Rational design and preparation of core-shell nanomaterials to boost their catalytic performance

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From the morphological point of view, catalysts can be classified into zero-dimensional (nanoparticle or quantum dot), one-dimensional (nanowire), two-dimensional (nanosheet), three-dimensional, and a combination of them. Among the varieties of morphology, core-shell structural catalysts with three-dimensional configuration stand out due to their unique construction and rich forms of interaction between the core and the shell, as well as their abundant ways of interaction with the catalytic intermediates. Constructing high-performance core-shell structural catalysts relies on the comprehensive understanding of the catalytic process and precise control over the catalyst structure. Here in this review, we attempt to sort out common synthetic methods for catalysts with core-shell structures from basic techniques to complex multiple processes. We will analyze how the core-shell configuration affects the catalytic performance from the microscopic to mesoscopic scales. We



would resolve the structure-property relationship from the aspects of activity, selectivity, and durability, respectively. Finally, we would end this review with perspectives on the future development of core-shell catalysts.

he rapid development of energy storage and conversion techniques calls for highly efficient catalysts. For this reason, noble metals such as Pt, Pd, Ru, Ir, and their alloys have been extensively investigated in various catalytic systems such as electrocatalysis, photocatalysis, and thermocatalysis.^[1-5] The reason why noble metals are selected is that they generally possess more appropriate adsorption energy and better durability than other elements.^[6–8] However, the use of noble metals severely hinders their practical application on large scale due to their scarcity in the crust of the earth. Besides, even for noble metal catalysts, their activity and durability need further improvement for commercial requirements.^[9] The performance of catalysts strongly relies on their structure, so the rational design of catalysts mainly focuses on the construction of novel structures. Among the variety of interesting structures, core-shell nanomaterials stand out due to their unique heterogeneous

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structures and large numbers of adjustable structural parameters that are determinants of optimized performance. Core-shell structure could be a perfect strategy to decrease the use of noble metals by forming an ultrathin noble metal shell with several atomic layers of thickness.^[2] The adsorption property of the catalysts could also be further modified by the electronic interaction between the core and the shell.^[6] Furthermore, the durability of catalysts could be enhanced by various forms of synergistic interaction between the core and the shell.^[10–14]

From a certain point of view, core-shell structure can be considered a wise combination of two components. Compared to single-structured materials, the adjustable parameters of core-shell nanomaterials have been greatly expanded. In addition to the regulation of core and shell separately, the interaction between the core and the shell, as well as the mass transport on the core-shell catalysts can be regulated, which allows more tunable parameters for improved performance. For core-shell catalysts that use shell as the active site, the electronic interaction from the core could be prominent, especially when the shell is ultrathin. On the other hand, for core-shell catalysts that use core as the active site, the mass transport of reactants through the shell will have a great impact on the catalytic performance. Since the thickness of shell can range from sub-nanometer to micrometers, the effect of the core-shell structure on the catalytic reaction can be extended from the microscopic scale to the mesoscopic scale. This makes core-shell catalysts not only a simple contact sur-

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face in conventional surface catalysis, but more likely a catalytic nanoreactor, which provides more possibilities for optimizing catalytic performance, and allows for more complex catalytic processes such as tandem catalysis.^[15–17]

The rational utilization of core-shell catalysts relies on the comprehensive understanding of catalytic process on the core-shell structure and the precise synthetic control during the preparation of core-shell catalysts. Here in this review, we would discuss the general synthesis of core-shell nanomaterials, which are classified as: sol-gel method, liquid-phase deposition, gas-phase deposition, and dynamic evolution. Then we would discuss how the configurations of core-shell structure affect the performance of catalysts, which would be subdivided into three aspects: activity, selectivity, and durability. We will conclude this review with the perspective on the future development of core-shell nanomaterials. We believe that with the development of new techniques and advancement in the understanding of multiscale chemical reactions, new developments related to core-shell nanomaterials in catalysis could occur.

