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Design of Hollow Structured Nanoreactors for Liquid-Phase Hydrogenations

Yutong Pi,[a] Haitao Li [b] and Jian Liu *[a]

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Inspired by the charming structures and functions of natural matter (such as cell, organel and enzyme), chemists constantly explore innovative materials platform to mimic natural catalytic systems, particularly liquid-phase hydrogenations, which are of great significance for chemical upgrading and synthesis. Hollow structured nanoreactors (HSNRs), featuring unique nanoarchitectures and advantageous properties, offer new opportunities for achieving excellent catalytic activity, selectivity, stability and sustainability. Notwithstanding great processes have been made in HSNRs, it still remains the challenges of precise synthetic chemistry, mesoscale catalytic kinetic investigation as well as smart catalysis. To this extent, we overview the recent developments in the synthetic chemistry of HSNRs, unique characteristics of these materials, and catalytic mechanisms in HSNRs. Finally, a brief outlook, challenges and further opportunities of their synthetic methodologies and catalytic application are discussed. This review might promote the further creation of HSNRs, realize sustainable production of fine chemicals and phamarcuticals, and contribute to the development of materials science.

1. Introduction

Hollow nanoreactors (HSNRs) are small reaction vessels designed and synthesized artificially, which can allow chemical reactions to occur within their nanospace and be distinguished from other materials by their unique structures and customizable functions.[1,2] HSNRs can either alter the basic chemical properties of molecules or change their behaviours in chemical transformations, thus accelerating the reaction, acquiring new understanding of chemical systems, and accordingly being subject to versatile research areas, such as catalysis, biomedicine, energy storage and conversion, and so forth.[3-7]

Nowadays, HSNRs have emerged as exceptional alternatives to traditional catalytic materials, especially in liquid-phase hydrogenation reactions, because the isolated space offer nanoscale environments partitioned from the surrounding bulk space.[8,9] The morphology and chemical contents of this nanospace dictate reaction chemical/spatial microenvironment, reactant enrichment, compartmentalization of active sites, and diffusion processes, thus improving its activity, long-term stability and regulating product selectivity, making it an ideal catalyst. To control and boost their catalytic performances, and even generate distinct and intriguing properties, the morphological and compositional control of HSNRs is particularly interesting. Several recent reviews have discussed the advances in the synthetic strategies of HSNRs.[10-12] Wan and coworkers outlined the new synthetic strategies by manipulating particle chemistry for the creation of hollow carbon-based nanospheres.[11] The fabrication of other hollow nanostructured materials, such as hollow metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), have also been focused.[13-15] Largely, most reviews and perspectives focus on the construction of specific materials, systematic summary on the engineering of HSNRs with various materials is still insufficient. Additionally, when considering the application researches, a number of comprehensive reviews have been thoroughly summarized. For example, the updated and critical investigation of hollow nanostructures in all catalytic branches (including, bio-, electro, and photocatalysis) presented by Schüth et al., and promising application on sensing, separation and storage reported by Zou and coworkers.[5] Despite many general and potential applications of HSNRs have been summarized in previous literatures, a review covering HSNRs for liquid-phase hydrogenations and emphasis on the structure-performance correlation is reported limitedly.

In this review, we systematically summarize the controllable and precise synthetic chemistry of HSNRs, detailly discuss their unique properties and how these properties affect liquid-phase hydrogenation performances. Finally, we further put forward a brief outlook for future developments and challenges of these synthetic principles and applications of HSNRs. These systematically review and in-depth understandings are expected to open new avenues for the rational design of advanced HSNRs, and inspire further development for broad application fields.

2. Synthetic Strategies for Hollow structured Nanoreactors

To date, tremendous research work has been devoted to constructing various hollow nanostructures in pursuit of their charming physical-chemical properties. Even so, the developing preparation processes can be categorized into two general paradigms: bottom-up and top-down (Figure 1). Similar to assembling building blocks, the bottom-up strategy is starting

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[a] College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, Inner Mongolia 010021, PR China
* E-mail: jian.liu@surrey.ac.uk; jian.liu@imu.edu.cn

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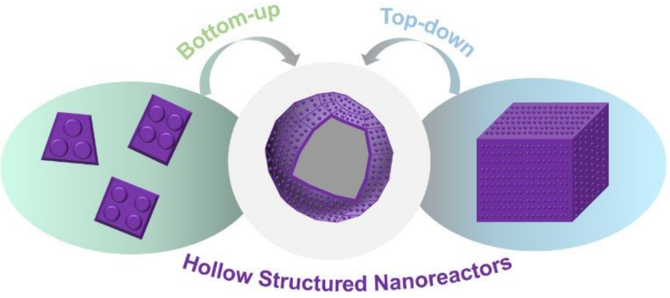

Figure 1. Scheme illustration of two main strategies for the synthesis of HSNRs.

from each small part and finally assembling it into an ideal nanostructure; Contrarily, the process of top-down strategy is to extract unnecessary parts from a built monolith, leaving the desired hollow nanostructure.

2.1 Bottom-up Strategy

Very recently, bottom-up strategy, typically soft-template directed protocols are widely used to fabricate various hollow materials with unique structures, pore configuration as well as fascinating physical-chemical properties.[16,17] The synthetic methods can be categorized into micelles-directed assembly, emulsion-guided assembly, and interfacial assembly methods.

The micelles-directed assembly method relies on the ordered arrangement and assembly of amphiphilic surfactants and block copolymers, for example, cationic cetyltrimethyl ammonium bromide (CTAB), Pluronic F127 ($EO_{106}PO_{70}EO_{106}$), poly(styreneblock-4-vinylpyridine) (PS-b-P4VP), and so on.[18] After assembled with precursors, like polymer oligomers, metal ions and silanes, the micelle-oligomers composites can be formed.[19] Finally, these composites proceed crosslinking and synthesize desirable hollow structures. The detailed morphology and mesostructure of hollow materials are highly depended on the structure of micelle, type of surfactants and other reaction parameters. Zhao et al. reported a lamellar micelle assembled by Pluronic P123 block copolymer and dopamine (Figure 2a).[20] Followed by continuously growing and self-assembling, the hollow multi-shelled nanospheres can be created. Meanwhile, changing the P123 to F108, F127, and P105, nanospheres with single cavity, ordered mesochannels, dendritic mesopores can be formed. The micelles-directed assembly method enables extending the library of hollow materials, such as hollow CaP,[21] WO_3,[22] and Au[23] nanospheres, etc.

