Hollow multishelled structures (HoMSs) have gained numerous achievements in broad scientific research fields. In the past decade, the rapid developments of synthetic methods and advanced characterization technologies have enriched HoMS family with abundant chemical compositions and geometric structures. In addition, the control in phase structure and surface structure of HoMSs have also been reported in recent years. With great efforts devoted to controlling the compositional and structural characteristics, such as shell composition, shell number, shell thickness, and intershell space, HoMSs have displayed their intrinsic temporal–spatial nature and proven to be fruitful in optimizing mass transport, storage, and release. This review first summarizes the compositional and structural control of HoMSs in three levels, that is, building subunits, assembled functional shells, and HoMSs. Subsequently, the essential influence of composition and structure on mass transport, storage, and release is deeply discussed by highlighting the application of HoMSs in energy storage, catalysis, electromagnetic wave absorption, and drug delivery. Finally, the challenges and opportunities in the future development of HoMSs are forecasted.

1. Introduction

As a new star of functional materials, hollow multishelled structures (HoMSs) are built up with at least two shells and corresponding two internal voids arranged from outside to inside. It is worth noting that these porous shells can provide channels for the mass transport between the adjacent voids. Such spatial-ordered arrangements of shells and voids in HoMSs endow them with temporal–spatial-ordered mass transfer. which has been formally defined as that mass can only successively go through shells and voids within HoMSs in a defined sequence. Designed with abundant chemical components, HoMSs are widely applied for electromagnetic wave (EW) absorption, catalysis, lithium ion battery (LIB), medicine therapy, and sensors. To meet the growing practical requirements in broad applications, great efforts have been devoted to the precise synthesis of HoMSs with complex chemical compositions and structures. Given this situation, our group reported the first synthesis example of MFe$_2$O$_4$ (M = Zn, Co, Ni, and Cd) HoMSs in 2009 by using carbonaceous microspheres’ (CMSs) templates, which was inspired by the programmed temperature approach of Xie’s group and the CMS templated method of Li’s group. Right after that, we formally defined such a synthetic strategy as sequential templating approach (STA) in 2011. Then, HoMSs with abundant chemical compositions as well as various geometry structures, phase structures, and surface structures have been successfully designed and fabricated. Despite the numerous achievements of HoMSs, the exploration for the structure–performance correlation of HoMSs has never stopped.

Surface reaction and mass transfer are two parts that are mainly considered in the discussion of structure–performance correlation of HoMSs. Therefore, it is necessary to deeply understand the intrinsic effect of composition and structure of HoMSs on these two processes. The reaction efficiency is closely related to the surface adsorption/desorption of ions and molecules, which is highly associated with the surface electronic structure of materials. As a result, HoMSs can be precisely designed with individual chemical component, surface structure (exposed active facet, etc.), phase structure (crystalline or amorphous), and crystal structure (body centered cubic, face centered cubic, hexagonal close packed, etc.).

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can also be loaded through stacking in cavities of HoMSs, which is related to the geometric structures of HoMSs.

In addition, optimizing the mass transfer of ions, electrons, and molecules in HoMSs also deserves attentive consideration. The geometric structure of HoMSs such as the shell morphology, shell number, shell thickness, pore size, orientation of pore channels, and the intershell space can significantly affect the mass transport in HoMSs. As we know, electrons can transfer not only on the surface but also in the bulk. For example, heterogenous interface can accelerate the separation of photoinduced electrons and holes, sequentially enhancing the photoelectric conversion efficiency. And the exposed facet, lattice distortion, etc. can also affect the surface transmission of electrons.

In addition, when adopted as electrodes, multiple shells of HoMSs can also form an equivalent parallel circuit, which will decrease the charge transport resistance. In addition, the relatively thin shell can also decrease the transfer resistance of electrons in the bulk. In case of ions and molecules, they can transfer in space of HoMSs (e.g., pore channels and intershell space) as well as by the surface movement. In this article, we would like to point out that there are many driving forces such as the concentration gradient, the surface hydrophobicity, the capillary force (suitable pore channel), the pressure difference, the electrostatic interaction, π–π stacking interaction, etc., which can strongly drive the mass transfer of ions and molecules.

Some review articles have summarized the history and development status of HoMSs, but barely reviewed the structure–performance correlation of HoMSs, especially in aspect of their phase structures, surface structures, and geometric structures. In this article, we will first summarize the synthetic methodologies for HoMSs with tunable chemical compositions and structures ranging from the basic building subunits to the assembled functional shells and HoMSs. Subsequently, case studies are conducted to discuss the essential influence of chemical composition and structure on mass transport (e.g., insertion and extraction of ions, separation and transmission of electrons, adsorption and desorption of molecules) in energy storage, catalysis, EW absorption, and drug delivery, respectively. In the final part, we will make a conclusion and give an outlook of HoMSs’ future development. We believe this review will display the special nature of HoMSs to the readers from a new perspective and can help to guide the design of HoMSs materials targeted to particular requirements in practical applications.

2. Control of Composition and Structure

A HoMS features with multiple shells (≥2) that are separated with intershell gap and assembled with building subunits. Benefited from the tunable building subunits and hierarchical architecture of multiple shells, HoMSs with the abundant compositional and structural parameters are demonstrating great opportunities in practical applications. As shown in Scheme 1, the building subunits can be designed with various basic functional properties by tuning their elemental composition, phase structure, morphology, and size. These functional building subunits assemble to various shell structures with diverse pore structures, shell compositions, shell thickness, and shell morphologies, etc. Then, multiple shells are hierarchically structured to form a HoMS with gaps between each shell, where the shell number, the intershell space, the morphology of shells, the core number, and the shells’ compositions can be precisely controlled. As a result, one can accurately control the compositional and structural characteristics of HoMSs by controlling the chemical compositions, structures, and assembly of building subunits and shells.

