Noble-Metal-Based Hollow Mesoporous Nanoparticles: Synthesis Strategies and Applications

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As second-generation mesoporous materials, mesoporous noble metals (NMs) are of significant interest for their wide applications in catalysis, sensing, bioimaging, and biotherapy owing to their structural and metallic features. The introduction of interior hollow cavity into NM-based mesoporous nanoparticles (MNs), which subtly integrate hierarchical hollow and mesoporous structure into one nanoparticle, produces a new type of hollow MNs (HMNs). Benefiting from their higher active surface, better electron/mass transfer, optimum electronic structure, and nanoconfinement space, NM-based HMNs exhibit their high efficiency in enhancing catalytic activity and stability and tuning catalytic selectivity. In this review, recent progress in the design, synthesis, and catalytic applications of NM-based HMNs is summarized, including the findings of the groups. Five main strategies for synthesizing NM-based HMNs, namely silica-assisted surfactant-templated nucleation, surfactant-templated sequential nucleation, soft “dual”-template, Kirkendall effect in synergistic template, and galvanic-replacement-assisted surfactant template, are described in detail. In addition, the applications in ethanol oxidation electrocatalysis and hydrogenation reactions are discussed to highlight the high activity, enhanced stability, and optimal selectivity of NM-based HMNs in (electro)catalysis. Finally, the further outlook that may lead the directions of synthesis and applications of NM-based HMNs is prospected.

1. Introduction

Over the past three decades, we have witnessed the rapid development of mesoporous materials. Owing to their rich structural features, such as large specific surface areas and pore volumes, adjustable pore sizes and structures, and diversity of frameworks, mesoporous materials have widely been applied in catalysis, energy storage, sensing, and biomedicine.[1] Recently, mesoporous materials have gradually advanced from first-generation carbon and oxides/sulfides/phosphates to second-generation noble metals (NMs) with more compositional functions.[2] NM-based mesoporous nanoparticles (MNs), particularly Pt, Pd, and Au, are of great interest in catalysis and (electro/photo) catalysis. This is because the d-band electron structure of NMs can optimize the adsorption/desorption of the reactants/electrons/photons, which enhances the catalytic and optical performances of NM-based MNs.[2j,3] In catalysis, NM-based MNs have multiple advantages of both “big” and “small” nanoparticles. “Big” nanoparticles facilitate fast electron transfer and endow high stability of catalysts, while “small” nanoparticles provide large surface area and expose more catalytically active sites. However, NM-based MNs still present some challenges. In particular, owing to the deep mesopores in a solid MN, transporting the reactants into the internal NM catalytic sites and withdrawing the products out of the mesochannels are extremely difficult.[4]
These limitations of NM-based MNs result in huge wastage of internal active sites and a decrease in catalytic activity, particularly considering that they are precious NMs. Recent reports have shown that introducing nanoscale interior cavities into NM-based MNs is a new and highly efficient way to resolve the above drawbacks. NM-based hollow MNs (HMNs) that subtly integrate hierarchical hollow and mesoporous structures into one nanoparticle exhibit add-in structural functions, including exposing more catalytically active sites, accelerating diffusion of the reactants within mesoporous channels, and providing an interior void space. These structural functions thus synergistically enhance their catalytic and electrocatalytic performances.[8] More interestingly, the crystalline mesoporosity and nanocavity of NM-based HMNs could also optimize their electronic and steric structures and provide nanoscale confined environments, potentially tuning their (electro)catalytic selectivity for certain products (Figure 1).[5a,b]

The most critical issue in the synthesis of NM-based HMNs is design of a method for introducing hollow structures into mesoporous nanocrystals.[7] Basically, there are three general ideas for introducing hollow structures in NM-based MNs. One is to first form a core–shell MN with a sacrificial core and dissolve the core using a chemical method. The other is to take advantage of the diversity of template molecular self-assembly and directly form a hollow structure with a mesoporous shell.[5a,b] The last approach is to use the mesoporous nanocrystal itself as a template, and transport the materials in the middle through a chemical reaction.[5e,6e] Galvanic replacement and Kirkendall effect are involved in the hollowing process. In general, the first route requires two steps for the synthesis of NM-based HMNs, and the remaining routes integrate the formation of mesopores and hollow structures into a one-step reaction. Overall, the mesopore sizes of NM-based HMNs depend on the mesopore-forming agents (e.g., surfactants, block copolymers, and sacrificial hard templates). In general, sacrificial hard templates and small-molecule surfactants template the formation of NM-based HMNs with smaller sizes (2–8 nm), whereas macromolecule block copolymers template the synthesis of HMNs with larger pore sizes (10–50 nm). The classic and first example is the synthesis of Pt HMNs by using silica nanoparticles as the sacrificial cavity-forming template and Pluronic F127 as the mesopore-forming template, which was developed by our group in 2011.[7] We named this strategy silica-assisted surfactant-templated nucleation (SSTN). Since then, several other synthetic strategies have been explored to prepare NM-based HMNs with different elemental compositions, mesostructures, and morphologies. Moreover, their synergistic functions for catalysis and electrocatalysis have been further studied. Compared to the synthesis of simple hollow or mesoporous structures, the synthetic systems of NM-based HMNs are more complicated and require more design. In addition, hollowing process, metal composition, surfactant composition, self-assembled structure, and reaction kinetics should be carefully considered to successfully synthesize NM-based HMNs.