Synthesis

Core-shell catalysts can be prepared using various bottomup techniques such as sol-gel, hydrothermal, solvothermal, chemical/electrochemical deposition, and atomic layer deposition (ALD) with the aid of a series of external stimuli such as heat,^[18] light,^[19] microwave,^[20] and ultrasound.^[21] Topdown approaches such as lithographic techniques, laserbeam processing, and mechanical techniques have also been reported.^[22] For convenience, we would sort out the methods into four categories (Figure 1): i. sol-gel method, which is extensively employed for the synthesis of SiO₂ and TiO₂. Solgel method also represents the most popular method for the preparation of porous metal oxide-based shells. ii. Liquidphase chemical deposition, which represents one of the most common techniques because most chemical reactions need to be carried out in liquids for easier control. iii. Gas-phase vacuum deposition, which requires expensive vacuum equipment with high energy consumption for precise thickness control. This approach is mainly used for semiconductorbased core-shell materials in fabricating photoelectronic devices. iv. Dynamic evolution, which means that core-shell structures are formed *in situ*, intentionally or unintentionally. Notably, core-shell structures can exist in multiple configurations such as core-shell structure hence needs to be adjusted accordingly for different configurations.

Sol-gel Condensation

Sol-gel method is mainly adopted for the synthesis of metal oxides such as SiO₂,^[23] TiO₂,^[24] Al₂O₃,^[25] CeO₂,^[26] ZrO₂,^[27] and CuO^[28] that could either serve as the core or the shell. A sol-gel reaction generally proceeds through the hydrolysis of precursors in a liquid medium followed by the condensation of the hydrolyzed products. The classical sol-gel method is the stber method reported in the late 1960s, which involves the hydrolysis of tetraethyl orthosilicate (TEOS) followed by condensation in ethanol/water solvent with ammonia as the catalyst at room temperature.^[23] Although the stber method is initially reported to synthesize SiO₂ nanoparticles, the universality of this method soon made it guite suitable for the synthesis of core-shell structure. For instance, Liz-Marzan et al. first reported the synthesis of Au@SiO2 core-shell structure using pre-synthesized Au nanoparticles as seeds and SiO₂ as shell with the stber method in 1996.^[29] After that, numerous studies have been carried out on the construction of core@SiO₂ shell for various applications. Considering SiO₂ is chemically inert and the classical stber method yields nonporous SiO₂ shell, constructing porous SiO₂ shell is thus meaningful to provide abundant channels for extensive applications. Buchel thus reported the construction of non-porous SiO₂@porous SiO₂ by coating porous SiO₂ on non-porous SiO₂ nanoparticles.^[30] Porous SiO₂ was synthesized using noctadecyltrimethoxysilane (C18TMS) as the mesostructured-





directing agent. Zhao et al. further proposed a cetyltrimethylammonium bromide (CTAB) templating-stber method followed by acetone refluxing.^[31] This modified stber method generated an ordered porous SiO₂ shell due to the function of CTAB soft template. TiO₂ is another extensively reported metal oxide due to its fascinating electronic and optical properties that can be potentially applied in photocatalysis.^[32] The construction of core@TiO2 shell generally follows a similar strategy to the formation of core@SiO2 shell using sol-gel method. Tertbutyl titanate (TBOT) is commonly used as the precursor for hydrolysis followed by condensation in ethanol/ammonia solvents.^[33] The porous TiO₂ structure can be obtained via the formation of voids between aggregated nanocrystals without the use of pore-directing agents such as CTAB. Other metal oxides can also be synthesized via a similar approach.

Liquid-phase Deposition

Liquid-phase deposition refers to the process of forming core-shell structures through chemical reactions or electrochemical reactions in liquid and represents the one of the most important approaches for the synthesis of core-shell structures due to its well control over reaction kinetics, most studies involve the sequential growth of core and shell via two steps. In the work reported by Tsang et al., Ag@Pd coreshell structure was prepared by reducing Pd(NO₃)₂ in the presence of Ag seed nanoparticles.[34] Another advantage of liquid-phase deposition is its superior advantage to obtain large amounts of uniform core-shell particles through cautious thermodynamic and kinetic control. Xia et al. reported the synthesis of Pd@Pt core-shell icosahedra by reducing Na₂PtCl₆ in the presence of ethylene glycol on Pd icosahedra.[35] The formation of core-shell structure can also be realized through the one-pot approach. Zhuang and coworkers reported the preparation of IrNi@Ir core-shell particles in OAm solution. The key to the formation of IrNi@Ir particles is the employment of two different Ir precursors with different reactivity.^[36] During the reaction, Ir(acac)₃ and Ni(acac)₂ were first co-reduced to form IrNi core, and IrCl₃ was later reduced to form Ir shell due to the strong binding between Ir and CI. The liquid-phase deposition has been extensively studied for the synthesis of core-shell structure with monolayer noble metals as the shell. For instance, Adzic and co-workers reported the preparation of Pt monolayer shell covered on bimetallic Ir-M (M=Fe, Co, Ni, or Cu) cores. They adopted an under-potential deposition of Cu monolayer followed by galvanic replacement by Pt. Since the growth of shell on core proceed through atom by atom, perfect interface between core and shell could be formed and thus provide ideal models for the study of core-shell interaction.^[37]