However, compared to the single-shelled counterparts, the fabrication of HoMSs is of greater challenge as well as important because of the complex composition and structure. Therefore, it urgently demands facile and general synthetic approaches to achieve the rational design and precise control of HoMSs targeted to the practical requirements in applications. In the past decades, various methods have been developed. According to different forms of templates, traditional methods can be divided into self-templating method, soft-templating method, and hard-templating method, respectively. The self-templating synthetic strategies are usually based on Ostwald ripening and Kirkendall effect. In case of soft-templating method, vesicles with multiple-layered structures built by surfactants can serve as templates for the fabrication of HoMSs. In addition, we can also directly control the geometric parameters (e.g., morphology, shell numbers, intershell space, etc.) of HoMSs in an efficient way by using hard templates.

In addition to the aforementioned traditional methods, our group has developed the STA for HoMSs, which is facile and general for the synthesis of HoMSs. It is worth noting that during the template-removal process using STA, the templates rich in precursors can act as “sequential template” multiple times to form HoMSs. In detail, building subunits can evolve from precursors, and their sizes are related to the Gibbs free energy of the system. There is a critical size of the crystal, whereas...
those with size larger than \( r_c \) can continue to grow steadily.\[^{48}\] With the reaction going on, the subunits of nanoparticles are assembled into shell structure, and the way how they are assembled can affect the HoMS morphology. For example, the pore size of shell structure is highly related to the nanoparticle size and the way nanoparticles are assembled. Nanoparticles with bigger size are potentially assembled into bigger pore size. And pore size is smaller when the nanoparticles are arranged more tightly. The atomic arrangements determine the crystal facet of nanoparticles as well as the crystal facet of HoMSs.\[^{49}\] Then, the hierarchical assembly of multiple shells will form the HoMS. Shell number can be well controlled by the template removal rate \( (R_{\text{rem}}) \) and the shell formation rate \( (R_{\text{sf}}) \).\[^{[1]}\] When \( R_{\text{sf}} \) matches well with \( R_{\text{rem}} \), more shells are formed. And a bigger difference between them will lead to less shell.\[^{50}\] And intershell space is sensitive to the heating rate. A fast heating rate will probably create a big intershell space, whereas a slow heating rate will make two proximate shells closer. In addition, with the similar \( R_{\text{sf}} \) and \( R_{\text{sf}} \), the higher precursor concentration in the template, the thicker shell can be formed. The morphology of HoMSs generally maintains that of the template.\[^{51-54}\] In this section, the case studies will be highlighted to discuss the composition and structure control of HoMSs, respectively.

### 2.1. Composition Control of HoMSs

The elemental compositions of the HoMSs can be directly determined by the adopted precursors during the synthetic process. Up to now, diverse HoMSs including metal oxides,\[^{34}\] sulfides,\[^{43}\] phosphides,\[^{55}\] carbides,\[^{56}\] carbonates,\[^{57}\] perovskite,\[^{58}\] carbon materials,\[^{59}\] organic polymers,\[^{60}\] etc. have been successfully fabricated. In this section, the composition control of HoMSs is discussed in a bottom–up way: from the basic building subunits to the assembled shells and then to the HoMSs.

The chemical composition of the subunits can be either homogeneous or heterogeneous. In the early studies, lots of work has been done on homogeneous case where each subunit has the same homogeneous composition.\[^{49}\] Since many review articles have discussed the homogeneous case, we will skip this situation and focus on the discussion of heterogeneous subunits. A recent work is about the HoMSs assembled with heterogeneous subunits of SnS\(_2\)/SnO\(_2\) for efficient photocatalytic CO\(_2\) reduction (Figure 1).\[^{43}\] In detail, SnO\(_2\) HoMSs were first fabricated through STA. Then, a hydrothermal process was performed with mixed solution containing thioacetamide and SnO\(_2\) HoMSs, sequentially producing heterogenous HoMSs assembled with SnS\(_2\)/SnO\(_2\) subunits. The lattice fringes of SnO\(_2\) and SnS\(_2\) are investigated by the high-resolution transmission electron microscopy (HRTEM) image (Figure 1b) showing that the lattice fringes of SnO\(_2\) and SnS\(_2\) form a heterogenous interface. Figure 1c shows a schematic representation of the heterojunction formed by SnO\(_2\) and SnS\(_2\) at the atomic scale.

The building subunits can further assemble the shells of a HoMS. As a result, the shell component is associated with the subunits. In the past decades, HoMSs have been widely designed with shells in homogeneous component. Building heterogeneity within the shell is of great challenges and opportunities. HoMSs with TiO\(_2\)/SrTiO\(_3\) heterogenous shells were fabricated by a two-step process for photocatalytic solar water splitting (Figure 1d).\[^{54}\] TiO\(_2\) HoMSs were utilized as both templates and precursors. In addition, with Sr\[^{41}\] precursors in the hydrothermal system, the SrTiO\(_3\) layer will form on the surface of TiO\(_2\). After that, the TiO\(_2\)/SrTiO\(_3\) heterogenous shell structure was realized in HoMSs. Note that shells in the HoMSs possess the same “heterogenous structure”. Transmission electron microscopy (TEM) image (Figure 1e) shows that the shell thickness becomes thicker after the transfer of TiO\(_2\) to TiO\(_2\)/SrTiO\(_3\).\[^{54}\]

In addition to the composition control of a single shell, multiple shells of HoMSs can also be designed with the same or different compositions. Wei fabricated an amazing heterogeneous HoMSs structure with heterogeneous compositions between shells. In detail, CMSs were used as templates to adsorb Ti and Cu precursors, followed by a calcination treatment. Due to the gradient concentration distribution of Ti and Cu precursors in templates, the quadruple-shelled TiO\(_2\)–Cu\(_x\)O HoMSs (4S–TCHOs) (Figure 1f,g) were fabricated with different Ti/Cu values in different shells (Figure 1h). As a result, shells with different Ti/Cu values can absorb solar light of different wavelengths.\[^{8}\]

### 2.2. Structure Control of HoMSs

In addition to the tunable chemical compositions of HoMSs, the structures such as phase structure, surface structure, and geometric structure can also be accurately controlled.