Another typical and facile synthetic method is emulsion-guided assembly, which is one of the most potential strategies for synthesizing nanomaterials with various nanostructures, especially hollow nanoarchitectures.[24,25] The emulsion involves the mixing of two immiscible liquids, generally water and oil, with the presence of surfactants.[13] An oil/water or water/oil emulsion system provides the template for tailoring the multiple architectures of the materials.[5,26] Recently, Ma et al. reported a nanodroplet remodeling method in water/oil emulsion system and synthesized multi-chambered (from single to tri-chambers) silica nanoparticles.[27] In this method, tetrahydeofuran (THF), a new solvent, was introduced to trigger the expansion of water nanodroplets in n-pentanol, causing the formation of muti-chambers silica nanoparticles with the continuous hydrolysis of silicate precursor adsorbed on nanodroplets surface. Wang and coworkers adopted the similar emulsion-guided strategy and synthesized various hollow

Yutong Pi received her Ph.D. degree in physical chemistry from the Dalian Institute of Chemical Physics, Chinese Academy of Science, in 2023. Now she is a researcher at the School of Chemistry and Chemical Engineering, Inner Mongolia University. Her research interests focus on the design and synthesis of nanoreactors for heterogeneous catalysis.

Haitao Li received his Ph.D. degree in materials science and engineering from China University of Geosciences (Wuhan, China) in 2021, and then conducted postdoctoral fellow in the Micro-Nano Reactor & Reaction Engineering Science Group led by Prof. Jian Liu in Dalian Institute of Chemical Physics, Chinese Academy of Science, China. Subsequently, he joined the College of Chemistry and Chemical Engineering of Inner Mongolia University. His research interests primarily focus on the rational design of functional transition-metal-/carbon-based nanoreactors for applications of heterogeneous catalysis including artificial production of H2O2 and advanced oxidation processes.

Jian Liu received his PhD degree in physical chemistry from the Dalian Institute of Chemical Physics, Chinese Academy of Science, China, in 2008. Now he is a chair professor and head of the School of Chemistry and Chemical Engineering, Inner Mongolia University, China. He also held an adjunct Reader position in the Department of Chemical and Process Engineering, University of Surrey, UK. His research focuses on the design of micro–nanoreactors, porous carbon spheres, and industrialization of homogeneouscatalysis in heterogeneous systems. His h-index is71 (Web of Science).

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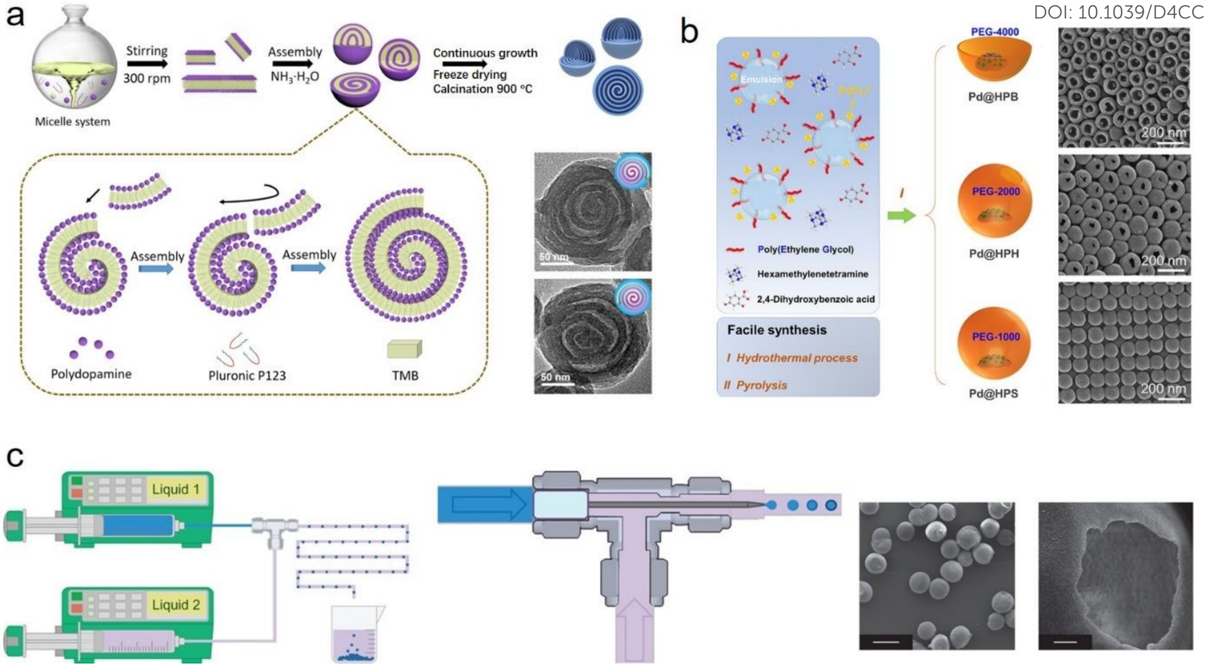

Figure 2. Schematic illustration of various bottom-up methods and transmission electron microscopy images of corresponding hollow nanomaterials: (a) micelles-directed assembly,[20] Copyright 2021, Science, (b) emulsion-guided assembly,[28] Copyright 2023, American Chemical Society, and (c) interfacial assembly methods,[29] Copyright 2011, Nature Publishing Group.

carbon nanoparticles, where P123/Sodium oleate served as emulsion precursor, polyethylene glycol as reverse demulsifier, 2,4-dihydroxybenzoic acid/hexamethylentetramine as polymer precursor (Figure 2b).[28] This strategy is applicable for building other types of hollow materials with multilevel structures, shapes, and functions.