Gas-phase Deposition

Gas-phase deposition mainly contains chemical vapor deposition (CVD) and pulsed laser deposition (PLD). They generally proceed through the generation of gas-phase precursors through heat, laser, or other methods, followed by deposition reaction under specific conditions. Since the concentration of gas-phase precursor could be controlled at an extremely low level, the thickness of the deposited layer could be well controlled in consequence. Although gas-phase deposition is mainly employed in the fabrication of semiconductor materials-based photo electronics, its application in catalyst preparation is also feasible. Cho and coworkers reported the preparation of Co@Pt core-shell structure via chemical vapor deposition of Pt on the external surface of Co using $Pt(PF_3)_4$ as the precursor. Co@Pt core-shell catalyst presented an elevated activity toward oxygen reduction reaction due to the strong Pt-Co interactions and large Pt surface area.^[38] Xie et al. reported the synthesis of $SrTiO_3$ @graphene via direct growth of high-grade graphene on the outer surface of $SrTiO_3$ via chemical vapor deposition using CH_4 as the carbon precursor. The as-obtained $SrTiO_3$ @graphene shows enhanced photocatalytic activity than that of the $SrTiO_3$ @rGO reference. The authors ascribed the improved performance to the special core-shell structure and perfect interface that promote interfacial charge transfer and electron-hole separation.^[39]

Dynamic Evolution

Core-shell structures could also be formed under special conditions during catalytic reactions, namely dynamic evolution, wherein selective leaching and phase segregation are the two most common mechanisms. Phase segregation is the separation of one phase into two phases driven by the reduction of free energy and prone to occur during the heat treatment at elevated temperatures. Abruna et al. reported that Pt₃Co@Pt could be formed during the heat treatment of Pt₃Co at 700 °C due to the surface segregation of Pt.^[40] Phase segregation might also be driven via the interaction from adsorbates. For example, Pt₃Co alloy was reported to transform to Pt_xCo_y@Pt after annealing in the presence of CO, which is due to the strong binding between Pt and CO leading to the surface enrichment of $Pt.^{[41]}$ Other adsorbates such as NO, O_2 , and H₂ have also been reported to show the same effect.^[42] Notably, such a process means the possible formation of core-shell structures during thermal catalysis. Selective leaching is most common in noble/non-noble metal alloys where non-noble metals are preferentially etched away by the corrosive electrolytes to form the alloy@noble metal core-shell structures, which is also referred as the de-alloy process. The preferential etching is due to the relatively low dissolution potential of non-noble metals compared with noble metals and the behavior has been observed in a series of systems such as PtCu, PtNi, AuCu, and PdCu. For instance, Xia et al. reported that PtNi@Pt can be formed by selective etching of Ni on PtNi alloy in 0.5 M nitric acid (HNO₃) solution at 60 °C.^[43] Nilson and co-workers reported that PtCu@Pt core-shell structure can be formed via selective etching of Cu from PtCu alloy via potential cycling in 0.1 M HCIO₄.^[44] Such a selective etching process indicates that core-shell structure could be formed from alloy electrocatalysts during catalysis in the presence of corrosive electrolytes or under positive potentials. The in situ formed catalysts with noble metal shells generally possess improved activity due to the compressive strained noble metals and enhanced durability due to the protection from the compact noble metal shells.