#### 2.2.1. Phase Structure Control

The phase structure of HoMSs can be the transition between crystalline phase and amorphous phase, or between different crystal forms, which can be achieved by adjusting the synthetic conditions, such as calcination temperature, calcination atmospheres, precursor species, etc. Compared to homogeneous phase structure control, the heterogenous cases attract much more attentions. For example, by optimizing the hydrothermal temperature, Wang’s group fabricated the double-shelled TiO\(_2\) HoMSs with mixed anatase TiO\(_2\) and TiO\(_2\) (B) (2S–AB–TiO\(_2\)–HoMS) (Figure 2a,b).\[^{10}\] Compared to the anatase and rutile TiO\(_2\), TiO\(_2\) (B) structure exhibited almost no volumetric expansion during the lithium intercalation/deintercalation processes, which makes TiO\(_2\) (B) a promising anode material for LIBs.

#### 2.2.2. Surface Crystal Facet Structure Control

The chemical reaction efficiency is closely related to the molecule adsorption and desorption processes which are strongly associated with surface crystal facet structures of materials.\[^{61,62}\] Although the facet engineering in nanocrystals has been widely discussed, it is still of great challenge to accurately expose one specific crystal facet in HoMSs. In case of nanocrystals, the surfactants and polar anions are popularly utilized to regulate the surface energy through adsorbing on the specific surface of material to lower the crystal facet surface energy. As a result, it will slow down the crystal growth speed along the direction, which is perpendicular to this target facet, thus producing nanocrystals with specific crystal facet exposed. In addition, the breaking and bonding of chemical bonds should also be considered during...
the evolution of HoMSs from the precursors and templates, which demand energy to drive. Metal–organic frameworks (MOFs) possess abundant metal ions with periodic arrangement and organic ligands in partial. As a result, they can be used as templates rich in metal precursors for fabricating HoMSs. Based on this, the zeolitic imidazolate framework-67 (ZIF-67) were reasonably adopted as both the precursors and the templates to fabricate Co$_3$O$_4$ HoMSs with dominant (111) facet of Co$_3$O$_4$ (Figure 2c). The spatial arrangement of Co atoms on (001) and (011) crystal facets of ZIF-67 was similar to that on (111) crystal facets in Co$_3$O$_4$ so that it demanded a gentle process to achieve the transformation. Therefore, the mild reaction conditions of a relative low calcination temperature and a low oxygen partial pressure were adopted in the synthetic process. It indicates that the surface facet structure of the HoMSs is related to the exposed facet of building subunits which can be regulated by the atomic arrangement mode of precursors in the template.

2.2.3. Geometric Structure Control

In addition to the phase structure and surface facet structure, geometric structure of HoMS can also be controlled by tuning the geometric characteristics of nanoparticle subunits, and the shells as well as the hierarchically assembly forms of multiple shells.

The geometric structures of HoMSs are closely related to that of the building subunits. To the best of our knowledge, it usually tends to form spherical subunits that assemble shells of HoMSs, because the sphere with the lowest surface energy is the most...
and then, Co\textsubscript{3}O\textsubscript{4} HoMSs were obtained after calcination under assembled to form multilayer structure by hydrothermal method, shown in the where Co precursor and poly(vinylpyrrolidone) (PVP) were spherical nanoparticle with a certain facet exposed.\cite{70,71} As changes in subunit morphology are often accompanied by changes in their exposed facets. Regularly, the surfactants are often added to the synthesis process to regulate the surface energy of the product. Furthermore, it also controls Gibbs free energy of the reaction system, subsequently forming the nonspherical nanoparticle with a certain facet exposed.\cite{70,71} As shown in the Figure 3a, the Co\textsubscript{3}O\textsubscript{4} nanosheets were assembled to form Co\textsubscript{3}O\textsubscript{4} HoMSs using a soft-template method (Figure 3a), where Co precursor and poly(vinylpyrrolidone) (PVP) were first assembled to form multilayer structure by hydrothermal method, and then, Co\textsubscript{3}O\textsubscript{4} HoMSs were obtained after calcination under 400–600 °C. It is evident from TEM (Figure 3b) and scanning electron microscopy (SEM) (Figure 3c) results that the assembly units are sheet-like structures.\cite{71} In addition, Cu\textsubscript{2}O HoMSs assembled by platelet-like Cu\textsubscript{2}O building subunits were prepared by a self-templating method, where Cu precursors were self-assembled into multilayer structure through Ostwald ripening process by hydrothermal approach, and then, Cu\textsubscript{2}O HoMSs were obtained after calcination treatment (Figure 3d). By controlling the reaction time, Cu\textsubscript{2}O hollow structures with single shell (Figure 3e) and double shells (Figure 3f) can be fabricated. When the content of glutamic acid added to the reaction system gradually decreased to zero, the morphology of the subunit nanoparticles changed from rod-like to plate-like, and finally to spherical structure.\cite{63} It is because that the glutamic acid will regulate the surface energy of subunit nanocrystal, resulting in an optimized crystal facet growth with different morphologies.\cite{73}

