

Precise Synthesis of Hollow Mesoporous Palladium–Sulfur Alloy Nanoparticles for Selective Catalytic Hydrogenation

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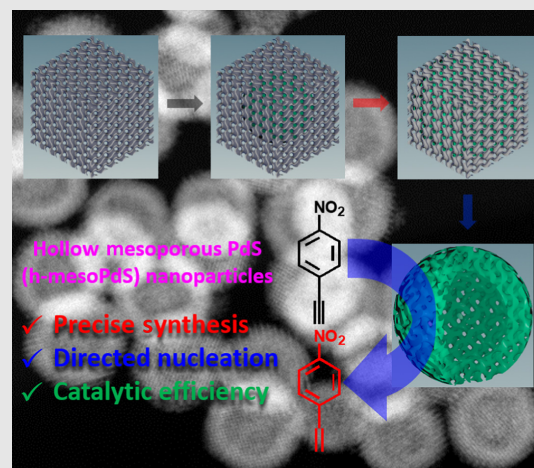
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Hollow mesoporous metals have unique potential for catalysis, but their precise synthesis and further elaboration of their structure–performance relationships are still huge challenges. Herein, we report a new synthetic strategy, named the Kirkendall effect in synergistic template (KEST), for the desired preparation of hollow mesoporous palladium–sulfur (h-mesoPdS) alloy nanoparticles. The KEST strategy combines the Kirkendall cavitation synthesis of hollow PdS alloys at the atomic level and the nanocasting growth of a highly ordered mesoporous framework at the mesoscopic level, resulting in one-step solid-phase synthesis of binary h-mesoPdS alloy nanoparticles under ambient conditions. The h-mesoPdS possesses hollow and mesoporous geometry as well as binary PdS alloy composition, which synergistically optimize their electronic structures and energetically adjust the hydrogenation reaction trends. The h-mesoPdS alloy nanoparticles show a remarkable selectivity of 94% for semi-hydrogenating 4-nitrophenylacetylene to industrially important 4-nitrostyrene without hydrogenating the nitro group or over-hydrogenating the alkynyl group. Because of the significant advances in both synthesis and catalysis, this work paves a new route for realizing the targeted synthesis of highly efficient nanomaterials in various applications.



A new synthetic strategy, named as the Kirkendall effect in synergistic template (KEST), is reported for precise preparation of hollow mesoporous palladium–sulfur alloy nanoparticles (h-mesoPdS) with well-defined geometry and ordered mesostructure. Benefiting from geometric and compositional synergies that energetically change the reaction trends, binary h-mesoPdS alloy nanoparticles exhibit remarkably high activity and stability for selective hydrogenation of 4-nitrophenylacetylene toward industrially important 4-nitrostyrene.

Keywords: mesoporous material, hollow cavity, palladium, hydrogenation, selective catalysis

Introduction

Selective hydrogenation is among the central strategies of academic and industrial manufacture of fine chemicals, petrochemicals, and environmental industries.^{1–3} One typical example is the chemoselective hydrogenation of nitrophenylacetylenes to produce nitrostyrenes, which are industrially important nitro compounds.^{4,5} Unfortunately, due to energetically favorable reaction pathways, commercial heterogeneous metal nanocatalysts inevitably cause consecutive over-hydrogenation of desired products into unfavorable wastes. To obtain high-value products and avoid unnecessary wastes, therefore, rational design of highly selective catalysts that can change the hydrogenation reaction trends is greatly important in catalysis science. Several strategies, including the formation of metallic alloys, the fabrication of metal-support interactions, and the surface functionalization of organic ligands, have recently been devoted to electronically optimize the hydrogen dissociation on catalysts surfaces and to enhance their selectivity of hydrogenation reactions at present.^{3,6–14} Although some advances have been made, it is still desirable to develop other, easier routes to enhance the selectivity for the products in the hydrogenation reactions.