Other Common Methods

Except for the above-mentioned methods, there are a number of other approaches that are commonly adopted for the synthesis of core-shell catalysts. Cation and anion exchange, known as the exchange between guest ions and ions within a lattice driven by thermodynamics and diffusion kinetics, leads to the formation of core-shell structure by controlling the extent of exchange progress. The synthesis of core-shell structured PbSe@CdSe,[45] CdTe@HgTe,[46] and Cd_xZn_{1-x}Se@CdyZn_{1-v}S^[47] are reported via cation exchange and β -Bi₂O₃@Bi₂S₃,^[48] Ag₂S@Ag₃PO₄^[49] via anion exchange. Galvanic exchange, driven by the redox potential, produces a similar effect and has been reported for the synthesis of Cu@Ag^[50] and Ag_xAu_{1-x}@CeO₂.^[51] The commercial application of core-shell catalysts relies on the industrial synthesis at large scale, which requires robust synthetic strategies that would not be affected by the expansion of the reaction system. Continuous-flow synthesis represents a typical methodology circumventing the mass and heat transfer issue in amplified batch reactor synthesis and therefore should be a promising approach. As typical examples, the successful fabrication of core-shell aerogel microparticles and up-conversion nanoparticles have been reported by Teo et al.^[52] and Liu et al.^[53]

Effects on Catalysis

The design of catalysts should be guided by the balance between activity, selectivity, and durability, which is also applicable to the design of core-shell catalysts. Herein, the effect of core-shell configurations on catalysis would be discussed separately as depicted in Figure 2, providing the basic design principles in the construction of core-shell catalysts. The schematic diagram describes eight different configuration-performance relationships: 1) electronic interaction-induced adsorption modification, 2) lattice mismatch-induced geometric effect, 3) single atom dispersion resulted improved atom utilization, 4) hydrophobic-hydrophilic modification-induced specific adsorption, 5) pore diameter difference determined size-selectivity, 6) active sites spatial separation resulted tandem catalysis, 7) confined active sites and 8) strongly bonded active shell that enhance the durability.

Activity

Core-shell structure influences catalytic performance on



Schematic illustration shows the configuration of core-Fig. 2 shell structure on the effects of catalysis.

both microscopic and mesoscopic scales. At the microscopic scale, the effect of core-shell structure is the same as that of the non-core-shell structural catalysts, which is achieved by changing the adsorption strength with the intermediates via the electronic effect. At the mesoscopic scale, the influence of the core-shell structure on catalytic performance can be quite complex, the main mechanisms affecting the activity of coreshell structure can be generally categorized into the following three types:

Improved Atom Utilization

Generally, catalysts are prepared as nanoparticles with small diameters to improve the atom utilization efficiency, which is especially true when noble metals are used as catalysts. However, no matter how small the nanoparticles are, there is always an inner part of the nanoparticle that cannot be accessed during the catalytic reaction. Moreover, smaller nanoparticles are more prone to dissolution and sintering due to their higher chemical potential. Core-shell nanoparticles hence provide an ideal solution to this challenge by using ultrathin shells as catalysts. By adopting such a strategy, the catalyst with ultrathin thickness could be uniformly deposited on the surface of the core with high utilization efficiency. Recent advancements in single atomic layer deposition could even realize the 100% utilization of catalysts.^[2]

Modified Adsorption Property

In most core-shell structures with atomic thin layers as the shell, the adsorption property of the exposed shell is strongly modulated by the core via the electronic interaction, which is otherwise called the ligand effect. The classical Sabatier principle states that the binding energy between the catalysts and the reaction intermediates should be neither too strong nor too weak. Such a strategy has been widely adopted for the design of various core-shell catalysts. The Sabatier principle was later internalized as the d-band theory by Norskov et al. on the consideration that the adsorption property is determined by the electronic structure.^[54] Jaramillo et al. reported that the activity of Pt toward oxygen reduction can be significantly improved via the construction of Ir@Pt core-shell structure, where the oxygen binding energy to the Pt surface, is weakened due to the electronic effect of Ir core (Figures 3a and 3b).^[55] Jongh et al. reported a shell thickness-dependent catalytic activity, highlighting the influence of subsurface layers, they concluded that the effect of Au core could affect the Pd shell even up to six atomic Pd-layers (Figures 3c and 3d). Their monocrystalline Au@Pd core-shell nanorods were up to 50 times more efficient than their alloyed and monometallic counterparts. This work also stresses that the effect of electronic modification could be quite different in alloy and coreshell structures.^[56] Ye et al. reported a Co@BCN core-shell structural catalysts via a bottom-up approach using MOF as the precursor and sacrificing template. The excellent activity toward hydrogen evolution, as revealed by DFT calculation, is due to the modified adsorption property of C sites from the Co core.[57]

Geometric Effect

Because of the lattice mismatch between the core and the shell in a core-shell nanoparticle, the core alters the lattice constant of the shell due to the lattice matching principle, introducing compressive or tensile strain to the shell, and alter-