Shell is the advanced structure composed of subunits. The geometric properties of shell mainly include shell thickness and shell morphology. Shell thickness is an important index of shell geometric parameter. Thinner shell can expose more active sites, provide a shorter mass transfer path, and smaller mass transfer resistance, thus improving reaction kinetics. Normally, the more of adsorbed precursors is, the thicker shell can be obtained. For instance, ethanol (ETOH) has been used to design Fe\textsubscript{3}O\textsubscript{4} HoMSs with controllable shell thicknesses (Figure 4a). It is because that the ETOH can efficiently lower the surface tension and enhance the wettability of CMS templates, sequentially promoting the absorption of precursors. With the increased ETOH content, the shell thickness of Fe\textsubscript{3}O\textsubscript{4} HoMSs ranges from 35 nm (adding 0% ETOH), 80 nm (adding 33% ETOH), to 180 nm (adding 67% ETOH).\cite{74}

The shell morphologies are often consistent with the corresponding templates.\cite{75} Since MOF materials possess tunable metals and organic ligands, they are popularly adopted as precursors as well as templates in HoMSs fabrication. The dodecahedral ZIF-67 crystals were adopted as precursors and templates to fabricate the mixed Co/Mn metal oxide HoMSs with dodecahedral morphology.\cite{60} In addition, by etching of the MIL-101 (Cr) large crystals with glacial acetic acid, the MIL-101 (Cr) HoMSs can be fabricated with the same morphology as the original MIL-101 (Cr).\cite{76} In addition, the mixed ZIF-8/ZIF-67 crystals were synthesized by a hard-templating method through the alternate growth of ZIF-8 and ZIF-67 on the template (Figure 4b). Since Zn in ZIF-8 is much easier to sublime than Co in ZIF-67, cobalt/nitrogen/carbon dodecahedrons (Co–NC) HoMSs were obtained by calcining the previously mixed MOFs at 600 °C under argon atmosphere.\cite{56}

Furthermore, multiple shells hierarchically assemble to form the HoMSs. During the formation process of HoMSs through the STA, CMS templates adsorbing precursors will first form subunits on the surface during calcination, and integration of subunits will occur during the inward contraction to form a shell. At the same time, the template continues to shrink inward as a template for the next formation of shell. When subunits integrate to form a solid shell, the spherical shape of the template continues, this process can repeat for several times, forming HoMSs. Zhao et al. synthesized cobalt–manganese oxides from single-shelled to septuple-shelled hollow spheres through STA by using CMS as templates for alkaline rechargeable battery.\cite{77} As shown in the mechanism diagram of Figure 5a, the shell number of Co–Mn oxide HoMSs is associated with Co/Mn molar ratio of precursors. And the maximum shell number of seven was achieved when the molar ratio of Co/Mn was 3.75. In addition to the effect of precursor concentration on shell numbers, the removal rate of the template \( \text{R}_{\text{t}} \) and the formation rate of the shell \( \text{R}_{\text{f}} \) can also affect the shell number during the formation of HoMS through STA. More shells are fabricated with well-matched \( \text{R}_{\text{t}} \) and \( \text{R}_{\text{f}} \) which can be adjusted by the heating rate.
and the calcination atmosphere.\cite{77} Intershell space is another important factor that will affect the reaction process. By adjusting the calcination procedure, HoMSs with two outer shells closer to each other can be also constructed. Figure 5b shows the synthesis schematic diagram of quintuple-shelled SnO$_2$ HoMSs with close double shells in the exterior. The heating rate is the main factor affecting intershell space, generally, the slower the heating rate is, the closer intershell spacing is.\cite{78}

It is worth noting that HoMSs possess temporal–spatial ordered mass transfer. In addition, uncommon structures such as heterogenous geometric structures,\cite{79} Janus structure, and heterogenous composition, multiple cores, etc. can enhance such temporal–spatial ordered nature, which will widen the application area and improve the application performance. CdS@C$_3$N$_4$ double-shell structure (Figure 5c) where the inner shell possesses spherical morphology and the outer shell is octahedral is synthesized through in situ supramolecular self-assembly. It is reported that double-shelled CdS@C$_3$N$_4$ octahedron (2-CSCN) has better photocatalytic activity than that of single component and single-shelled CdS@C$_3$N$_4$ octahedron (1-CSCN).\cite{80} HoMSs with multiple cores inside are also very fascinating. As shown in Figure 5d, ZnO nanoparticles were first produced by hydrothermal method, and then they were assembled to form hollow ZnO with symmetrical double egg-yolk structure after 24 h reaction.\cite{81} When applied for photocatalysis and photodetection, it is found that the double egg-yolk structure can improve the utilization of light, thereby improving the photocatalytic efficiency.\cite{81}
3. Structure–Performance Correlation of HoMSs

In this section, the in-depth discussion on structure–performance correlation of HoMSs will be conducted by case studies of diverse applications in aspect of surface reaction and mass transfer. The effects of chemical compositions and structures on performance properties will be discussed, respectively. Surface reaction efficiency is closely related to the surface adsorption and desorption of ions and molecules, which are associated with the surface energy and surface steric hindrance. In addition, the mass transfer efficiency of electrons, ions, molecules, and photons will also influence the application performance properties. Generally, HoMSs with larger shell number can provide more sites for ion insertions, active sites for catalytic reactions, or drug loading. Shell with abundant pore structure can promote substances to enter into the inner part of HoMS under capillary attraction and promote mass transport, whereas the thin shell makes the transmission path shorter, thus improving the power transfer efficiency.
density in energy storage and the activity in catalytic reaction. And it should also be noted that the performance is a comprehensive result of many aspects including chemical compositions, phase structure, surface facet structure, and geometric structures.