Interfacial assembly, micelles and framework precursors self-assembled on the two-phase interface, allows the controllable synthesis of unique hollow architectures, greatly enriching those structures and functionality. Usually, three interfaces, liquid-liquid, solid-liquid and liquid-gas interfaces, are utilized for manipulating the assembly. In liquid-liquid interfacial assembly, two immiscible liquids provide the interface as reaction space and strongly confine the construction of various hollow nanomaterials. As a typical example, De Vos's group developed a microfluidic environment that enables the formation of spherical liquid-liquid interface and spherical MOF shell (Figure 2c).[29] Through a capillary, the generated monodispersed droplets containing aqueous cupric solution can react with the ligand molecules at the interface, and then form the $Cu_3(BTC)_2$ hollow capsule. As another useful interface, solid-liquid interface can effectively architect hollow nanomaterials. Yu et al. reported a novel anisotropic hollow carbon material by this solid-liquid interface assembly method.[30] The approach allows regioselective surface assembly of carbon precursor, dopamine, on the different positions of slicalite-1. Upon carbonization and removal of these hard substrates, the hollow carbon with anisotropic were successfully achieved. Zhao et al. proposed a monomicelle interface confined assembly approach to synthesize 3D hierarchical mesoporous superstructure, where colloidal silica nanospheres as hard substrate, PS−PVP−PEO as monomicelles and dopamine as carbon precursor.[31] Furthermore, gas-liquid interface also shows huge potential for fabrication of hollow nanomaterials. For instance, Zhang et al. added CO_2 bubbles into continuous ionic liquid, and allowed the assemble of organic linkers and metal ions on the solid-liquid interface, resulting in the generation of hollow Zn-BTC.[32]

On the basis of the above-mentioned synthetic methods, numerous hollow materials with diverse morphology, shape, composition and functionality have been prepared. Whereas, in pursuit of enhanced properties and functionality, and meeting the requirements for broad applications, the design and synthesis of hollow nanostructures are still of great significance.

2.2 Top-down Strategy

The top-down strategy underscores the control of particles themselves with labile chemical structure and the removal process: (1) by delicately regulating reaction condition, solid nanomaterials with unstable inner parts and stable outer parts are constructed, in which the unstable parts are easier to be removed; (2) removing the labile interior with the assistant of extra solvent (such as acetone, ethanol, H_2O, and metal salt solution, etc.), and transforming these solid nanoparticles into hollow nanostructured materials. Generally, the labile chemical structure can be constructed by building inner constitutional inhomogeneity, surface protecting method, and architecting of core shell materials.

For manipulating particle chemistry, Chen and coworkers firstly revisited the Stöber method of silica synthesis and demonstrated the inhomogeneous nature of silica shell.[33] Due

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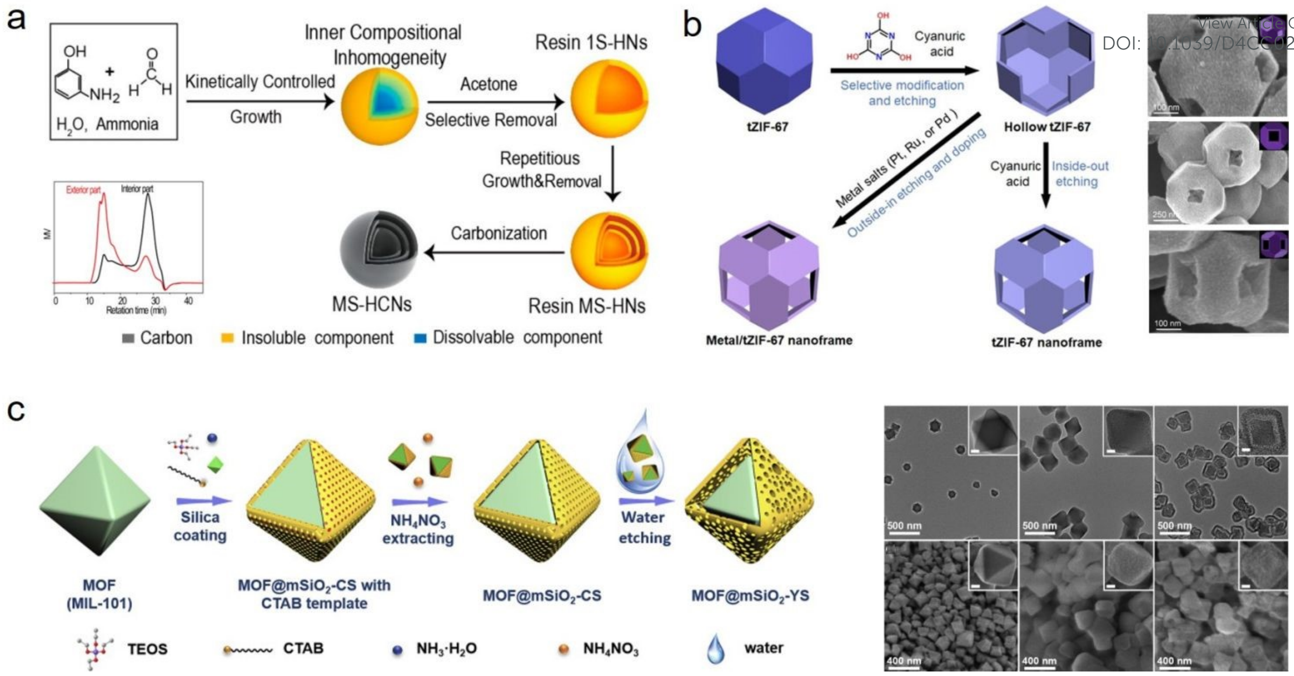

Figure 3. Schematic illustration of the formation of hollow nanomaterials based on various top-down methods and corresponding transmission electron microscopy: (a) building inner constitutional inhomogeneity,[34] Copyright 2017, American Chemical Society, (b) surface protecting method,[35] Copyright 2021, Wiley-VCH, and (c) architecting of core shell materials,[36] Copyright 2020, Elsevier.

to the presence of a more robust outer layer, the weakened inner layer is easier to be etched by hot water and forming hollow nanostructures. Recently, focus is laid on the synthesis of hollow nanostructured phenolic resins by controlling their compositional chemistry.[11] Because the tailorable growth kinetics of polymerization process, different polymerization degree or distribution of different polymeric components within a single phenolic particle can be prepared. Wan's group demonstrated that through tunning the time and temperature of polymerization process, the synthesized 3-aminophenol formaldehyde (APF) resin nanospheres have a location-specified different of molecular weight, exterior part higher than that interior part (Figure 3a).[34] Therefore, after acetone treatment, the core of these nanospheres was able to be selectively dissolved, forming hollow particles. Very recently, we reported another method to control growth kinetics by molecular-level design to build phenolic resins nanospheres with periodic variation in polymerization.[37] By simply changing the mole ratio of different phenol precursors 3-AP and R, the solid phenolic resins with wave-like polymerization degree can be successfully obtained, enabling construction of hollow multishelled structure with the combination of subsequent ethanol scissoring process. In addition to managing polymerization degree, the followed removal process is equally important in expanding the diversity and complexity of phenolic resins. In our previous work, a nanoscale chemical scissoring strategy has been developed which relies on the utilization of ethanol as chemical scalpel to tailor the nanostructure and chemical composition of APF.[38] Due to the facile and reliable strategy, multilevel hollow structure APF nanoparticles with accurately positioning of organic functional groups are successfully prepared. Similarly, Yu et al. successfully constructed charming concave hollow APF spheres via the acetone guided deflation-inflation asymmetric growth process.[39] The synthetic concept of constructing single particle with inhomogeneous chemistry for hollow nanostructure is suitable for other material system. So far, increasing attention and efforts have been paid to the nanoengineering of hollow MOFs.[40,41] Usually, due to the incomplete coordination between metal nodes and grain boundaries, more defects are present in the inner region of MOFs, resulting in their inhomogeneity. The presence of defects allows preferential etching of core parts and formation of hollow MOFs. Besides, incorporating extra agent during synthesis makes the internal core with weak coordination less stable than the external surface, which helps to architect hollow MOFs. Furthermore, by means of crystallization degree and chemical reactivity control, hollow organic−inorganic composite (such as hollow TiO_2−C, ZrO_2−C, SnO_2−C, and CeO_2−C), metal oxides and COFs can also be successfully achieved.[11,42-44]