Fig. 3 a Atomic model and TEM image of Ir@Pt core-shell nanoparticle. **b** Mass activity and specific activity of Pt/C and Ir@Pt at 0.9 V_{RHE} before and after 10000 stability cycles.^[55] Copyright 2016, American Chemical Society. **c** TEM image and EDX maps show the structure and composition of Au@Pd core-shell nanorod. **d** TOF and selectivity at 98% butadiene conversion as functions of the Pd fraction.^[56] Copyright 2021, Springer Nature Limited.

ing the symmetry of the shell lattice. All these phenomena impose an evident change in the electronic structure of the shell and alter the catalytic property. Li and co-workers reported that core-shell CuPd@Pd (Figure 4a) could present Pt-like activity for both hydrogen evolution (Figure 4b) and oxygen reduction (Figure 4c). Their analysis shows that the improved activity could be ascribed to the compressed strain of the Pd shell due to the smaller lattice constant of CuPd core that downshifts the d-band center of Pd by 2.0%, which weakens the binding strength toward H* and O* species and hence facilitates the reaction kinetics.^[58] In the work reported by Zeng et al., the high conversion efficiency of CO₂ to HCOOH could be achieved on Bi@Sn core-shell nanoparticles (Figures 4d and 4e) with faradaic efficiency of 91% (Figure 4f) and a current density of 31 mA cm⁻² at -1.1 V_{RHE} in 0.5 M KHCO₃ electrolyte, much higher than that of Sn nanoparticles at the same conditions. DFT calculations indicated that the energy barrier of the determining step for the production of HCOOH is lowered due to the compressed strain in the Sn shell, leading to improved catalytic performance.^[59] Huang et al. reported a AuCu₃@Au core-shell nanocrystal that is highly efficient for CO₂ reduction to CO. The improved faradaic efficiency was analyzed due to the formation of unconventional fct Au shell as stabilized by the strain effect of ordered $AuCu_3$ core (Figures 4g and 4h).^[60]

Selectivity

Unlike non-core-shell catalysts that only affect catalytic performance via the adsorption strength, which is severely restricted by the scaling relationship. Core-shell catalysts affect catalytic performance via extensive mechanisms such as sizeselectivity, combined hydrophobic-hydrophilic effect, and tandem process. These mechanisms altogether provide additional tools for the optimization of core-shell catalysts that are expected to break the classical scaling relationships.

Size-selectivity

The most form of selectivity improvement could be attributed to the size-selective effect when mesoporous shell and active core are employed. In such a situation, only the reactants of the right size could transport through the channels in the shell and react on the core, thus greatly suppressing side reactions. The most common catalyst is the core-shell structure with tunable pore-size zeolite as the shell. Farrusseng et al. reported that core-shell Pt/Al₂O₃@SIM-1 catalyst shows an exceptional molecular sieving effect for the hydrogenation of C=C (Figure 5a). SIM-1 with a channel size of ca. 5 completely suppressed the hydrogenation of toluene (5.8) (Figure 5c)

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Fig. 4 a TEM image of a representative CuPd@Pd nanoparticle. **b** HER polarization curves of Cu/C, Cu@Pd/C, Pd/C, and Pt/C catalysts in 0.5 M H_2SO_4 electrolyte. **c** ORR polarization curves of Cu@Pd/C, Pd/C, and Pt/C catalysts in 0.1 M HClO₄ electrolyte.^[58] Copyright 2021, Wiley-VCH GmbH. **d** TEM image of Bi@Sn core-shell nanoparticle. **e** HAADF-STEM image of Bi@Sn nanoparticle. **f** Faradaic efficiency of HCOOH on Bi@Sn nanoparticles and Sn nanoparticles.^[59] Copyright 2020, The Authors. **g** Schematic illustration shows the geometric interaction between ordered AuCu₃ core and *fct* Au shell. **h** Faradaic efficiency of HCOOH on o-AuCu₃@*fct* Au nanoparticle and *fcc* Au nanoparticle.^[60] Copyright 2021, American Chemical Society.