What is more, due to the spatial relationships between multiple shells of HoMSs, they demonstrate the inherent temporal–spatial ordered nature, which will endow them temporal–spatial ordered mass transfer properties in practical applications. Fabricating HoMSs with heterogenous geometric structures as well as heterogenous composition, etc. will further enhance such temporal–spatial ordered mass transfer, which will bring breakthrough in applications of sequential drug release, tandem catalysis, sequential solar light harvesting, etc. In this section, we will discuss the structure–performance correlation of HoMSs in application fields of energy storage, catalysis, electromagnetic absorption, and sustained drug release (Table 1).

| Application            | Material                        | Morphology parameters | Ref.  |
|------------------------|---------------------------------|-----------------------|-------|
| Sensor                 | Dye degradation                 | Co₃O₄@ Co–Fe oxide    | Sphere |
|                        |                                  | Size: 800–900 nm      | [149] |
| Detection of xylene    | Co–Fe oxide HoMSs               | Sphere                | Sphere |
|                        |                                  | Size: 1–1.2 μm        | [150] |
| Nonenzymatic glucose sensor | Co₃O₄ HoMSs               | Sphere                | Sphere |
|                        |                                  | Size: 20–30 nm        | [151] |
| Methanol detection     | Y₂O₃ HoMSs                      | Sphere                | Sphere |
|                        |                                  | Size: 0.9 μm          | [152] |
| Ammonia detection      | CoFe₂O₄ HoMSs                   | Sphere                | Sphere |
|                        |                                  | Shell thickness: 50 nm| [153] |
| Gas sensing            | Hematite                        | Sphere                | Sphere |
|                        |                                  | Size: 200–300 nm      | [154] |
| Isopropanol sensing    | SnO₂ HoMSs                      | Sphere                | Sphere |
|                        |                                  | Size: 2 μm            | [155] |
| Energy storage         | LIB                             | CoFe₂O₄@GC           | Sphere |
|                        |                                  | Tube                  | [156] |
|                        | LIB Carbon-coated NiCo₂S₄ HoMSs | Sphere               | Sphere |
|                        |                                  | Shell thickness: 7–11 nm (carbon layer) | [157] |
| Zn-ion batteries       | Zn₃V₂O₇                        | Sphere                | Sphere |
|                        |                                  | Size: 10–30 nm        | [158] |
| Mg–Li hybrid ion batteries | (NiCoMn)₃O₄ HoMSs          | Sphere                | Sphere |
|                        |                                  | Size: 5–6 μm          | [159] |
| Sodium ion battery     | Cobalt sulfide HoMSs            | Sphere                | Sphere |
|                        |                                  | Size: 800–900 nm      | [160] |
| Dye-sensitized solar cells | SnO₂@TiO₂ HoMSs           | Sphere                | Sphere |
|                        |                                  | Size: 500 nm          | [161] |
| Li–S battery           | Co₉S₈@CNT                      | Sphere                | Sphere |
|                        |                                  | Size: 500 nm          | [162] |
| Supercapacitor         | CuCo₃O₄                        | Sphere                | Sphere |
|                        |                                  | Size: 1 μm            | [163] |
Biomedicine Biosensors C@ZnCdS Sphere Dodecahedral

is a research hotspot.\[111\] Lou and coauthors fabricated hollow sites. Developing HoMSs with more shells for energy storage single-shelled and double-shelled zinc storage applications.\[34,82

have been intensively utilized as promising electrodes in energy with more exposed active sites for reactions. As a result, HoMSs molecules. In addition, more shells will provide more effective surface can provide abundant transmission access for ions and mole-

The pore channels in shells of HoMSs buffer the volume expansion during energy storage and improve the stability performance. The pore channels in shells of HoMSs can provide abundant transmission access for ions and molecules. In addition, more shells will provide more effective surface with more exposed active sites for reactions. As a result, HoMSs have been intensively utilized as promising electrodes in energy storage applications.\[14,82–110\]

3.1. Structure–Performance Correlation of HoMSs in Energy Storage

Electron and ion transport have great impact on the energy storage performance. According to the ion diffusion equation, \( t = \frac{L^2}{4D} \) (\( D \) is the diffusion constant), the diffusion time \( t \) is positively correlated with the diffusion length (L) of ions although the electron transfer is affected by the series resistance that is related to the thickness of electrode. In addition, the shells of HoMSs can form an equivalent parallel circuit to reduce the transmission length, thereby improving the electron and ion transmission rates. In addition, the inner void space of HoMSs can effectively buffer the volume expansion during energy storage and improve the stability performance. The pore channels in shells of HoMSs can provide abundant transmission access for ions and molecules. In addition, more shells will provide more effective surface with more exposed active sites for reactions. As a result, HoMSs have been intensively utilized as promising electrodes in energy storage applications.\[14,82–110\]

HoMSs with more shells can expose more volumetric active sites. Developing HoMSs with more shells for energy storage is a research hotspot.\[111\] Lou and coauthors fabricated hollow single-shelled and double-shelled zinc–cobalt sulfide (Zn–Co–S) rhombic dodecahedral cages (RDCs) for supercapacitors. Compared to the single-shelled hollow structure, double-shelled Zn–Co–S RDC exhibited superior specific capacitance (1266 F g\(^{-1}\) at 1 A g\(^{-1}\)), and excellent cyclic stability (91% retained after 10 000 cycles). It is because double-shelled structure exposed more volumetric active sites for chemical reactions, and more shells provided more transmission paths for ions and electrons to improve the transfer efficiency, subsequentially improving electrochemical performance.\[112\] However, too many shells would also induce a small void volume ratio, which can result in a poor cycling stability. Design of HoMSs with a suitable shell number can not only maintain the morphological stability but also obtain a high-specific capacity. As shown in Figure 6a–c, when Co\(_3\)O\(_4\) HoMSs is applied in lithium-ion batteries, the specific capacity of triple-shelled Co\(_3\)O\(_4\) is better than single- and double-shelled, but the performance of quadruple-shelled electrode is worse than that of triple-shelled. It is because that the quadruple-shelled electrode possesses a too small void volume ratio which cannot efficiently buffer the volume expansion during lithiation, thus inducing a poor cycling stability.\[82\]