In addition to controlling the inhomogeneous nature of nanoparticles, surface protecting method is commonly used to prepare hollow nanomaterials. By utilizing stabilizing agents, generally polymers, to shield the coordination bonds of surface, a more stable and anticorrosive surface can be created, which could be left after treated with extra etchants. In early research, Yin and coworkers proposed a "surface-protected etching" strategy to prepare hollow silica sphere, in which poly(vinyl pyrrolidone) (PVP) was used as protecting agent because of the formation of strong hydrogen bonds with silica surface.[45] Therefore, after treatment with NaOH, it can selectively etch the internal core of silica and form hollow nanostructure. Apart from PVP, other ligands include polyacrylic acid,[46] polyethylene glycol,[47] and polyethyleneimine,[33] have also been chosen to

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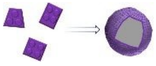
Table 1. Summary of various synthesis methods of HSNRs.

Strategies	**Synthetic Methods**	**Compositions**	**Advantages**
Bottom-up Strategy 	Micelles-directed assembly	PDAs, COFs, phenolic resins, MOFs, CaP, WO_3, Au, etc.	High complexity of designable structures
	Emulsion-guided assembly	PDAs, PS, COFs, phenolic resins, MOFs (ZIF-8, UiO-66), TiO_2, SiO_2, etc.	Controllable morphology, internal and external composition
	Interfacial assembly methods	PDAs, PS, COFs, phenolic resins, Composites (TiO_2-PDA, SiO_2-PDA), etc.	High operability and structural diversity
Top-down Strategy 	Building inner constitutional inhomogeneity	Phenolic resins, MOFs, SiO_2, COFs organic—inorganic composite, etc.	Precisely manipulating the nanostructure and composition
	Surface protecting method	SiO_2, ZIF-67, metal oxides (TiO_2, CeO_2, ZnO), etc	Convenient operation, high repeatability
	Architecting of core shell materials	MOF@mesoporous SiO_2, MOF-1@MOF-2, etc.	High expansibility, and well-defined nanostructures

enforce the surface of specific materials. Furthermore, the success of this strategy encourages researchers to explore the possibility of applying it to other materials systems. For instance, Yamauchi et al. demonstrated that cyanuric acid can anisotropically modify and protect the exposed crystal facets (111) of ZIF-67 from etching, thus constructing hollow nanoframes (Figure 3b).[35] Besides, hollow TiO_2, CeO_2, ZnO can also be obtained by applying this synthetic concept.[48]

Currently, building core-shell structured solid precursors with differentiable stability between inner part and outer part for creating hollow nanomaterials have been extensively investigated, since it is easy to manipulate the selective removal process. Tsung et al. first fabricated core-shell MOFs (UiO-66-$(OH)_2$@UiO-66) with controllable oxidizing capacity, and then introduced 2,5-dihydroxyterephthalic acid (DOBDC) as a sacrificial linker to selective engraving these MOFs.[49] Finally, depending on the degradation of DOBDC into small molecules to guide the controllable collapse of inner core, a series of hollow and yolk-shell MOFs were produced. By applying this facile top-down strategy, various hollow structured MOFs have been successfully prepared, such as hollow nanocages ZIF-67, hollow Zn-BTC, hollow MIL-88A, yolk-shell ZIF-67@ZIF-8, and so on.[50-52] Aside from MOFs, Yu and coworkers chose core-shell MOF@SiO_2 with a structure water-stable MOF core and water-unstable SiO_2 shell to synthesis yolk-shell MOF@mesoporous SiO_2 nanoparticles through a green water-etching approach (Figure 3c).[36] This method provides an idea for precisely changing the unstable core-shell to simple hollow structures, even complex hollow structures such as mutil-shell bowl-like, multi-cavity, and so forth.

In order to architect more charming and functional hollow MOFs, the family of post-treatment agent is gradually increasing and diversified, from liquid- to gas-phase agents (including tannic acid, gallic acid, amino acids, NaOH, ethanol, acetone, NH_3, CO_2, etc.). Noticeably, the kind and dosage of the above agents should be rationally considered to avoid destruction of whole structures. In brief, based on these different synthetic strategies, numerous hollow nanostructured materials with fascinating morphologies and compositions have been successfully constructed. The comparative table summarizing the key synthetic methods and the advantages of the representative HSNRs is listed in Table 1, which could provide guidance for rationally designing desired nanoreactors.

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3. Unique Properties directed Liquid-Phase Hydrogenations

Liquid-phase hydrogenations, one of the most challenging catalytic reactions, plays a significant role in petroleum refining, both bulk and fine chemicals production.[53] Although great enhancements have been made in designing catalysts and regulating catalytic performances, the requirements of catalysts are still remained and highly stringent, such as accurately controlling specific reaction steps to achieve target product, preventing the leaching and sintering of active metal nanoparticles to improve the long-term stability, improving mechanical strength.[54,55] The successful construction of HSNRs endow them particular properties and greatly enhance the catalytic performances thereafter.[56] In this section, we attempt to detailly illustrate the unique properties of HSNRs and how they affect the liquid-phase hydrogenations performances (Figure 4).