Mesoporous materials that have abundant mesopores within a solid framework have received growing attention because of their great potentials in catalysis, batteries, and biomedicines.^{15–19} Especially, mesoporous metal nanocrystals have evoked special research interest due to their novel physicochemical properties (e.g., good electrical and thermal conductivities, high catalytic activities) and functional geometric features (e.g., high surface areas, large exposed active sites, unique structures).^{19–27} Furthermore, the introduction of an interior hollow cavity into mesoporous metal nanocrystals, which subtly combines a mesoporous shell framework and interior hollow nanocavity into one geometry, is of fast-growing interest because of their better mass transport and permeability.^{28–32} In electrocatalysis, both mesopores and nanocavities can modify geometric structures that further optimize the electronic and steric effects of the catalysts and thus enhance the product selectivity to some extent.^{23,33–38} However, limited success has been achieved in applying the geometric effect of (hollow) mesoporous metals to adjust the selectivity of the products in hydrogenation reactions, although supported metal nanoclusters within mesoporous matrixes have been studied to enhance catalytic activity.^{39–41}

Hollow mesoporous metal nanocrystals were synthesized through templating strategies. Their mesoporous frameworks are formed by nucleation and growth of metal atoms around the self-assembled surfactants, while their interior nanocavity is generated by sequential removal of the sacrificial templates.^{28–30,42,43} However, the

feasibility of the method is limited to certain metals or their alloys with limited geometries due to the scant mesophase structures of the surfactants in the synthesis systems and the fast nucleation rates of metal precursors that fail to replicate the mesophases of the templates. In addition, mesoporous geometries of metal nanocrystals formed by the surfactant-templating method generally lack structure ordering and architecture control, which limit the applications of such materials in catalysis and disable the elucidation of their geometry-performance relationships. To address critical challenges and explore the application in selective hydrogenation reactions, new strategies to synthesize hollow mesoporous metal nanocrystals with ordered structures (porosity and cavity) and desired compositions (even metal-nonmetal) that have not been found are exceedingly necessary.

In this manuscript, we develop a new synthetic strategy, named the Kirkendall effect in synergistic template (KEST), to precisely prepare hollow mesoporous palladium-sulfur alloy nanoparticles (h-mesoPdS) with well-defined geometry and ordered mesostructure and investigate its catalytic performance toward selective hydrogenation of 4-nitrophenylacetylene (4-NPA). This novel method takes advantage of the Kirkendall cavitation that precisely tailors interior hollow nanocavities and elemental compositions at the atomic level and also the nanocasting synthesis which targets ordered mesostructures at the mesoscopic level (Figure 1a and Supporting Information Figures S1–S3). In the case of binary h-mesoPdS alloy nanoparticles, nanoscale Kirkendall effect happens in the synergistic template of mesoPd within a mesoporous molecular sieve (mesoPd/KIT-6), allowing the direct solid-phase synthesis of h-mesoPdS nanoparticles under mild conditions. When investigated as a heterogeneous catalyst, an impressive high selectivity of 94% toward industrially important 4-nitrostyrene (4-NS) in selective hydrogenation of 4-NPA is achieved over h-mesoPdS alloy nanoparticles, remarkably better than commercial Pd/C. Density functional theory (DFT) calculations further demonstrate that geometric and compositional synergies of h-mesoPdS optimize the surface electronic structures and thus change the hydrogenation trends that energetically suppress the over-hydrogenation of 4-NPA.

Experimental Methods and Calculation Setup

Synthesis of h-mesoPdS alloy nanoparticles

Binary h-mesoPdS alloy nanoparticles were synthesized by the KEST method with mesoPd/KIT-6 hybrid as the synergistic template and sulfur powder as the S source. Typically, 0.10 g of as-synthesized mesoPd/KIT-6 hybrid was mixed physically with 0.10 g of sulfur powder. Then, the mixture was calcined at 150 °C for 10 h in a