The mass transfer process can also be affected by the shell thickness of HoMSs. Fe\(_2\)O\(_3\) HoMSs (Figure 6d,e) with thinner shells can shorten the distance between the electrode and the electrolyte as well as provide more accessible active sites for charge storage, thereby increasing energy density. Lithium-ion batteries with thinner-shelled Fe\(_2\)O\(_3\) HoMSs display a higher discharge capacity than that of thicker-shelled Fe\(_2\)O\(_3\) HoMSs, and the triple-shelled Fe\(_2\)O\(_3\) with thin shells can achieve a stable capacity of 1702 mA h g\(^{-1}\) (Figure 6f).\[174\] In addition, the contact between multiple shells forms an equivalent parallel circuit, thus decreasing the electron transfer resistance. Generally,
more shells induce a lower electrochemical impedance (Figure 6g,h).\textsuperscript{[15]} In addition to the effect of geometric morphologies, the composition can also affect the energy storage performance. NiO HoMSs were obtained by calcining the carbon microsphere template after adsorbing Ni\textsuperscript{2+}, and then, (NiO)\textsubscript{x}(NiS)\textsubscript{1−x} (0 ≤ x ≤ 1) HoMSs were obtained under different sulfurization experimental conditions. The rate performance test showed that the supercapacitor performance of HoMSs can also be greatly affected by the composition.\textsuperscript{[113]} Among them, the performance of (NiO)\textsubscript{0.1}(NiS)\textsubscript{0.9} is the best, and can deliver a specific capacity of 1063 F g\textsuperscript{−1} at 2 A g\textsuperscript{−1}. This is because (NiO)\textsubscript{0.1}(NiS)\textsubscript{0.9} has abundant defects and can provide more effective surface active sites. Optimizing the composition of electrode (selecting high-performance materials, constructing heterostructures, defects, etc.) is also a promising way to improve the performance.

3.2. Structure–Performance Correlation of HoMSs in Catalysis

In the past decade, HoMSs have been widely adopted in diverse catalytic reactions, such as photocatalysis,\textsuperscript{[114–123]} electrocatalysis,\textsuperscript{[124–130]} gas sensors,\textsuperscript{[131]} and other catalytic fields.\textsuperscript{[131–138]} The hierarchical assembly of multiple shells within HoMSs can fully expose their volumetric effective surface for catalytic reactions. In general, designed with more shells, HoMSs can provide more volumetric active sites to adsorb more reactants and activate them. In addition, the adjustable porous shells can support suitable channels for reactants and products transmission, thus improving the mass transfer efficiency. In addition, the surface facet structure with the highest activity can be designed for enhanced adsorption of reactant molecules. In this part, detailed explorations on the structure–performance relationship of HoMSs in catalysis were conducted in aspects of surface facet structure and geometric structure.

The catalytic performance is closely related to surface adsorption and desorption processes, which can be strongly affected by the surface exposed crystal facets of catalysts. Co\textsubscript{3}O\textsubscript{4} HoMSs with prominent (111) crystal facet were prepared by using ZIF-67 as the template (Figure 7a). Meanwhile, as a control sample, Co\textsubscript{3}O\textsubscript{4} HoMS without prominent (111) crystal facet was prepared by using CMS as the template (Figure 7b). When applied for
photocatalytic CO₂ reduction, both catalysts exhibited the selectivity of 100% from CO₂ to CO. In addition, under the same test condition, Co₃O₄ HoMSs with a dominant exposure of Co₃O₄ (111) crystal facet exhibited a much higher CO yield than that of the control catalysts (Figure 7c), which benefited from the optimal adsorption/desorption processes on Co₃O₄ (111) crystal facets.

As the key parameters of geometric structures, shell number and shell thickness can also affect the catalytic performance through optimizing electron transmission efficiency. Multiple shells can connect with each other to form a parallel resistance, thus reducing the resistance and speeding up the electron transmission. Single-shelled and double-shelled Ni–Fe LDH nanocages (Figure 7d,e) were applied to electrocatalytic oxygen evolution reaction in alkaline systems. The double-shelled Ni–Fe LDH exhibited a better performance, achieving 20 mA cm⁻² current density and 71 mV dec⁻¹ Tafel...
slope at an even low overpotential of 246 mV and it also shows a good cycling performance in alkaline electrode. As shown in Figure 7f of electrochemical impedance spectroscopy (EIS) results, Ni–Fe LDH nanocages with two shells display a smaller semicircle than that of the catalysts with single shell, indicating a smaller electrochemical impedance and a faster electron transfer.[139]

It is worth noting that shell number not only affects the impedance of the catalysis but also affects the absorbance in the photocatalytic reaction. Au-based HoMSs with tunable shell numbers were applied to selective hydrogenation of 4-nitrostyrene.[140] The catalytic results showed that triple-shelled Au HoMSs exhibited a higher conversion efficiency and selectivity than those with single and double shells. To explain the reason for this phenomenon, Au HoMSs with different shell numbers were characterized by UV–Vis–near infrared, and the spectroscopic results showed that triple-shelled Au HoMSs can absorb more light at 300–1200 nm. This also means that materials with more shell numbers have a higher light utilization in photocatalysis, which may improve the catalytic activity.[141] However, blindly increasing shell numbers does not necessarily benefit the improvement of catalytic performance. Lou’s group prepared ZnS–CdS dodecahedral cage HoMSs for solar energy conversion.[142] The experimental results showed that the performance of the triple-shell layer was the highest, and the performance of the catalyst would be reduced when the number of shell layers increased. This may be because too many shells slowed down the material transport rate, which was not conducive to the adsorption and desorption of reactants. In addition to affecting the catalytic performance, shell number also has a significant impact on sensing fields such as gas sensitivity. Our group has found that Fe₂O₃ HoMSs can significantly improve the detection sensitivity of ETOH compared with bulk materials, and with the increase of the shell numbers, the sensitivity has been significantly improved. The reason is that Fe₂O₃ HoMSs with more shells can contact ETOH molecules more fully.[13]