while selectively allowing the hydrogenation of ethylene (4.16) (Figure 5b) with a conversion efficiency of ca. 94%.^[61] Zhang et al. reported a size-selective effect of Pt-CeO₂@UIO-66-NH₂ in the conversion of furfural to furfural alcohol. It is analyzed that the narrow Zn-Cr@SAPO windows compel the furfural across UIO-66-NH₂ to the Pt-CeO₂ surface vertically via the C=O group, and thus hampered the adsorption and hydrogenation of the C=C bond in the furfural ring.^[62] In another similar work, Liang et al. reported that the core-shell structure of Pt/CeO₂@alucone films presents a quite different selectivity toward the hydrogenation of n-hexene and cis-cyclooctene due to the size-selective effect.^[63]

Hydrophilic-hydrophobic Effect

The interaction between porous shells and reactants could greatly control the diffusion of reactants and products, thus greatly affecting selectivity. The hydrophilic/hydrophobic property of the shell could be easily tunned via the functionalization of surfactants, and thus the selectivity could be accordingly tunned. Li and co-workers constructed a core-shell structure with MOF NH₂-MIL-101(Fe) as the core and COF NUT-COF-1 as the shell, which exhibited improved conversion efficiency (32%) and selectivity (84%) for styrene oxidation compared with those of (24%) and (26%) for NH₂-MIL-101 (Fe). The authors attributed the improved performance to the gathering of the hydrophobic reactant styrene after the combination with the hydrophobic COF shell.^[64] Ding et al. reported an improved olefin selectivity (36.6%) and CO conversion efficiency (56.1%) through Fischer-Tropsch synthesis (FTS) on FeMn@Si core-shell catalyst with hydrophobic SiO₂ as the shell. The authors ascribed the improved performance to the protection of the iron carbide core from oxidation by water and the restrained side reactions related to water due to the presence of the hydrophobic shell.[65] Yang and coworkers reported that the selectivity of CO₂ to CH₄ could be greatly improved when Cu/Cu2O sphere core was covered with carbon shell due to the reduced local H₂O coverage on the hydrophobic shell (Figure 5d-5f). The efficiency of 81±3% for CO₂ to CH₄ could be obtained, completely different from the major products of H₂ when the hydrophilic shell is emploved.[66]



Fig. 5 a Schematic illustration for the preparation of the Pt/Al₂O₃@SIM-1 sphere. Ethylene **b** and Toluene **c** hydrogenation on Pt/Al₂O₃ and Pt/Al₂O₃@SIM-1 catalysts.^[61] Copyright 2016, The Royal Society of Chemistry. **d** Schematic illustration of the wettable Cu, hydrophobic Cu, and the atomic model of the interface between Cu and C coating. **e** From left to right: *CO desorption to form CO(g), *CO protonation to form *OCCO on Cu. **f** Free energies for the three competing reactions under different H₂O quantities.^[66] Copyright 2022, The Royal Society of Chemistry.

Tandem Catalysis

Core-shell structures provide the possibility for tandem catalysis due to the multiple components and hierarchical structures, which is appealing for the synthesis of products that need to proceed through multiple steps, and greatly decreases the complexity of catalytic facilities. Herein, core-shell catalysts not only provide the different components for different catalytic reactions in a multiple-step reaction but also act as the nanoreactor to distribute different reactions at different times and spaces (Figure 6a). Tang et al. reported the successful cascade reaction on Pd@IRMOF-3 (Figure 6b), where the reaction of 4-nitrobenzaldehyde and malononitrile toward 2-(2-nitrobenzylidene)malononitrile first occurred on alkaline IRMOF-3 shells (Figure 6c), followed by selective hydrogenation of -NO₂ group of the intermediates on the Pd core (Figure 6d).^[17] In another case, Huang et al. reported that the selectivity toward C₂ from CO₂ could be significantly improved on the Cu@Ag core-shell nanoparticles using the tandem catalysis mechanism in which CO₂ was first converted to

CO on the Ag shell followed by further C-C coupling on the Cu core (Figures 6e-6g). Notably, the incomplete coverage of Ag on Cu is required for the spillover of CO to Cu.[67] In a similar work, Thomas et al. reported that the conversion of CO₂ to CH₄ or light hydrocarbon could be realized on SiO₂-Pt@m-SiO₂-Co in a tandem catalysis mechanism, where the CO₂ and H₂ were first converted to CO on the Pt core through a reverse water gas shift, followed by the conversion of CO to light olefins through Fischer-Tropsch process.[15] It has been reported that a multi-step reaction could be realized in one volk-shell catalyst. Zhao et al. developed a volk-shell Pd@Fe catalyst that features atomically dispersed Fe sites in a Ndoped carbon shell and Pd sites in a yolk derived from a metal-organic framework. The as-prepared yolk-shell catalyst could simultaneously catalyze nitroaromatic hydrogenation and alkene epoxidation when a mixture of H₂/O₂ is introduced and finally lead to a cascade reaction towards amino alcohols.[68]