Herein, we aim to summarize the progress in the synthesis and applications of NM-based HMNs, mainly focusing on the results of studies conducted by our two groups (Table 1).[5a–f,6e,7–22] For the synthesis of NM-based HMNs, hollow cavities are introduced into MNs. Herein, we discuss five strategies to introduce hollow cavities into MNs: SSTN, surfactant-templated sequential nucleation (STSN), soft “dual”-template (SDT), Kirkendall effect in synergistic template (KEST), and galvanic-replacement-assisted surfactant-template (GRST) (Figure 2). The detailed procedures and reaction mechanisms for five strategies will be discussed thoroughly. Furthermore, we provide detailed case studies using electrocatalytic ethanol oxidation reaction (EOR) and selective hydrogenation of 4-nitrophenylacetylene (4-NPA) as model catalysis reactions. Based on these reactions, we further demonstrate how the structural add-in features of NM-based HMNs significantly enhance catalytic activity and stability and precisely tailor catalytic selectivity. Finally, we provide a brief summary of the synthesis and applications of NM-based HMNs and a future outlook on the potential and further developments in this research area. This review can provide insights into the challenges associated with precise synthesis and targeted applications of NM-based HMNs, and it may help the readership in finding their respective solutions. However, the synthesis and applications of non-NM-based HMNs (silica, carbon, metal–organic frameworks, and derived materials, etc.) and hollow...
NM-based alloys with random holes have not been covered in this review. For more detailed results, readers are encouraged to refer to other corresponding reviews.

2. Synthesis Strategies and their Underlying Mechanisms

2.1. SSTN Strategy

In 2011, Ataee-Esfahani et al. reported a simple SSTN strategy for the controllable synthesis of Pt HMNs. In general, SiO$_2$ nanoparticles with functionalized surfaces (e.g., amino groups) are first prepared and further utilized as a colloidal template to direct in situ surface nucleation and growth of mesoporous NMs in the presence of a mesopore-forming surfactant template. After the nucleation growth of the NM framework, the silica nanoparticles and surfactant template are completely removed, and NM-based HMNs with hollow interiors and nanosponge shells are thus obtained. This is the first successful example of NM-based HMN synthesis. This opens new opportunities to prepare other NM-based HMNs and further explore their high catalytic performance. In a subsequent study, Ataee-Esfahani et al. extended the SSTN strategy to synthesize bimetallic Pt–Ru HMNs with multiple elemental functions and thoroughly demonstrated their corresponding formation mechanism (Figure 3a). Based on the strong electrostatic affinity between the amino-functionalized colloidal silica and the metal seeds, Pt–Ru nanoparticles were first deposited randomly on the silica particles (0.5 h). When nucleated for longer times, more Pt–Ru nanocrystals were deposited and subsequently formed a mesoporous framework owing to the template effect of F127 (1–2 h). The adsorption of F127 on the silica surface was promoted by the formation of hydrogen bonds between the terminal hydroxyl group of F127 and the amino groups on the silica surface. As a result, the F127 micelles assembled into ordered arrays on the silica surface, and the formation of the Pt–Ru mesoporous framework was confirmed through energy-dispersive X-ray spectroscopy (EDS) line scan analysis (Figure 3e). In addition, the sizes (thicknesses) of the mesopores, hollow cavities, and HMNs were precisely controlled (Figure 3f). By easily adjusting the sizes of the colloidal silicas and feeding amounts of the metal precursors, Pt–Ru HMNs with an overall size in the range of 160–520 nm and a framework thickness in the range of 13–42 nm were achieved. This achievement confirmed the high feasibility of the SSTN strategy for the synthesis of NM-based HMNs.

