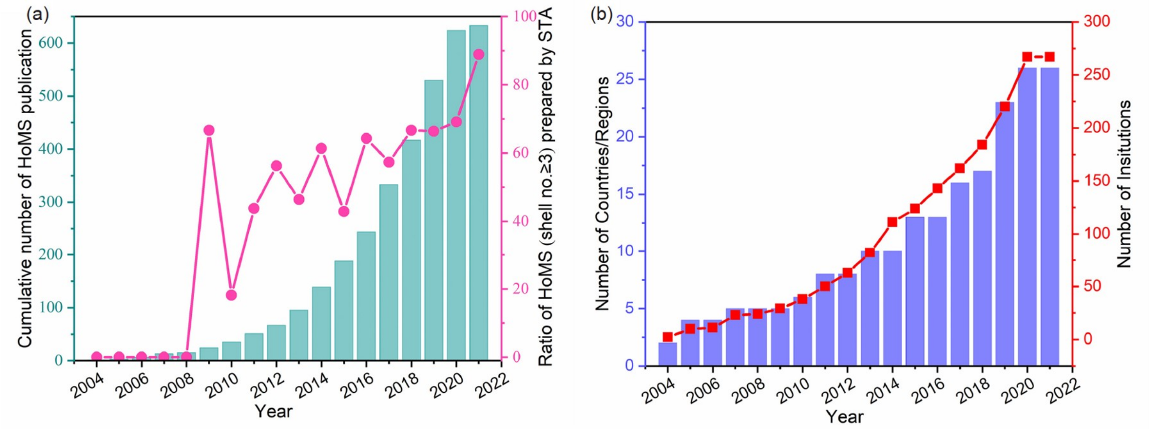

Figure 8 (a) Statistical number of published papers about HoMSs in each year. (b) Statistical number of countries/regions and institutes that work on HoMSs (color online).

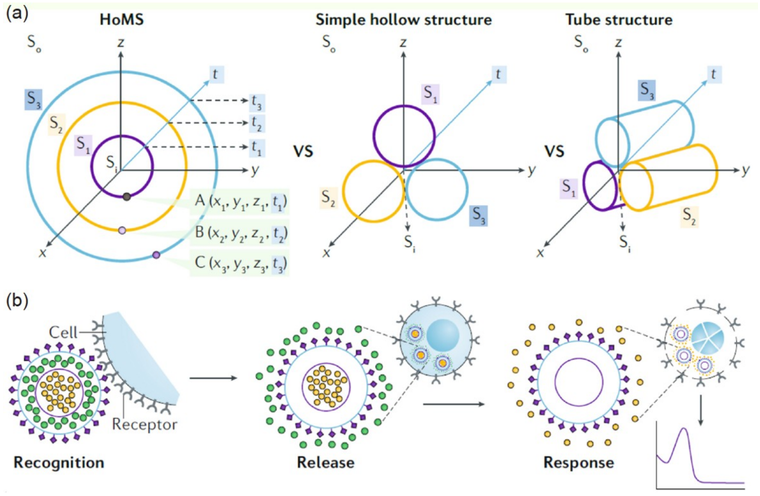

Figure 9 (a) Temporal-spatial control means that small molecules encounter spaces in a set order, something which cannot be said for other materials like non-concentric microspheres or cylinders. (b) A dynamic smart HoMS in drug delivery that can recognize overexpressed cell receptors to target certain cells. Adapted with permission from Ref. [4], copyright by Nature Publishing Group (2020) (color online).

its temporal-spatial ordering nature, HoMS-based catalyst is highly suitable for tandem reactions by making the transmission of multiple reactants, complex interactions of multiple catalysts and multistep catalytic transformations take place in a specific sequence to achieve better mass transfer, excellent compatibility and improved selectivity. For example, the selective epoxidation of alkenes through *in situ* generated H_2O_2 can be achieved on TiO_2/Pd@Void@TiO_2/Mo(VI) HoMS (Figure 10) [4]. First, H_2 and O_2 diffuse into the inner TiO_2/Pd shell to produce H_2O_2. Then this instable H_2O_2 intermediate diffuses out, driven by the concentration gradient and interacts with alkene on the outer shell of TiO_2/Mo(VI) before decomposes or escapes away, resulting in high activity. The tiny pores in HoMS shell allow H_2, O_2 and H_2O_2 to pass through yet stop large alkene molecules from entering, thus avoiding the byproducts from the catalysis of an alkene by Pd. As a result, the selectivity is significantly improved.