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Fig. 6 a Schematic illustration shows the integration of two catalysts into one particle by constructing the core-shell structure. **b** TEM image of Pd@IRMOF-3 nanocomposites. **c** Synthetic route for Pd@IRMOF-3 hybrids. **d** cascade reactions involving Knoevenagel condensation of A and Malononitrile via the IRMOF-3 shell and subsequent selective hydrogenation of intermediate product B to C via the Pd nanoparticle core.^[17] Copyright 2014, American Chemical Society. **e-f** Elemental mappings images for Cu@Ag, red for copper and green for silver. **g** Schematic illustration of tandem catalysis for CO₂ reduction to C₂ over Cu@Ag core-shell nanoparticle.^[67] Copyright 2021, Wiley-VCH GmbH.

Durability

Catalysts degrade in various forms such as dissolution in electrolyte, Ostwald ripening, agglomeration, coalescence, and poisoning. Core-shell catalysts intrinsically protect the catalysts from degradation in different ways according to the configuration of the core-shell structure. For instance, confining active components in stable shells with porous channels so the active components are physically isolated and no coalescence could happen, or immobilizing active catalysts on the stable core through the strong core-shell interaction so the diffusion and dissolution of catalysts could be suppressed. In the following, we would discuss these two behaviors in detail.

Physical Barrier

The growth of nanoparticles, either through Ostwald ripening or direct coalescence, is the main form of catalyst degradation. Core-shell structures could significantly increase the durability of catalysts through an intrinsic physical barrier that prevents the growth of nanoparticles. This is especially true when the active catalysts are confined in the porous shell in the thermocatalysis situation. Since the active core is strictly confined in the shell, the Ostwald ripening or coalescence of catalysts could be much harder due to the physical barrier of the shell. Other core-shell configurations could achieve the same effect as shown in Figure 2. Somorjai et al. reported that Pt@mSiO₂ with Pt core and mesoporous SiO₂ shell (Figure 7a) could effectively prevent the aggregation of Pt at high temperatures. The Pt@mSiO₂ nanoparticles were well maintained after calcination at 350 °C, 550 °C, and even up to 750 °C (Figures 7b-7d) as well as presented remarkable activity for ethylene hydrogenation and CO oxidation.^[10] Vohs et al. reported that core-shell Pd@CeO2 shows no sintering upon temperature up to 973 K, and little moderate sintering at temperature as high as 1373 K, while extensive sintering of Pd without CeO₂ shell was observed at 1373 K, demonstrating the excellent protection of CeO₂ shell against sintering (Figures 7e and 7f).^[69] Kwon et al. reported that carbon-coated Pt loaded on the surface of carbon nanofiber (Figures 7g and 7h) shows excellent durability with a slight voltage loss at the impressive current density of 0.8 A cm⁻² for 30000 accelerated stability test cycles (Figure 7i). The authors attributed the enhanced durability to the protection of the carbon coatings that shield the Pt nanoparticles.^[70]



Fig. 7 a Schematic illustration of the synthesis of $Pt@mSiO_2$ nanoparticles. Thermal stability of $Pt@mSiO_2$ nanoparticles after heat treatment at **b** 350 °C, **c** 550 °C, and **d** 750 °C.^[10] Copyright 2009, Macmillan Publishers Limited. **e** $Pd@CeO_2$ loaded on alkyl-siloxane functionalized YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine YSZ (100) after heat treatment in air at 1373 K. **f** $Pd@CeO_2$ loaded on pristine Y