The macroscopic morphology and atomic elemental composition strongly correspond to the physicochemical properties of NM-based HMNs, except for the mesoscopic nanostructures. This SSTN strategy is synthetically simple and can be extended to customize the morphology and composition of NM-based HMNs. For example, 1D HMNs with rod-like hollow cavities and abundant mesopores were formed by replacing colloid silica nanoparticles with nanorods as the cavity-forming template (Figure 3g). Furthermore, the as-synthesized NM-based HMNs were utilized as the parent template, and more functional compositional elements can be introduced into the nanostructure. For example, quaternary PtPdSP HMNs with bi-nonmetal cocyclotes (more functions) were obtained through in situ modification of PtPd HMNs with S and P sources (Figure 3h).

2.2. STSN Strategy

The sequential nucleation strategy benefits from the different reduction potentials and nucleation kinetics of various metal precursors, producing core–shell nanoparticles by precisely
controlling the reduction kinetics.\cite{24} Hollow nanostructures are then generated through selective etching of interior metal nanocrystals.\cite{25} In 2013, Wang et al. applied this sequential nucleation strategy for the surfactant-templated synthesis of mesoporous NMs and successfully prepared Pt-rich PtPd HMNs (Figure 4a).\cite{13} The STSN synthesis of NM-based HMNs was completed in two steps. The first step was the formation of M1-on-M2 (Pt-on-Pd) MNs by utilizing the temporal separation of Pd and Pt deposits in an F127 solution. It is worth emphasizing that during the growth of Pt, amphiphilic Pluronic F127 was adsorbed on the Pt surface through its hydrophobic group (PPO), thereby forming mesoporous Pt.\cite{26} The TEM and dark-field STEM images confirmed that the metal nanocrystals were composed of a Pd core and a dendritic mesoporous Pt shell (Figure 4b–e). The second step was the selective chemical etching of the Pd core while simultaneously retaining the mesoporous Pt framework. Based on the fact that Pd is less stable than Pt against the acid etching, successful removal of the Pd core in a concentrated nitric acid solution was demonstrated after 5 days of incubation (Figure 4f,g). The STEM EDS mapping images of the final products implied that Pd was slightly concentrated in the interior of the PtPd HMNs rather than being uniformly dispersed throughout whole HMNs (Figure 4h,i), further suggesting sequential nucleation in the first step. This pioneering work produced dendritic porous PtPd HMNs; however, the mesopores were not ordered because of the absence of control over the self-assembly of Pluronic F127.

The STSN strategy was recently extended to control the macroscopic morphology, mesoscopic structure, and elemental composition of NM-based HMNs. All of these parameters strongly correspond to the physicochemical properties of NM-based HMNs and optimize their catalytic performance. Wang et al. reported a series of NM-based HMNs with controlled morphologies and ordered spherical mesopores, such as truncated octahedral PtPdNi and octahedral PtPdRh (Figure 4j–o).\cite{5c,18} The sequential nucleation of metals, the formation of polyhedral nanoparticles, and mesoporous shells were controlled by optimizing the concentrations of the F127 template, the reduction potentials of the reducing agents, and the metal precursor combinations. In these syntheses, the mild reducing agent facilitated the formation of (truncated) octahedral Pd nanocrystals before the nucleation of other metal species. The Pd nanocrystals then served as seeds for subsequent nucleation and growth of Pt/Ni and Pt/Rh. Pluronic F127 increased the dispersity of the nanocrystals and templated the formation of mesoporous shells. Finally, the selective etching of Pd with nitric acid released the core materials, thereby forming NM-based HMNs with different morphologies.
2.3. SDT Strategy