5.2.2 Temporal-spatial ordering in electromagnetic wave absorption

The temporal-spatial ordering nature of HoMS enables "sequential light harvesting" to enhance the solar light-harvesting similar to the antenna system of *Cyanobacteria* [122]. HoMS with broader bandgap semiconductor in the outer shell could absorb weakly penetrable short-wavelength light, whereas the inner part consisting of narrower-bandgap semiconductor absorbs strongly penetrable long-wavelength light (Figure 11). Consequently, broader coverage of solar spectrum is achieved, which results in enhanced absorption of incident light. Such sequential harvesting of light in a single HoMS particle leads to much-enhanced quantum efficiency (6 times higher at 400 nm than nanoparticles with similar composition). To further demonstrate the effect of such HoMS structure with different design sequences, TiO_2-Cu_xO HoMS materials with reversed shell composition are fabricated, which shows a clear decrease in photocatalytic hydrogen evolution and apparent quantum efficiency. Moreover, the sequence of the hetero-shells is proved to be crucial in light-harvesting. When the compositions in different shells of the HoMSs are reversed, the hydrogen evolution efficiency is only one-fifth the biomimetic sequence. Furthermore, introducing surface oxygen vacancies in each building block of HoMS is also proven to be beneficial for the sequential light absorption in the nanoscale. Strikingly, with this novel HoMS, overall water splitting is realized, which would not be possible using nanoparticles with the same composition. This is a significant step forward for applications of HoMS in light-harvesting, and it symbolically exemplifies the superior properties of temporal-spatial ordering in HoMS.

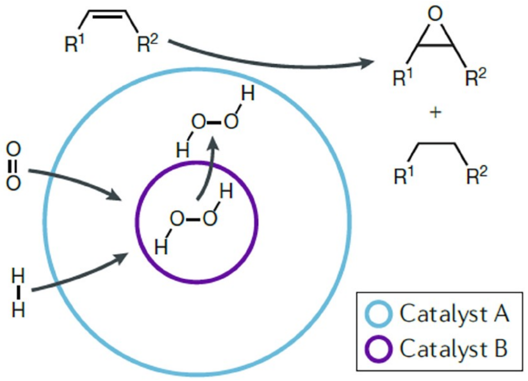

Figure 10 Schematic showing that a cascade reaction ensures that an alkene undergoes epoxidation at a Mo catalyst (A) instead of hydrogenation at a Pd catalyst (B). Adapted with permission from Ref. [4], copyright by Nature Publishing Group (2020) (color online).

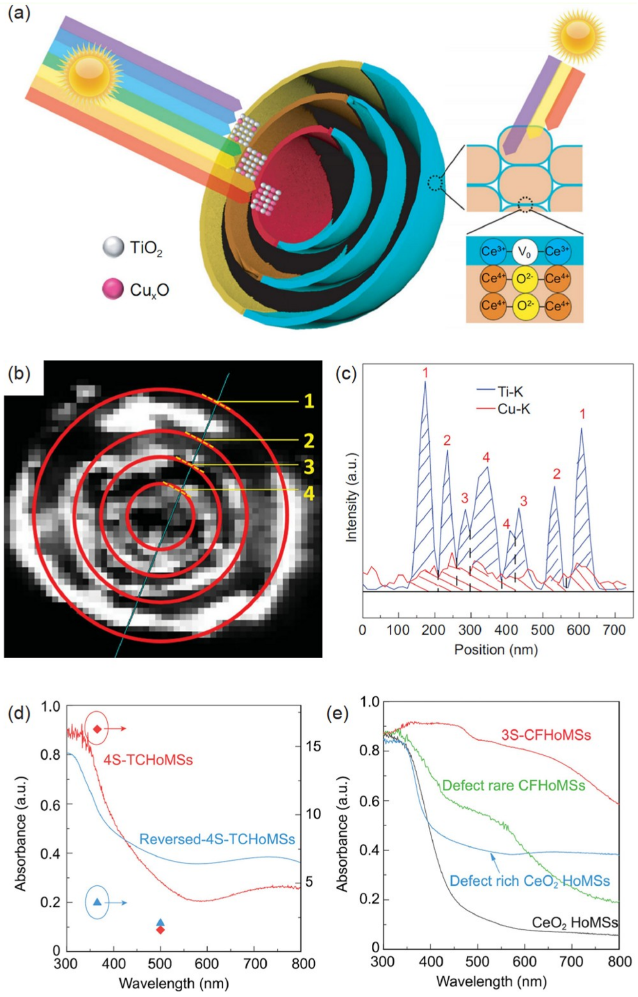

Figure 11 (a) Illustration of two designed heterogeneous HoMSs for efficient sequential harvesting of solar light. (b) Dark-field TEM image of a slice of 4S-TCHoMSs. (c) EDS line scanning along the cyan line in (b), showing the Ti/Cu ratios in different shells. (d) UV-Vis absorption curves and apparent quantum efficiency of 4S-TCHoMSs (red diamonds) and reversed 4S-TCHoMSs (blue triangles). (e) UV-Vis absorption curves of 3S-CFHoMSs, CeO_2 HoMSs and the corresponding samples with surface defect control. Adapted with permission from Ref. [122], copyright by Chinese Academy of Sciences (2020) (color online).