Strong Core-shell Interaction

The immobilization of catalysts on the substrate is another effective strategy to suppress the diffusion and coalescence of catalysts, which can be realized by strong core-shell interaction via the elaborate design of core/shell configuration. In the work reported by Jin et al., the stability of the Pt shell was significantly enhanced by the strong interaction of Pt-P between the amorphous Pd-P core and Pt shell (Figure 8a). Theoretical analysis reveals that the vacancy formation energies of Pt and Pd are significantly improved due to the presence of P (Figures 8b and 8c), with that of Pd increased from 6.27 eV to 8.59 eV and Pt from 7.91 eV to 8.89 eV.[71] Tilley et al. reported that the stability of Ru in the oxygen evolution reaction could be enhanced due to the electronic interaction from the Pd core as evidenced by XPS. They explained that Pd@Ru presents a similar 3d binding energy to Ru bulk metal without oxide peaks present, whereas Ru oxides are commonly observed for Ru nanoparticles by XPS because Ru nanoparticles are susceptible to oxidation thereby unstable compared with Ru bulk in OER.^[72] By employing the principle that strong bonds could be formed between early transition metal carbides (TMCs)/transition metal nitrides (TMNs) and Pt, Ledendecker et al. reported the durable electrocatalysts employing strong interaction between carbide cores and Pt shells, which present well-maintained core-shell structure and atomic composition during 10000 potential cycles in accelerated electrochemical studies. The authors also proposed that the full coverage of Pt is critical for enhanced durability (Figure 8d).^[11]

Conclusion and Perspectives

This review aims to sort out general synthetic methods for core-shell nanomaterials and illustrate how core-shell configurations affect catalytic performance in terms of activity, selectivity, and durability. After almost thirty years of develop-



Fig. 8 a TEM images of Pd@Pt and Pd@a-Pd-P@Pt and the corresponding mass activity upon potential cycles. **b** Theoretical models showing the formation energies of Pt vacancy and Pd vacancy for Pd@Pt_{2L}. **c** Theoretical models showing the formation energies of Pt vacancy and Pd vacancy for Pd@a-Pd-P@Pt_{2L}.^[71] Copyright 2021, American Chemical Society. **d** Schematic showing the evolution of the partially and fully covered core-shell particles during potential cycling.^[11] Copyright 2019, Springer Nature Limited.

ment since the early 1990s, core-shell structure has become an essential type of morphology for various catalytic systems. A series of synthetic methods have been developed to specifically prepare core-shell nanomaterials. A range of substructures has been derived according to the configuration of the core and the shell. The influence of core-shell structure on the effects of catalytic performance has also been extensively explored. Nevertheless, some remaining challenges still exist which we would like to discuss in the following.

1. The precise synthetic control over size and shape toward core-shell catalysts. The performance optimization of catalysts strongly relies on the precise control of catalyst structure via advanced synthetic methodologies. Compared with simple structural catalysts, core-shell catalysts with complex hier-archical structures require much more complicated synthetic processes. Hence, developing more advanced synthetic methods for core-shell catalysts is of great importance.

2. Large-scale synthesis of core-shell catalysts with low cost. The commercial application of catalysts requires large-scale and low-cost synthesis, which poses great challenges to coreshell catalysts that intrinsically require multiple synthetic steps and dealing with compatibility between different steps. Nevertheless, some up-to-date synthetic scheme such as programmable synthesis which enables highly designable structure and broad composition range via a general strategy has emerged and show great potential for scalable applications.

3. Advanced understanding of core-shell configuration effects on catalytic performance. The influence of core-shell structure on catalytic performance is not limited to the traditional adsorption/desorption process but involves the mass transfer behavior through the shell. Thus, it is critical to evaluate the transfer behavior such as diffusion direction and rate with effective experimental and numerical methods. Experimentally, in situ infrared spectroscopy has been reported to evaluate mass transport by detecting the adsorption of reactants on the surface of core and shell in yolk-shell structure. Establishing mass transfer kinetics at the micro/mesoscopic scale for core-shell structure will be of great significance.

In summary, Catalysts with core-shell structure via rational design and precise synthesis provide an excellent strategy for improved catalytic performance. Further advancement in the construction of novel core-shell structures lies in the exact control over size, shape, spatial arrangement, and interface engineering. A deeper understanding of catalytic mechanisms relies on the insight into the adsorption/desorption of catalytic intermediates and the mass transfer behavior in the core-shell structure. We believe that with the development of new synthetic techniques and new understandings of the detail of catalytic reaction steps, more advanced core-shell catalysts with elevated performance will be developed.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Yuliang Yuan, Xuli Chen, and Hongwen Huang proposed the layout; Yuliang Yuan and Zhilong Yang drafted the manuscript; all authors joined the discussion, edition, and approved the final version.

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