TiO₂/FeₓTiO₂ HoMSs with different intershell space exhibited different catalytic activities in solar water oxidation. It turns out that the close double-shelled (CDSHS) sample exhibits the best performance among all the prepared samples (Figure 7j). CDSHS can absorb more light in the UV–visible light at 300–700 nm (Figure 7k) and has the lowest fluorescence quenching efficiency, i.e., lower recombination efficiency of electrons and holes (Figure 7l). In photocatalytic reaction system, intershell space affects the reflection and refraction of EW between shells and thus affects efficiency. HoMSs with closer shell space can absorb more EWs, and would boost photogenerated electrons and holes’ separation efficiency, thereby improving the photocatalytic efficiency. Shell thickness of HoMSs also affects electron transmission in catalysis, according to theoretical analysis, the thinner shell of the same quality HoMSs catalyst will expose more active sites, which is conducive to improving electron transmission efficiency.[114]

Shell space, porosity, and pore size greatly affect mass transmission. The high porosity can facilitate the mass transmission; however, it is worth noting that too high porosity can weaken the mechanical stability of the structure. Pore size also affects mass transmission. The larger the pore size is, the easier the macromolecule transport. By controlling the pore size, the transportable molecules can be tuned, thus improving the selectivity of reactions. Umegaki used hollow silica–aluminum composite microspheres in the hydrolytic dehydrogenation of borane ammonia.[138] Hollow silica–aluminum composite spheres with different pore sizes were prepared by changing the surfactants added in the synthesis process. It is found that hollow microspheres with a larger size had a higher catalytic activity for the hydrolytic dehydrogenation of borane ammonia. This is because hydrated ammonia borane would diffuse more easily through the inner surface of hollow spheres with larger channels.

3.3. Structure–Performance Correlation of HoMSs in EW Absorption

According to different wavelength, EWs can be divided into radio waves, microwaves, ultraviolet light, visible light, infrared light, etc. which have been widely applied in daily life and production. A good absorption performance is demanded of the EWs absorbers. For example, the radar stealth material must possess a good microwave absorption performance. In addition, solar light is another important EW of which the absorption we will mainly discuss in this section. Due to the excellent properties in scattering process of multishell structure and internal cavities of HoMSs, it can greatly enhance the light-scattering effect and increase the optical path of the incident light in HoMSs, subsequently increasing the absorption of incident light. As a result, HoMSs have been considered as promising candidates for solar light absorption, especially for photovoltaic devices and photocatalysis. The photoelectric conversion efficiency and photocatalytic efficiency are closely related to the solar light absorption performance.

Light-harvesting process can be greatly affected by shell number as well as intershell space.[144] For example, it is found that the quadruple-shelled ZnO HoMSs can absorb more UV EW than double- and triple-shelled ZnO HoMSs. Generally, the smaller the shell number is, the worse the absorption performance is.[69] Moreover, HoMSs with closer intershell space can absorb more UV since the scattering of light is higher in shells with closer shell space.[69] The separation and utilization efficiencies of photogenerated electron–hole pairs, which will be influenced by the shell components, greatly affect the photocatalytic activity. For instance, the heterojunctions in shells will promote the separation of electron–hole pairs and reduce the recombination of electrons.

Since the light with different wavelengths displays different properties of penetration depth in medium, they can be absorbed by shells with heterogeneous chemical compositions at different positions, achieving an efficient sequential solar light harvesting. Figure 8a shows a quadruple-shelled TiO₂–CuO HoMSs (TCHoMSs) with an increased molar ratio gradient of Ti/Cu along outside-in TiO₂–CuO shells. As a result, solar light in short wavelength with weak penetration can only be absorbed by the outmost shell, whereas long-wavelength solar light with strong penetration can be absorbed by the inner shell. Despite the sequential light-harvesting process displayed by shells with heterogeneous compositions, the nanoparticles’ subunits can also be designed with the function of sequential light harvesting. A quadruple-shelled CeO₂–CeFeO₃ HoMSs were fabricated with large amount of oxygen vacancies on the surface of CeO₂–CeFeO₃
subunits, where there is a decreased concentration gradient of oxygen vacancy along outside-in subunits. Therefore, the outer surface of CeO$_2$–CeFeO$_3$ subunits prefer to absorb visible light, whereas the inner part of these subunits harvest UV light. Interestingly, the light-harvesting performance of TCHoMSs in UV–Vis region was greatly superior to those of randomly mixed TiO$_2$/Cu$_x$O particles, TiO$_2$ HoMSs, and crushed TCHoMSs (Figure 8b). The result showed a little decrease in the crushed TCHoMSs in visible light harvesting, although the concentration of Cu$_x$O in the inner shells was larger than the outside. Furthermore, contrasted HoMSs with reversed order of TiO$_2$ and Cu$_x$O from the outside-in were synthesized. As a result, the reversed TCHoMSs demonstrated an enhanced light-harvesting intensity in the visible light region, but hindered the UV light absorption efficiency (Figure 8c). All the aforementioned discussions illustrated the conception of efficient sequential light harvesting of heterogenous HoMSs.[8]

3.4. Structure–Performance Correlation of HoMSs in Drug Delivery

Dynamic smart behavior in HoMSs endows them great promise in drug delivery. The sustained drug release performance of HoMSs is mainly measured by three aspects, loading capacity, release rate, and sequential release. Among them, loading capacity and release rate are related to shell number, porosity, and pore size.[57,144–148] In general, for HoMSs of the same size, the one with more shells can achieve a larger drug loading capacity.