5.2.3 Temporal-spatial ordering in drug delivery

HoMS, with a high drug loading capacity and a sustained release profile, has been used in many drug delivery systems [115,123–126]. But only recently, the controlled release mode of HoMS based on temporal-spatial ordering was developed. By analyzing the behavior of HoMSs during drug release, Wang's group [127] discovered that the release of the molecules from HoMSs went through sequential release stages, namely burst release, sustained release, and stimulus-responsive release (Figure 12). In detail, by simply adjusting the amount of MIT-HoMSs introduced into the environment, the desired drug concentration can be quickly reached in the burst release stage. The sustained release of MIT molecules in π-π stacking state in the cavity of HoMSs could maintain the required concentration and inhibit the growth of bacteria for a long period. The triple-shelled HoMS could provide a long sterility period in a bacteria-rich environment that is nearly eight times longer than that of the pure antimicrobial agent under the same condition. When the foreign pathogens were added to the HoMSs system, the driving force was strong enough to break the energy barrier, and the drug molecules stored in HoMS were released, resulting in the responsive release. Owing to different adsorption characteristics in HoMSs and physical barriers from the multiple shells, drug molecules in different locations of HoMSs have different release times. All these advantages could be attributed to chemical diffusion- and physical barrier-driven sequential drug release, providing a route for the design of smart nanomaterials. In addition, HoMS is promising for the delivery of multiple drugs. By loading multidrug with different functionalities in different spaces in one HoMS, it is promising to control their release time, the number of released drugs, release order, and release kinetics, thus increasing the efficacy of various drugs for complex health purposes.

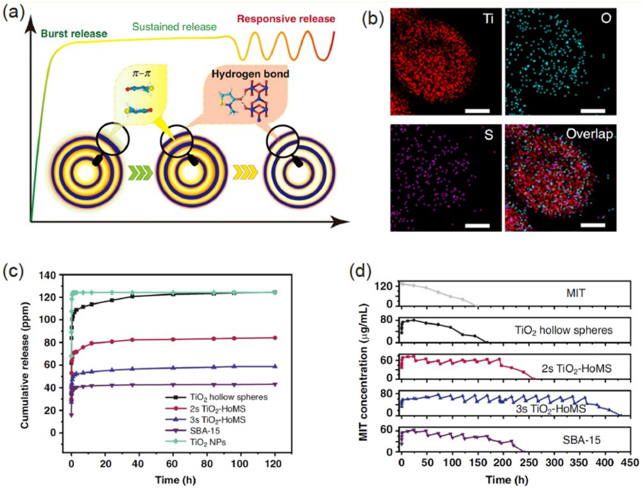

Figure 12 (a) Schematic illustration of the spatially dependent drug release by HoMS. (b) TEM-EDX mapping images of MIT-3s-TiO_2-HoMS. (c) Cumulative release performance of MIT in buffer with the same amount of MIT in different carriers. (d) Bacterial-responsive release profiles of MIT, MIT-TiO_2 hollow spheres, MIT-2s-TiO_2-HoMS, MIT-3s-TiO_2-HoMS, and SBA-15. Adapted with permission from Ref. [127], copyright by Nature Publishing Group (2020) (color online).