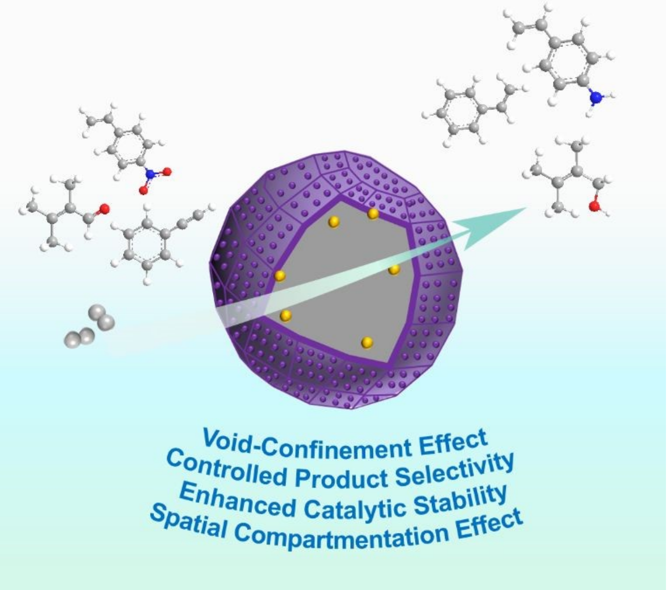

Figure 4. Schematic illustration of the properties of HSNRs applied in liquid-phase hydrogenation reactions.

3.1 Void-Confinement Effect

One of the main characteristics of HSNRs is the presence of nanospace, which allows the storage and catalytic reaction of reactants within them. It is exactly because of the existence of nanosize vessel that the unique cavity confinement effect appears, which can be specifically divided into reactant enrichment effect and controllable molecular activation processes. Recently, Li et al. studied the reactant enrichment behavior in hollow nanoreactor, Pt NPs@MnOx, in detail (Figure 5a-d).[57] Compared to crushed nanomaterials (Pt NPs&MnOx) without hollow cavity, the as obtained Pt NPs@MnOx showed better catalytic performance in selective hydrogenation of α,β-unsaturated aldehydes, highlighting the structural superiority of hollow nanospace in boosting hydrogenation performance. Besides, by conducting adsorption experiments, the authors demonstrated that the increased adsorption amount of reactant within the confined space derived from their directional diffusion via local concentration gradient. In addition, the enhanced reaction rate occurred in HSNRs can be illustrated in the rate equation. Obviously, in comparison with chemical reactions proceeding in bulk solution, the boosted reaction rate of HSNRs is assigned to the increased reactant concentration, $(\mathrm{NR} \supset \mathrm{A{\cdot}B}) > ([\mathrm{A}][\mathrm{B}])$, which indicates these reactants are well-preorganized and enriched in HSNRs.[8,58,59]

Reaction rate equation in bulk solution:

$$\mathrm{A{+}B} \overset{\mathrm{k_a}}{\rightarrow} \mathrm{C}$$

$$\mathrm{k}= \frac{\mathrm{d[C]}}{\mathrm{dt}} = \mathrm{k_a[A][B]}$$

Reaction rate equation in hollow nanoreactor:

$$NR+A+B= (\mathrm{NR} \supset \mathrm{A{\cdot}B}) \overset{\mathrm{k_b}}{\rightarrow} (\mathrm{NR} \supset \mathrm{C}) = NR+C$$

$$k= \frac{\mathrm{d[C]}}{\mathrm{dt}} = \mathrm{k}_b[(NR \supset A{\cdot}B)]$$

Aside from the reactant enrichment effect, the hollow nanostructure can also affect molecular activation processes, providing relatively low Gibbs free energy (ΔG#) (Figure 5e, f).[59] For parallel reactions, by adjusting the interaction between HSNRs and specific molecules, HSNRs allow to regulate the ΔG# of different products, thus adjusting the catalytic selectivity. The void-confinement effect in boosting catalytic behavior can also be observed in Ru@HCS hollow spheres for hydrogenation of levulinic acid,[60] PdCu@HCS for alkenes and alkynes hydrogenation,[61] Pt@CeO_2 nanoreactor for cinnamaldehyde selective hydrogenation,[62] and so forth. Furthermore, the void-confinement effect is highly dependent on the nanostructures of HSNRs, such as shell curvature, particle size, shell composition, and interior structure, etc.

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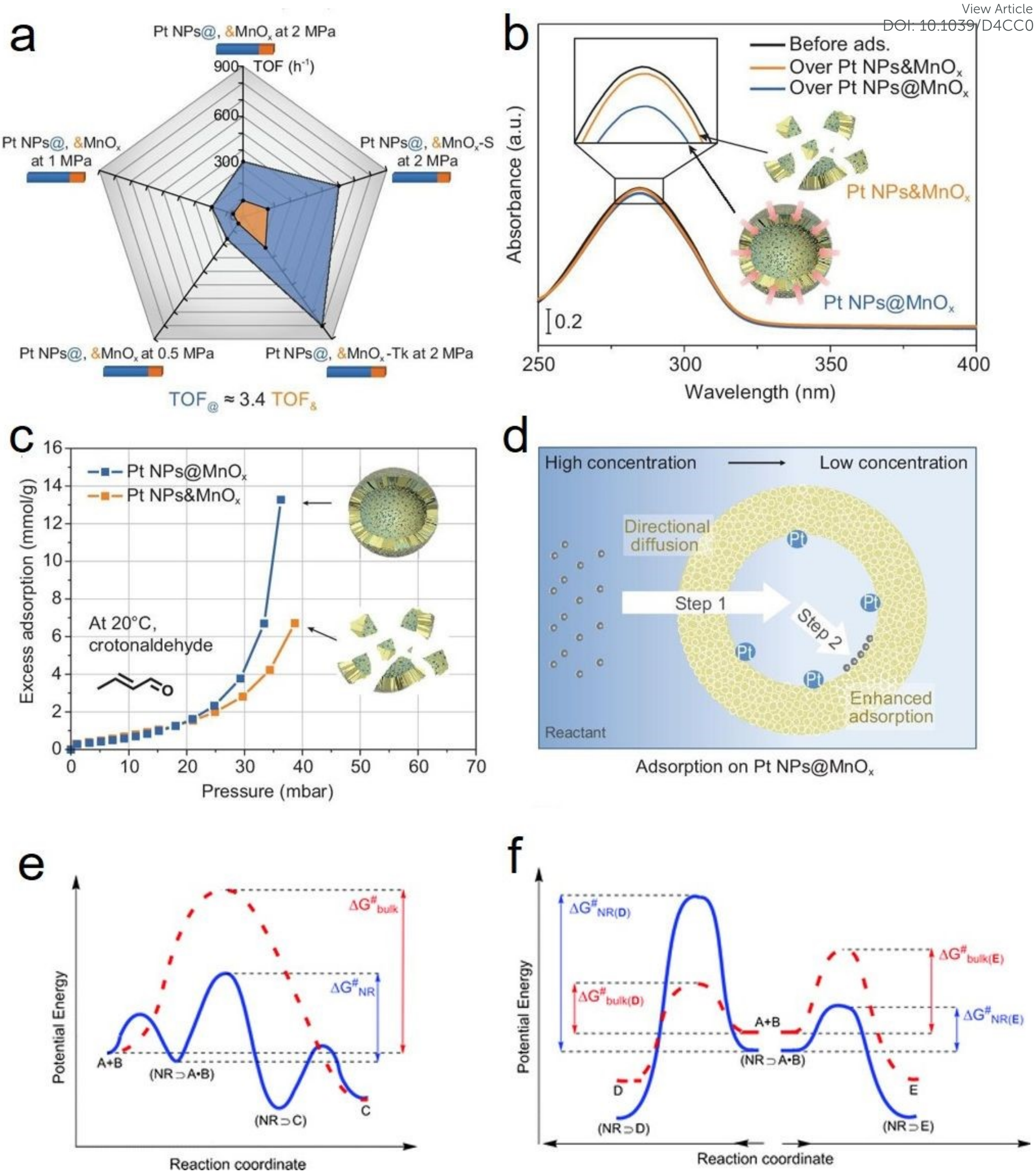