Soft amphiphilic surfactants self-assemble into diverse nanostructures, which can be predicted using the molecular packing parameters.[27] The molecular packing parameter ($p$) is defined as $p = v_o/a_{e}l_0$, where $a_e$ is the equilibrium area per molecule at the aggregate surface, $v_o$ is the surfactant tail volume, and $l_0$ is the tail length. Under the conditions $0 \leq p \leq 1/3$, $1/3 \leq p \leq 1/2$, and $1/2 \leq p \leq 1$, the surfactants self-assemble into spheres, cylinders, and vesicles (bilayers), respectively. Therefore, the composition of the template molecules or the solvent conditions can be adjusted to achieve the desired nanostructures. The adjustability of the assemblies provides another route for the preparation of NM-based HMNs. It is believed that these assembled structures coexist in certain boundary regions. In other words, the formation of cylinder micelles on a vesicle micelle can be induced. Such assemblies serve as perfect templates for growing NM-based nanocrystals in one step. This method saves...
synthetic steps and significantly reduces material consumption, as no sacrificial core is formed. Following this design, Lv et al. reported an SDT strategy for synthesizing NM-based HMNs (Figure 5a).[5b] In this synthesis, dioctadecyldimethylammonium chloride (DODAC) with two hydrophobic tails is important because it can self-assemble into “dual” templates
of cylinder and vesicle micelles simultaneously in the presence of metal precursors. Moreover, its strong hydrophobicity inhibits the mobility of the metal precursors and confines the nucleation of NMs along the surfactant templates. For example, under the reduction of ascorbic acid, smaller PdAg alloy cores were first grown in situ on the surface of spherical vesicles. Then, the PdAg alloys gradually nucleated into a continuous framework and grew larger with cylindrical micelles to form a mesoporous framework. Compared to the SSTN strategy that homogeneously nucleates NMs on a colloidal silica template, the SDT strategy first forms bowl-like nanoparticles, which epitaxially grow into whole nanoparticles (Figure 5b). Finally, PdAg HMNs with clean surface sites were obtained by easily removing the surfactant template using H2O/ethanol. The combination of hollow and mesoporous structures as well as bimetallic compositions in one nanoparticle was confirmed using TEM, dark-field STEM, STEM EDS mapping, and line scanning images (Figure 5c–e). In addition, mesoporous nanochannels in PdAg HMNs were cylindrical and radially open, implying that cylindrical micelles of DODAC templated the formation of a mesoporous structure. Such a hierarchical structure would be highly beneficial for the transport of reactants, enhancing the catalytic performance of PdAg HMNs. As a control, adding a small amount of ethanol to the reaction solution destroyed the...
vesicle micelles, which resulted in the synthesis of solid MSs.\cite{4} Interestingly, the SDT strategy can be extended to synthesize other NM-based HMNs with different elemental compositions (or functions), such as PdAgCu HMNs (Figure 5f–h) and PdAgAuCu HMNs, by easily changing the initial feed solutions, indicating the generality of the SDT method.\cite{5a}

Inspired by the epitaxial growth of asymmetric bowllike nanoparticles into symmetric HMNs, NM-based asymmetric HMNs (AHMNs) were obtained by controlling the nucleation kinetics (reaction parameters) (Figure 5i,j).\cite{19} For example, increasing the concentration of DODAC from 0.6 to 3.0 mg mL$^{-1}$ gradually increased the structural asymmetry of PdAgCu AHMNs from 7/8 (AHMNs-7/8) to 1/8 (AHMNs-1/8) (Figure 5k). This is possibly because the higher concentration of DODAC decreased the local concentration of metal precursors along the templates, resulting in the partial nucleation of HMNs with high asymmetry. On the other hand, symmetric HMNs were formed at a low DODAC concentration (<0.1 mg mL$^{-1}$). Both AHMNs and symmetric HMNs have similar hollow structures and sizes, indicating that they are formed through the SDT strategy. In addition, the precursor concentrations, reaction temperatures, and pH of the solution also played important roles in tailoring the structures of the assemblies and the nucleation kinetics of the NM nanocrystals. Catalytic results confirmed that PdAgCu AHMNs exhibited a recordable EOR activity of 6.4 A mgPd$^{-1}$ and remarkable stability compared to symmetric counterparts. This is because the asymmetric structure exposes more active sites and accelerates the removal of poisonous species (the rate-determining step of EOR electrocatalysis). The SDT strategy is a universal method that can be easily extended to multimetallic AHMNs, such as tetrametallic PdAgPtCu and PdAgCuFe (Figure 5l,m), and 1D interconnected nanochains of Pt AHMNs.\cite{28} The SDT strategy thus provides a new and simple route for designing nanomaterials containing NM-based AHMNs with different structural and compositional functions.

2.4. KEST Strategy

The Kirkendall effect is one of the most common mechanisms in the formation of hollow nanoparticles.\cite{29} This includes the formation of a compound (M$_1$M$_2$) on the surface of the metal nanocrystal (M$_1$) and the diffusion of M$_1$ and M$_2$ through the interface of M$_1$ and M$_2$M$_2$. Owing to the faster outward diffusion of M$_1$ compared to the inward diffusion of M$_2$, the M$_1$@M$_1$M$_2$ nanocrystal gradually converts to a hollow structure. Recently, Lv et al. developed a novel synthetic strategy, named KEST, for the synthesis of binary PdS nanoparticles with well-defined morphology and periodically ordered mesostructure (Figure 6a).\cite{6e} The KEST strategy combines the advantages of Kirkendall cavitation, which precisely controls the formation of hollow nanoparticles at the atomic level, and nanocasting synthesis, which templates the confinement nucleation of a periodically ordered mesoporous framework at the mesoscopic level. Considering the synthesis of PdS HMNs, the authors first prepared mesoporous Pd nanoparticles confined in a KIT-6 template (Pd/KIT-6) using a traditional hard template method (Figure 6b). When the mixture of Pd/KIT-6 was directly treated with solid sulfur at a high temperature, the fast outward diffusion of Pd and slow inward diffusion of S resulted in Kirkendall cavitation of PdS in the KIT-6 template. At the beginning of this reaction, the mesoporous Pd gradually diffused outward and recrystallized in the KIT-6 channels with sulfur vapors, producing a yolk–shell Pd–PdS structure (Figure 6c,d). As the reaction proceeded, the interior Pd diffused out completely, forming binary PdS HMNs with hollow cavities. Meanwhile, the KIT-6 template confined Kirkendall cavitation and formed mesoporous shells (Figure 6e). Interestingly, some bowl-like HMNs were observed in PdS/KIT-6, indicating that Kirkendall cavitation proceeded along the pores due to the capillary effect.\cite{10} Moreover, the changes in the HMN sizes (shell thickness, yolk, and overall nanoparticle) and PdS compositions further confirmed the successful synthesis of PdS HMNs using the KEST strategy (Figure 6f,g).