As shown in Figure 9a–c, the porous structure provides access for drug molecules (DOX·HCl) to go through the shell and enter the inner of HoMSs, thus increasing the loading efficiency. When double-shelled and triple-shelled SiO$_2$ are loaded with codeliver fluorescein 5(6)-isothiocyanate (FITC) fluorophore, the release rate of the triple-shelled is lower than that of the double-shelled, (Figure 9f,g). It takes 50 and 300 h, respectively, for double-shelled and triple-shelled SiO$_2$ to reach release plateau period. Regardless of double-shelled and triple-shelled SiO$_2$, the drug release rate is related to solution pH value. In this experiment, FITC releases faster in neutral environment (pH = 7.4) than acid environment (pH = 4.3),

Figure 8. a) Illustration of designed two heterogeneous HoMSs for efficient sequential harvesting of solar light. The left part represents TCHoMSs, whereas the right part represents CeO$_2$–CeFeO$_3$ HoMSs (CFHoMSs). VO indicates oxygen vacancy. The left part of the scheme shows an increased molar ratio gradient of Ti/Cu along outside-in TiO$_2$-Cu$_x$O shells, which enables sequential harvesting of weak-penetrable short wavelength light by the outer part and strong-penetrable long wavelength light by the inner part. The different colors of the multiple shells indicate their different compositions. The right part of the scheme shows that abundant oxygen vacancies exists at the surface of CeO$_2$–CeFeO$_3$ nanoparticle subunits, thus realizing sequential light harvesting on each nanoparticle subunit from the edge to the inside. b) UV–vis absorption curves of 4S-TCHoMSs, TiO$_2$–Cu$_x$O nanoparticles, crushed 4S-TCHoMSs, and TiO$_2$ HoMSs; c) UV–vis absorption curves of 4S-TCHoMSs and reversed 4S-TCHoMSs with apparent quantum efficiency. Reproduced under the terms of the Creative Commons CC-BY license.[8] Copyright 2020, Oxford University Press.
and DOX releases faster in acidic environment (pH = 4.3) than in neutral environment (pH = 7.4). [145]

4. Conclusion

Benefiting from the large effective surface area, temporal–spatial ordered mass transport, and enrichment of substances in the cavities between shells, etc., HoMSs have demonstrated impressive performance in broad applications. In this article, we focused on the deep discussion of the structure–performance correlation of HoMSs in diverse applications. To achieve the composition and structure control of HoMSs, we first summarized the synthetic methods for the fabrication ranging from the basic building subunits to the constructed shell structure, and then to HoMSs hierarchically assembled by multiple shells. Next, in terms of phase structure, surface facet structure, and geometric structures, the structure–performance correlation of HoMSs are highlighted by case studies in energy storage, catalysis, EW absorption, and drug delivery. By precise control of subunit nanoparticles exposed with active facets, we can fabricate shell structures as well as HoMSs with the same exposed active facets, which will significantly optimize the adsorption/desorption of reactants/products. With more shells, HoMSs can provide more accessible active sites for ion insertion, catalytic reaction, and drug loading, etc. When adopted as electrodes, multishells in HoMSs can form the equivalent parallel circuit, subsequently providing with a parallel electronic transmission route. Together with the advantages of thinner shell and the optimized pore structure, it can also facilitate the transport of ions or molecules, sequentially promoting the rate capability of batteries or the treatment effect of drug delivery.

In our recent report, we highlighted the intrinsic temporal–spatial ordered nature of HoMSs in mass transfer, storage, and release. [2] In the future development, we can predict that a better temporal–spatial ordered properties of HoMSs can be achieved by designing these spatial-ordered shells with heterogeneous compositions (e.g., metal oxides, carbides,
nitrides, phosphides, selenides, metal salts, etc.) and heterogeneous structures (e.g., phase structure, surface facet structure, geometric structure, etc.), so as to achieve a multistep, multiple, and continuous response of HoMSs in mass transfer, storage, and release. In addition, fabricating HoMSs with a greater number of spatial-ordered shells is promising to bring breakthrough in traditional areas and to open new application fields. Furthermore, dynamic smart heterogenous HoMSs may be another promising future direction that heterogenous HoMSs can enable target-responsive dynamic smart actions in response to the external signals and stimuli. Therefore, the target-responsive behaviors can happen in a sequential and repetitive way. The well-designed HoMSs with dynamic smart properties may be helpful for sequential drug release and tandem catalysis. So that the facile and scalable synthetic methods and advanced characterization techniques are highly desirable and urgently needed in the future development of heterogenous HoMSs.

In future, we can also develop the bottom–up synthetic approach for fabricating HoMSs with functional building subunits. These tunable functional building subunits can be easily designed with suitable compositions and geometric structures. By precise assembly of the subunits to HoMSs, we can regulate the chemical compositions, phase structure, surface facet structure, and geometric structures of HoMSs materials targeted to the practical requirements. Moreover, the smart subunits can also be designed with dynamic geometric configurations in response to the environmental stimuli for HoMSs’ fabrication and application. In addition, HoMSs themselves can also function as the functional “subunits” to build HoMSs-based functional superstructures which are promising to enrich the family of HoMSs and open new areas. Finally, but most importantly, the better understanding of HoMSs’ structure–performance correlation can be realized with more advanced characterization techniques and theoretical calculation methods, which is also a promising future direction.

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Conflict of Interest

The authors declare no conflict of interest.

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