Figure 5. Reactant enrichment effect of HSNRs: (a) Comparison of catalytic hydrogenation activity between a series of Pt NPs@MnOx HSNRs with crushed samples, (b) UV–vis spectrum of cinnamaldehyde adsorption experiment, (c) in situ gravimetric adsorption analysis profiles, (d) schematic illustration of reactant enrichment effect on Pt NPs@MnOx nanoreactor.[57] Copyright 2023. The controlled molecular activation processes: Comparsion of reaction energy profiles over HSNRs and bulk phase in (e) A and B as reactants to produce C, and (f) A and B as reactants to produce D and E.[59] Copyright 2008, Royal Society of Chemistr

3.2 Controlled Product Selectivity

Owning to their adjustable pore size/length, composition, and spatial position of active sites, HSNRs are ideal catalysts to achieve the goal of regulating catalytic selectivity.[63,64] For example, the channels or porous shell of HSNRs can strongly determine the mass transfer behavior by the steric hindrance and diffusion rate, thus endowing them molecular sieving effect. Fang et al. prepared various hollow COFs, and encapsulated Pd nanoparticles within their hollow cavities, forming efficient size-selective catalysis in nitroarenes hydrogenation (Figure 6a, b).[65] Because of its narrow pore diameter (1 nm), the Pd@AB-HCONs showed better activity in hydrogenation of nitrobenzene with

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small molecule size (0.46*0.66 nm) than that of 2,4,6-triphenylnitrobenzene with large molecule size substrate (1.01*1.16 nm). Otherwise, Zheng and cowokers demonstrated that reactants are very sensitive to the shell thickness of HSNRs in p-nitrophenol hydrogenation, where reaction rates decreased dramatically from 0.21 to 0.08 min^{-1} with the size of carbon shell increased from 3 to 13 nm.[66] Besides size selectivity, the HSNRs can also achieve chemoselectivity. Jiang et al. implanted PdAg nanocages into hollow ZIF-8, forming PdAg@ZIF yolk-shell nanoreactor.[67] The outer shell ZIF-8 not only allows efficient mass transfer, sufficient exposure of active metal, but also enhances substrate enrichment. As a result, owing to the nanostructure and plasmonic metal nanoparticles, the as-made nanoreactor displayed excellent chemoselectivity (97.5) in the hydrogenation of nitrostyrene to aminostyrene (Figure 6c, d). In addition to nanostructure, the precise position of active sites is equally important for controlling reaction pathway and even cascade reactions.[68,69] Xu et al. implanted Pt nanoparticles into MFI zeolites and demonstrated its efficient tandem aldol condensation and hydrogenation reaction of furfural and acetone with a high combine yield of 87% in C_8 products.[70] To be noted, it is important to maintain both excellent catalytic activity and mechanical strength of HSNRs, because of the ultra-thin shell in HSNRs is easy to be break and leads to the leaching of metal nanoparticles. Because the outer shell of HSNRs is vital for sieving substrates and molecules, enabling highly size- and shape-selectivity catalysis.

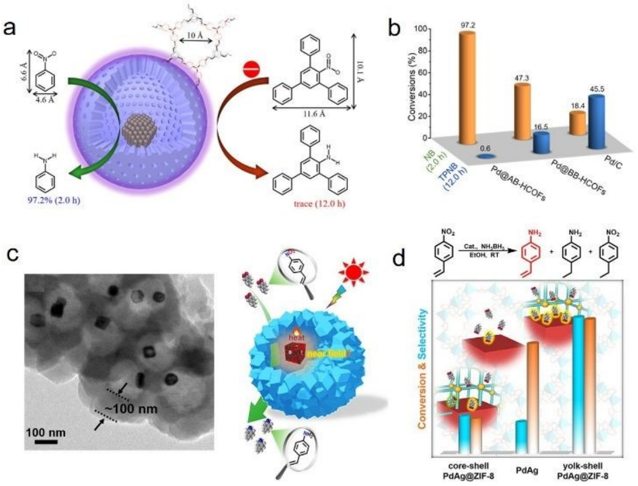

Figure 6. (a) Schematic illustration for the size-selectivity of Pd@AB-HCOFs nanoreactor in nitroarene hydrogenation, (b) Catalytic activity comparisons of varied catalysts.[65] Copyright 2022, American Chemical Society. (c) TEM image and structural model of core-shell PdAg@ZIF-8 nanoreactor, (d) chemoselective hydrogenation of nitrostyrene of different catalysts.[67] Copyright 2022, American Chemical Society.