The synthesis of PdS HMNs in the KIT-6 template was the first successful preparation of NM-based HMNs with periodically ordered mesostructures. This provides great opportunities to evaluate the mesostructure-related properties of NM nanocrystals. The KEST strategy can be extended to produce PdP HMNs with highly ordered mesopores by replacing the sulfur source with a phosphorous source (NaH$_2$PO$_2$). In addition, the KEST method is powerful for preparing metal alloys. Metal alloys can be divided into random solids and intermetallic compounds depending on their atomic order.\cite{21} The former has randomly distributed atoms of alloy composition across the lattice, whereas the latter is composed of the long-range ordered atoms, bonded by strong d-orbital interactions with a specific atom stoichiometry. Structurally ordered atomic arrangements of intermetallic compounds provide unique properties to intermetallic compounds. These properties stand out from those of other crystal structures, particularly in catalysis and electrocatalysis. Compared to random alloys, intermetallic compounds are generally synthesized at higher temperatures. Owing to the high thermal stability of the KIT-6 template, the KEST strategy was successfully applied to prepare ordered intermetallic HMNs, such as Pt$_5$Sn$_3$. In this synthesis, Kirkendall cavitation of the KIT-6-confined Pt mesoporous polyhedral was driven by the addition of SnCl$_2$ and heating under a reducing atmosphere (H$_2$/N$_2$). Precise control of the atomic ratios of Pt/Sn feeds and reaction temperatures resulted in a gradual evolution of the crystal structure from a PtSn random alloy to an ordered Pt$_5$Sn$_3$ intermetallic compound (Figure 6h,i).\cite{20} This report broadly expands the synthetic capability of the KEST strategy to a library of novel NM-based HMN materials with more compositional functions.

2.5. GRST Strategy

Over the past two decades, galvanic replacement reactions (GRRs) have been widely used for preparing hollow metal nanocrystals.\cite{32} The driving force of a GRR is the difference in the electrode potentials between two metals. Metal M$_1$ (anode), which has a lower electrode potential than metal M$_2$ (cathode), is oxidized by the salt form of metal M$_2$ and converted to its ionic form, generating holes/cavities in the original metal crystals. When the GRR takes place in a system with sufficient
mesopore-forming surfactants, it produces HMNs. This process is called the GRST strategy. The GRST strategy generally includes two steps: preparation of a sacrificial template (the anode material) and galvanic replacement growth of HMNs with a secondary metal salt (the cathode material) on the sacrificial template in the presence of a mesopore-forming template. Therefore, choosing the right metal is critical for using the GRST strategy to synthesize NM-based HMNs. Thus far, Ni, Ag, and Te are good choices as sacrificial templates, while Pt, Rh, and Au salts have been demonstrated as oxidizing agents.[33] As a typical example, Wang et al. developed a two-step GRST strategy and successfully synthesized 1D Rh HMNs (Figure 7a).[5e] In this synthesis, 1D Ni nanowires and amphiphilic micelles formed by poly(ethylene oxide)-block-poly(methyl methacrylate) (PEO-b-PMMA) were used as the anode sacrificial and mesopore-forming templates, respectively. The authors demonstrated that adding RhCl\textsubscript{6}^{3−} to the reaction solution containing Ni nanowires and polymer micelles gradually reduced RhCl\textsubscript{6}^{3−} into metallic Rh around the micelles on the surface of Ni nanowires, while oxidizing simultaneously metallic Ni to Ni\textsuperscript{2+} (3Ni + 2RhCl\textsubscript{6}^{3−} → 3Ni\textsuperscript{2+} + 2Rh + 12Cl\textsuperscript{−}). This is because the reduction potential of RhCl\textsubscript{6}^{3−}/Rh (+0.44 V versus standard hydrogen electrode (SHE)) is certainly higher than that of Ni\textsuperscript{2+}/Ni (−0.25 V). During GRST synthesis, the sacrificial Ni nanowires gradually dissolved into the reaction solution, while mesoporous Rh nucleated on the surface of the Ni template. Yolk–shell intermediates of Ni–Rh nanowires with a Ni-rich core and a mesoporous Rh shell were formed, confirming successful synthesis of HMNs using the GRST strategy (Figure 7b–e). The structure of Rh HMNs includes 1D tubular interiors and mesoporous exteriors (Figure 7f–i); therefore, they exhibited highly efficient electrocatalytic performance. In comparison, when an additional reducing agent was used, the dissolved metals recrystallized further with the secondary metals and formed multimetallic HMNs. This two-step GRST strategy has successfully prepared several 1D HMNs, including bimetallic PtTe (Figure 7l–m),[34] and IrTe HMNs,[34] and trimetallic PtRuTe HMNs.[22]