5.3 Dynamic smart HoMSs

In addition to temporal-spatial ordering, dynamic smart HoMS also holds great opportunities. Dynamic smart HoMS, which is composed of or surface-decorated with responsive materials, can perform mass release or capture when stimulated by external pressure, optical, electrical, thermal and magnetic stimuli. In the recent review of Wang's group [4], dynamic smart HoMS has been proposed as an ideal vehicle for targeted and selective drug delivery, as well as for efficient and economical chemical separation. Here we propose another interesting aspect that is the dynamic formation of HoMS during the drug delivery or other application processes. Considering that the big size of HoMS may make it difficult to enter into the cell, it would be quite interesting if nanoparticles can self-assemble into a HoMS after entering the body either driven by the pH environment, optical or thermal stimuli (Figure 13a), which would benefit the therapy effect and greatly promote the development of modern medicine. To be specific, firstly, the assembly of nanoparticles into a HoMS could enhance the retention in the body and extend the therapy time, thus benefiting the therapy effect [128]; secondly, the formation of HoMS could trap drugs inside it and enable sequential drug release, which would attain synergistic efficacy and avoid undesired drug-drug interaction; thirdly, the assembly of nanoparticles into a HoMS could achieve a greater heat accumulation and storage capability, which would benefit the photo-thermal or magnetic-heat therapy effect. Similarly, the shank multiple-layered bowl structure, which possesses a smaller size than HoMS, would be able to enter into the cell more easily. After reaching the inside of the cell, the bowl would be refilled and become a HoMS (Figure 13b), and then perform the unique temporal-spatial drug release behavior. In addition, a HoMS could be formed during other application processes. For example, a solid particle would expand and become a HoMS under thermal stimuli, thus isolating the combustible material from air, endowing its fire-retardant function. The dynamic formation of HoMS during the application process would make it better meet the application's requirements and improve the performance.

6 Summary and outlooks

In conclusion, the last decade has witnessed the burgeon and flourishment of HoMS. Great progress has been achieved in the synthetic methodology, the discovery of unique proper-

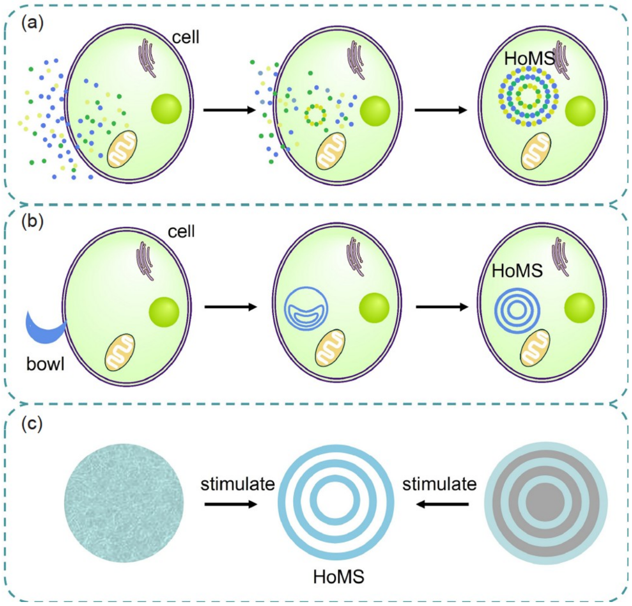

Figure 13 Dynamic smart HoMS. (a) Nanoparticles assembled into HoMS after entering into the cell. (b) A shrank bowl refilled and recovered to HoMS after entering into the cell. (c) A solid particle becomes a HoMS under extern stimulation (color online).

ties and exploration of new applications. Of all the fruitful outcomings, the latest advance in the controllable synthesis of HoMS by STA offers new opportunities in broadening the compositional, structural and functional diversity of HoMS. Furthermore, the implementation of some novel concepts, such as temporal-spatial ordering in HoMS, have laid the foundation for solving some complex yet important scientific problems in applications like energy conversion and storage, catalysis and drug delivery.

In the future, more efforts should be devoted to both the synthesis and application of HoMS. Future research could be focused on the exploration of general laws and theoretical models of HoMS synthesis. Besides, it is also highly promising to develop a gentler and greener synthesis process for HoMS fabrication. In addition, through a better understanding of the reaction mechanism in the HoMS fabrication *via* advanced *in situ* characterization techniques and calculation and modeling, one can better control the composition, crystallinity, pore structure and grain assembly of HoMSs. Typically, heterogeneous HoMSs with differential compositions for different shells, Janus HoMSs or HoMS superstructures with novel shapes (such as intricate hollow structures) are highly desired and are expected to bring novel properties.

As for the application, for sure, exploiting temporal-spatial ordering and target-responsive smart HoMSs is crucial for the further advancement of HoMS, which will further demonstrate the utility of this material. Although temporal-spatial ordering-based electromagnetic wave absorption has been verified, other promising applications, including cascade catalysis, sequential drug delivery and hybrid energy storage in HoMS remain proof-of-concept. To make them practical, one of the most desirable actions is to make heterogeneous HoMS with temporal-spatial ordering shell properties target to a specific application area. In addition, target-responsive smart HoMS is also highly attractive yet still remains to be confirmed. Ongoing research efforts are desired to be devoted to this area. Nevertheless, with continuous efforts, one could make the highly charming temporal-spatial ordering and dynamic smart HoMSs be realized by diverse materials and fully advance the targeted, practical applications.

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Conflict of interest The authors declare no conflict of interest.

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