3.3 Enhanced Catalytic Stability

Persistent catalytic stability for catalysts, especially for metal-loaded catalysts, is one of the key scientific issues and necessary prerequisites in the research and practice of nano-catalysis. Because metal nanoparticles are easily aggerated at harsh temperature and leached under recycling process, causing a rapid decline in catalytic activity.[71] The unique hollow architecture is ideal for confining metal nanoparticles and preventing them from pernicious aggregation and leaching, thus maintaining a long catalyst lifetime. Tsung et al. solitary confined Pd nanoparticles within a unique architecture MOF, multi-yolk-shell UiO-66-$(OH)_2$, and investigated its stability in catalytic conversion of allylbenzene (Figure 7a, b).[49] No obvious nanoparticles agglomeration was observed and marked hydrogenation reactivity was maintained after high-temperature treatment. Apart from multi-chamber structure, enhanced catalytic stability can also be observed in the multi-shelled HSNRs. Liu et al. encapsulated ultrafine Pd nanoparticles between the narrow space of inner shell reduced graphene oxide and outer shell carbon layer (Figure 7c, d).[72] The unique nanostructure of the as-obtained RGO@Pd@C can effectively prevent the aggregation and leaching of metal nanoparticles, and maintain excellent 4-nitrophenol hydrogenation performance after 10 cycles. Another example of catalytic stability controlled by HSNRs was demonstrated for Pt@hollow carbon shell (Pt@hmC) system. Compared to pure Pt nanoparticles and commercial Pt/C, the Pt@hmC showed remarkable reusability in nitrobenzene hydrogenation.

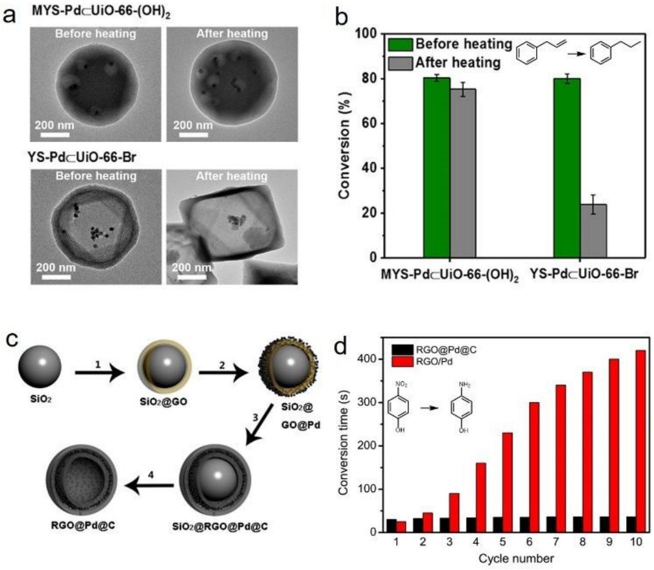

Figure 7. (a) TEM images of HSNRs with different nanostructures before and after heating, (b) catalytic conversion of allylbenzene on HSNRs.[49] Copyright 2019, American Chemical Society. (c) Schematics of the synthesis of RGO@Pd@C hollow sphere, (d) the stability test of these nanocatalysts.[72] Copyright 2014, Nature Publishing Group.

3.4 Spatial Compartmentation Effect

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Spatially positioning single or multiple active components into one support is the cutting edge of designing supported catalysts, which can promote rapid conversion of catalytic reactions, realize selective catalysis, and synergistic catalysis between different active sites.[73-76] As the nanostructure parameters of HSNRs can be ingenious controlled, it is possible to precisely locate metal nanoparticles in these nanostructures. Recently, we designed and synthesized a hollow multi-shelled carbon carrier, which provides an ideal platform to precise locate Pd nanoparticles, internally encapsulated (Pd@HoMS-C) or externally loaded (Pd/HoMS-C) (Figure 8a).[37] Combined the unique nanostructures and spatially comparted active sites, these HSNRs possessed size- and shape-selective catalytic hydrogenation performances, that is, Pd@HoMS-C tends to catalyze small aliphatic substrates while Pd/HoMS-C shows excellent catalytic performance toward large aromatic substrates (Figure 8b). Theoretical calculations demonstrated that the differential catalytic behaviors derive from the different adsorption energy barriers of substrates (Figure 8c). In localizing multiple metal nanoparticles, Zhao et al, spatially isolated Au and Pd nanoparticles at the bottom and upper chambers of dual-chambered silica nanoreactor (Figure 8d).[27] Due to the efficient transformation of reactants and intermediates, this nanoreactor can effectively convert 1-nitro-2-(phenylethynyl)benzene to 2-phenylindole with selectivity up to 76.5% (Figure 8e). Similarly, a multi-compartmentalized organosilica with co-localization of Pd and Ru nanoparticles was reported by Yang and coworkers.[68] Such unique catalyst exhibited excellent sequential hydrogenation behavior in converting nitroarenes into cyclohexylamines. In addition to active nanoparticles, HSNRs can also realize spatial compartmentation of nonmetallic active sites for efficient catalytic conversion. For instance, Ma et al. spatially separated QDNH$_2$/-SO$_3$H (or QNNH2/-SO$_3$H) and ProTMS/-CO$_2$H in the inner and outer shell of hollow nanospheres for catalyzing asymmetric organocascade.[77]