A sequential reduction strategy was developed to direct GRST synthesis of NM-based HMNs. Compared to the two-step GRST strategy, the sequential reduction-assisted GRST strategy is seedless and can be completed in one step. Lv et al. recently utilized this method to synthesize AuAg HMNs (Figure 8a).[5d] The key to the synthesis is to introduce a surfactant, which can

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**Figure 6.** The KEST strategy for synthesizing PdS HMNs. a) Schematic illustration of the synthesis of PdS HMNs using the KEST strategy. b–e) Time-dependent TEM images of PdS@KIT-6 intermediates. Insets in (b–e) are dark-field STEM and EDS mapping images of PdS HMNs after etching the KIT-6 template with different reaction times. f,g) The relationships between size (f) or atomic percentage (g) and reaction time. a–g) Reproduced with permission.[6e] Copyright 2021, Chinese Chemical Society. This figure has been published in CCS Chemistry 2021; “Precise Synthesis of Hollow Mesoporous Palladium–Sulfur Alloy Nanoparticles for Selective Catalytic Hydrogenation” is available online at https://doi.org/10.31635/ccschem.021.202101343. h) Dark-field STEM and EDS mapping images, i) XRD pattern, and (inset) high-resolution STEM image of intermetallic Pt\textsubscript{1}Sn\textsubscript{1} HMNs. h,i) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0).[20] Copyright 2022, The Authors, published by Wiley-VCH.
coordinate with Au and Ag precursors and self-assemble to form micelles as the mesopore-forming agent. The thiol-terminated multifunctional surfactant, \( \text{C}_{22}\text{H}_{45}\text{N}^+(\text{CH}_3)_2\text{C}_3\text{H}_6\text{SH} \) (Cl\( ^- \)) (C\( _{22}\text{N}-\text{SH} \)), was designed to form stable C\( _{22}\text{N}-\text{S-Au(I)} \) and C\( _{22}\text{N}-\text{S-Ag(I)} \) intermediates. Such intermediates limit the mobility of the Au/Ag precursors and also self-assemble into spherical micelles to form mesopores.\[^{[35]}\] The significant difference in the reduction potentials of C\( _{22}\text{N}-\text{S-Ag(I)}/\text{Ag} \) and C\( _{22}\text{N}-\text{S-Au(I)}/\text{Au} \) resulted in the sequential reduction and nucleation of Ag and Au nanocrystals. Initially, Ag nanoparticles were formed, which then reacted with C\( _{22}\text{N}-\text{S-Au(I)} \) (C\( _{22}\text{N}-\text{S-Au(I))} + \text{Ag} \rightarrow \text{Au} + \text{C}_{22}\text{N}-\text{S-Ag(I))}. \) This resulted in the direct formation of HMNs via GRR. It is noteworthy that the covalently stable C\( _{22}\text{N}-\text{S-Ag(I)} \) also avoided the formation of AgCl aggregates. The GRST formation mechanism of the AuAg HMNs was clearly revealed by the corresponding TEM images, ultraviolet-visible (UV–vis) absorption spectroscopy, and color changes of the reaction solution when collecting their intermediates at different reaction times (Figure 8b–d). AuAg HMNs exhibited well-controlled localized surface plasmon resonance signals, which expanded their applications in photochemistry. Advanced characterizations showed that the resultant AuAg HMNs are highly uniform in both structure and composition, confirming the power of one-step seedless GRST strategy for synthesizing NM-based HMNs (Figure 8e,f). Furthermore, the interior hollow cavity, mesoporous framework, and optical activities of AuAg HMNs were precisely controlled by easily tuning the feeding amount of Ag precursor (Figure 8g–i). Moreover, when changing the

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**Figure 7.** Two-step GRST strategy for synthesizing NM-based HMNs. a) Schematic illustration of the synthesis of Rh HMNs using a two-step GRST strategy. b–e) Time-dependent SEM or TEM images and (insets) corresponding schematic illustrations of yolk–shell Ni–Rh intermediates and Rh HMNs. f,g) SEM images and h,i) TEM images of Rh HMNs. a–i) Reproduced with permission.\[^{[5e]}\] Copyright 2021, Royal Society of Chemistry. j) SEM image, and k) TEM image, l) STEM EDS mapping image, and m) line scan profiles of PtTe HMNs. j–m) Reproduced with permission.\[^{[21]}\] Copyright 2019, Royal Society of Chemistry.
reduction kinetics, the resultant products can also evolve into well-alloyed MNs and core–shell MNs, confirming the importance of GRR in the formation of HMNs. This strategy does not require pre-synthesis of sacrificial seeds and provides a simple reference scheme for the design and synthesis of NM-based HMNs.

3. Catalytic Application

3.1. Enhancing Catalytic Activity and Stability

NM-based HMNs have attracted increasing attention in the fields of catalysis and electrocatalysis because of their multiple structural advantages, which expose more active sites and remarkably accelerate their catalytic kinetics, thus synergistically enhancing their activity and stability. Here, we discuss the electrochemical EOR, which is an anode reaction of a direct ethanol fuel cell (DEFC) in detail as proof-of-concept catalysis. Pd-based NMs are the most efficient catalysts for EOR electrocatalysis; however, their activity is significantly deactivated owing to the strong adsorption capacity of toxic ethoxy intermediates (CH$_3$COO$_{ads}$, CH$_3$CO$_{ads}$, etc.). Engineering the structure of NMs into hierarchical HMNs is an effective route to remove such toxic intermediates. Bimetallic PdAg HMNs developed by Lv et al. were chosen as an example catalyst to highlight the structural advantages in enhancing the EOR activity and stability (Figure 9a). Owing to their higher utilization efficiency and accelerated mass/electron transfer, the HMNs had a higher electrochemical surface area, which is significantly higher than that of their counterpart catalysts (PdAg MSs, PdAg NPs, and commercial Pd/C) (Figure 9b). Meanwhile, PdAg HMNs exhibited a much better CO anti-poisoning ability (imitating the rate-determining step of EOR electrocatalysis) (Figure 9c). These structural advantages synergistically boosted the EOR activity of the PdAg HMNs in alkaline solution. Compared to the counterpart catalysts, PdAg HMNs achieved the highest EOR activity of 4.61 A mgPd$^{-1}$ and the lowest onset potential of −0.7 V (Figure 9d). Meanwhile, compared to NPs and solid MSs, the higher electrocatalytic kinetics obtained in different scan rates (v) further confirmed that PdAg HMNs with add-in structural advantages exhibited an accelerated diffusion rate of the reactants and a higher EOR activity (Figure 9e).

Apart from the high activity, the EOR stability of PdAg HMNs has also been remarkably enhanced because of their structural advantages. Both EOR current–time (i–t) and cycling stability studies revealed that PdAg HMNs slowly declined their EOR activity and retained high activity after EOR electrocatalysis. In sharp contrast, the EOR activity of the commercial Pd/C quickly declined to nearly zero (Figure 9f,g). The high stability of PdAg HMNs mostly originates from their add-in structural advantage, which can enhance the anti-poisoning ability, suppress the surface atomic dissolution, and inhibit the physical Ostwald ripening process. Advanced characterizations...
revealed that the PdAg HMNs retained well their structure and composition after the stability tests, thereby confirming their synergistic advantages for EOR electrocatalysis (Figure 9h). Interestingly, NM-based HMNs are highly active and stable in various (electro)catalysis reactions, including the methanol oxidation reaction (MOR), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and oxygen evolution reaction (OER). These results confirmed the importance of designing and synthesizing novel NM-based HMNs for catalysis and electrocatalysis.