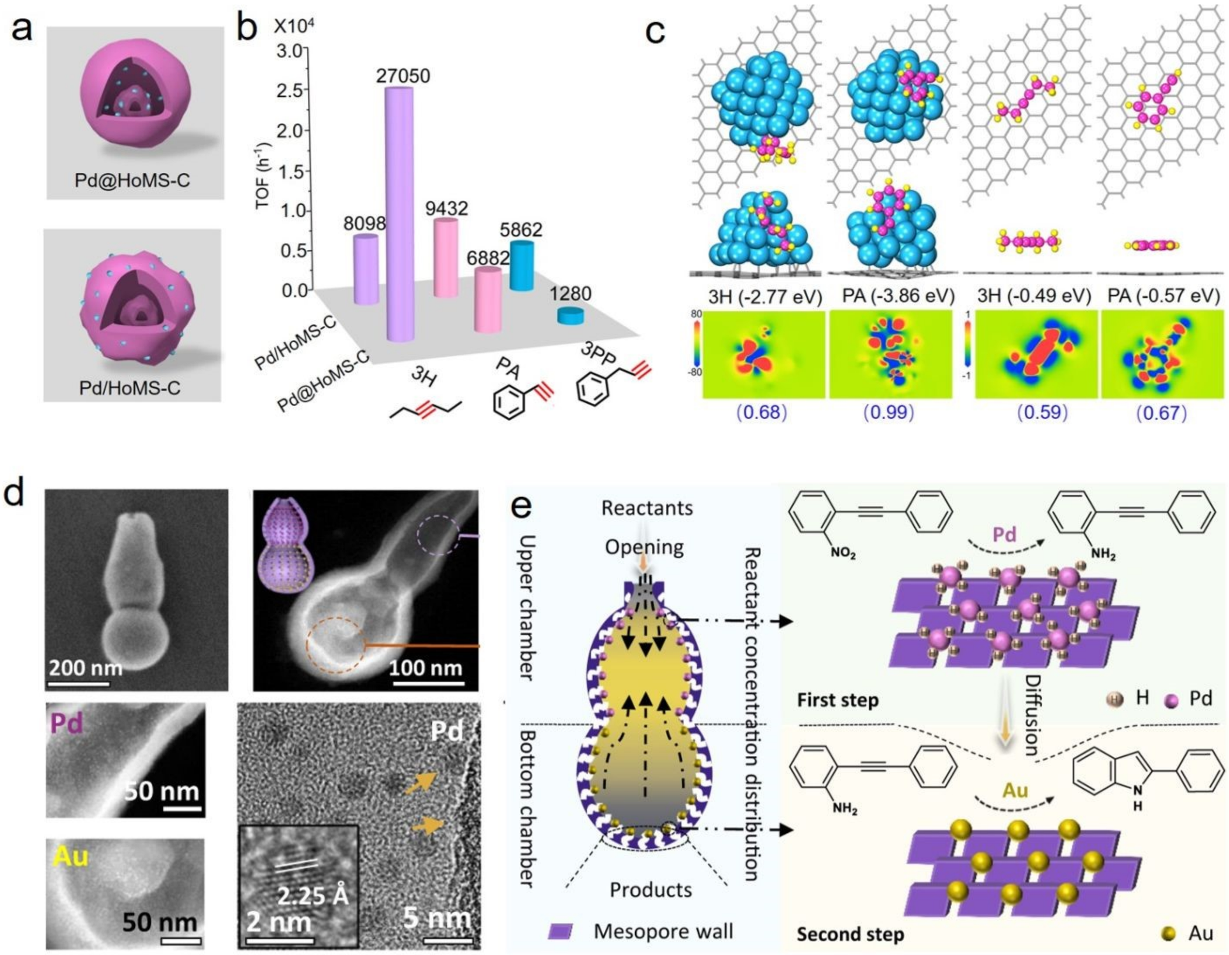

Figure 8. (a) Structural models for multi-shelled HSNRs with different Pd locations, (b) the corresponding TOF values of these nanoreactors in hydrogenation reactions, (c) theoretical calculations of the adsorption energies of different substrates on carbon carriers.[37] Copyright 2023, Wiley-VCH. (d) Structural characterization of dual-chambered silica nanoreactor with separated position of Au and Pd nanoparticles, and (e) concentration distribution of reactants as well as cascade reactions.[27] Copyright 2022, Nature Publishing Group.

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4. Conclusions and Perspectives

As a class of cell-mimicking materials that is attracting great attention, HSNRs are promising candidates for numerous scientific disciplines with enhanced efficiency. The advantageous nanostructures endow them with many unique properties, such as faster mass transport, highly dispersed metal nanoparticles, adjustable geometric and electronic characteristics, and more exposed active sites. So far, great processes have been made in preparation of novel HSNRs with distinct compositions/structure, as well as their advanced applications. However, the precise engineer of HSNRs with required functionality and properties is still at a relatively primary level. More universal synthetic methods and synthetic mechanism have not yet been systematically studies. Moreover, it also noted that the fundamental theory of HSNRs in driving catalysis requires increasing dedicated efforts and improvements.

In this review, main concerns are concentrated on the significant progress of construction of HSNRs and their unique properties in liquid-phase hydrogenations. Two general synthetic strategies, bottom-up and top-down strategies, are introduced, and their underlying formation mechanism, merits and limitations are emphatically discussed. Furthermore, a distinctive viewpoint on the unique effects and properties of HSNRs in hydrogenation reactions of alkenes, alkynes, aromatic and biomass have been illustrated and highlighted. Meanwhile, we also discussed the target of developing HSNRs in overcoming the difficulties of hydrogenations.

With respect to research passion toward architecting cell-mimicking systems, the increased level of controllable synthesis and mechanism exploration in both structure and application of HSNRs creates many opportunities for the development of the next generation of multifunctional heterogeneous catalysts. Despite many remarkable strides have been made, there are still much to do (Figure 9). (1) Precise synthetic chemistry, that is based on the specific reactions to construct HSNRs, is highly desired. The cavity and shell geometric parameters of HSNRs, e.g. the size and structure of internal cavities, pore structure, pore orientation, offer ideal models for modulating mass transfer, substrate enrichments and reaction efficiency/pathways. (2) Developing multi-functional HSNRs is urgent for intricate catalysis, such as cascade/chiral/molecular-sieve reactions. For effective cascade of multistep reactions (such as sequential hydrogenation of biomass/nitroaromatic compounds, and tandem oxidation of cinnamyl alcohol, etc.), HSNRs with multi-cavities and compartmentalizations would be an ideal platform for modifying multiple localized functional groups, spatially positioned reactive sites, and different composition within one single nanoreactor. These HSNRs enable efficient diffusion of reaction intermediates, effective synergistic catalysis between active sites, and finally boosted catalytic performance. (3) The synthesis mechanism of HSNRs, especially for complex hollow nanostructures, is still limitedly understood. It is necessary to develop advanced techniques to visualize and track the structural evolution process, reveal the synthesis mechanism in kinetic/thermodynamics, and finally guide and inspire researchers to construct next generation HSNRs. (4) Advanced characterization techniques, such as density functional theory (DFT) calculation, finite element analyses (FDTD), semi-in situ or ex situ approaches are highly desired to study nanoreactor effects and hydrogenation reaction mechanisms, which are beneficial for precise design of high performance HSNRs.

In short, the insights afforded by this Review contribute to the deep understanding of HSNRs in designing, fabricating, catalytic behavior, further development of multifunctional catalysts, and rational bridging of homogeneous and heterogeneous catalysis.

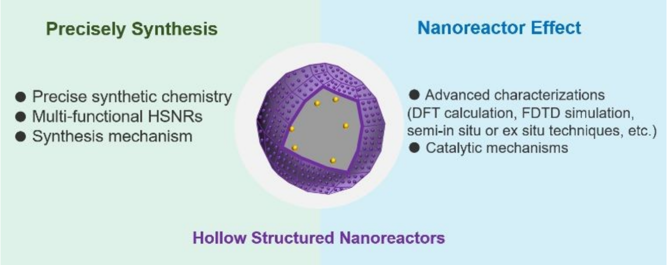

Figure 9. Schematic illustration of future research on HSNRs.

Author Contributions

Yutong Pi: writing-original draft. Haitao Li: visualization. Jian Liu: writing-review & editing, supervision.

Data Availability Statement

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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Data availability statements

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.