3.2. Optimizing Catalytic Selectivity

Crystalline mesoporosity and nanocavity of NM-based HMNs significantly change the surface tensile strain of their active sites and also provide a confined “nanopincer” environment. These structural functions could tune the adsorption and desorption properties of the reactants and optimize their selectivity in catalysis and electrocatalysis. Recently, Lv et al. demonstrated that PdS HMNs demonstrated catalytical efficiency of PdS HMNs in the selective hydrogenation of 4-nitrophenylacetylene (4-NPA) (Figure 10a). Density functional theory (DFT) calculations showed that, compared to their nanoparticle counterparts, PdS HMNs have a highly curved framework and abundant low-coordinated sites, thus producing strongly perturbed electronic structures (Figure 10b). Meanwhile, projected partial density of state (PDOS) studies revealed that the hollow and mesoporous structure of PdS HMNs would significantly close Pd sites to the Fermi level (Figure 10c). Such an electronic structure changes the adsorption features of the reactants on the PdS HMNs and thus optimizes their catalytic trends.
toward the desired products. In particular, for the selective hydrogenation of 4-NPA, PdS HMNs favorably hydrogenated the −C≡C group without hydrogenating the −NO2 group and over-hydrogenating the −C−C group (Figure 10d). A high catalytic selectivity of ~94% toward industrially important 4-nitrostyrene (4-NS) was achieved over PdS HMNs. In comparison, the 4-NS selectivity was decreased to 64% for mesoporous Pd (Figure 10e), confirming the positive effect of the hollow structure (and PdS composition) on the catalytic selectivity. As a control, commercial Pd/C favorably overhydrogenated 4-NPA toward 4-aminoethylbenzene (4-AE), suggesting low catalytic selectivity toward the high-value products (Figure 10f). The DFT calculations further showed that these catalysts had different reaction trends (barriers), which optimized their catalytic selectivity toward the targeted products (Figure 10g–i). These results provide a new possibility for tuning catalytic selectivity by engineering crystalline porosity of NM-based HMNs at the mesoscopic level.

4. Summary and Outlook

Since its first synthesis in 2011, NM-based HMNs have been rapidly developed. NM-based HMNs with controlled morphologies, structures, and compositions have been successfully prepared using various synthetic methods and are widely applied in catalysis and electrocatalysis. Compared to their counterparts of hollow NMs and mesoporous NMs, NM-based HMNs that concurrently combine an interior hollow cavity and a penetrated mesoporous framework in one nanoparticle exhibit multiple add-in synergies, making them more active, stable, and selective for catalysis and electrocatalysis. In this review, we summarized recent synthesis strategies for NM-based HMNs, including SSTN, STSN, SDT, KEST, and GRST. We further explored the control over the macroscopic morphology, mesoscopic structure, and atomic composition and arrangement of NM-based HMNs. More importantly, we systematically discussed the formation mechanisms of NM-based HMNs.
Meanwhile, two important catalytic reactions, EOR electrocatalysis and selective hydrogenation of 4-NPA, were used to demonstrate the importance of NM-based HMNs in enhancing catalytic activity and stability and optimizing catalytic selectivity.

Despite significant studies on NM-based HMNs, their synthesis and applications are still at an immature stage. First, there are a large number of synthesis strategies for preparing NM-based HNs and MNs and further engineering their hierarchical structures. For example, Ostwald ripening and the dissolution-regrowth are important strategies for synthesizing hollow-structured NMs with well-controlled morphologies;[37] however, these strategies have never been successful in synthesizing NM-based HMNs. Similarly, the power of synthesis strategies, particularly the liquid-crystal-templated route, refers to libraries of mesoporous NMs with controlled morphologies, structures, and compositions.[38] Meanwhile, the sizes of both mesopores and interior cavities of NM-based HMNs should be further regulated since they strongly correspond to their catalytic performance. Therefore, developing new synthesis methodologies and theories is highly desirable for the precise synthesis of NM-based HMNs with targeted functions. The reproducibility, price, and scale-up of the methods for synthesizing NM-based HMNs are of great concern.

Second, engineering the mesoscopic structures and atomic arrangements of NM-based HMNs by identifying more desired and novel functional materials is challenging. At the mesoscopic level, the periodically ordered crystalline porosity (mesopore and nanocavity) of NM-based HMNs is structurally beneficial for potential applications. At the atomic level, the crystalline phase of NM-based HMNs can be extended from traditional face-centered cubic (fcc) to hexagonal close-packed (hcp) and to body-centered cubic (bcc). Moreover, their atomic arrangement can be extended from random solids to highly ordered intermetallic compounds. These modifications would provide novel physicochemical properties and functions to the NM-based HMNs, thereby expanding their applications.

Finally, the applications of NM-based HMNs almost are limited to catalysis and electrocatalysis. Exploring new applications of NM-based HMNs with multiple structural and compositional advantages, particularly in photocatalysis, photoelectrical catalysis, sensing, surface-enhanced Raman scattering (SERS), bioimaging, and biotherapy, is urgently required. Elaborating on the general structure–performance relationships of NM-based HMNs is also highly desirable.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

catalysis, hollow mesoporous nanoparticles, noble metals, synthetic methods, template synthesis

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