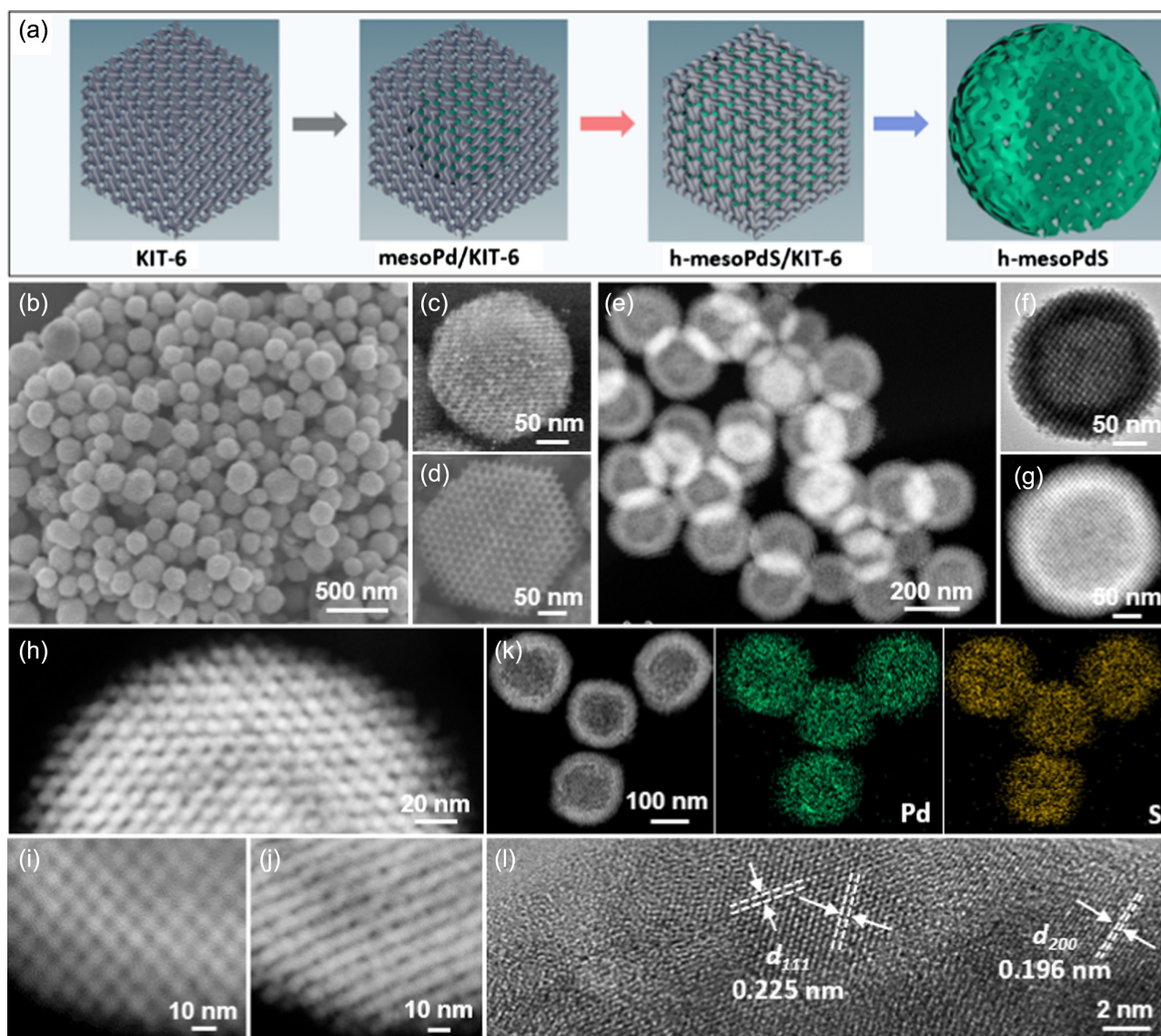


Figure 1 | Synthesis and characterizations. (a) Synthesis of binary *h*-mesoPdS alloy nanoparticles through a KEST route. (b–d) SEM, (e–g) STEM/TEM, and (h–j) high-magnification STEM images of the *h*-mesoPdS nanoparticles. (k) STEM image and corresponding STEM EDS elemental maps of the *h*-mesoPdS nanoparticles. (l) High-resolution TEM image of the *h*-mesoPdS nanoparticles.

pipe furnace under nitrogen atmosphere. Finally, *h*-mesoPdS alloy nanoparticles were obtained by washing with water/ethanol three times, etching with hydrofluoric acid (HF) three times, and drying at 50 °C.

Selective hydrogenation of 4-NPA

Selective hydrogenation reaction of 4-NPA was tested in a 15 mL pressure bottle with 0.25 mL (1.0 mg mL^{−1} in ethanol solution) of the catalyst, 10.0 mg of 4-NPA, 7.5 mg of ammonia borane, 0.025 mL of distilled water, and 0.70 mL of ethanol. The reaction was performed at 40 °C under magnetic stirring for different times. The products were finally analyzed by gas chromatography

(GC) with a Panna A91 Plus GC equipped with a flame ionization detector and a DB-WAX capillary column (Agilent J&W, California, USA; 30 m, 0.25 mm i.d.) with nitrogen as the carrier gas. After the catalysis, the catalyst can be recycled five times and washed for further structural and compositional characterizations.

Calculation setup

DFT calculations based on the Cambridge Serial Total Energy Package (CASTEP) package have been applied to investigate the electronic structures and energetic trend of the hydrogenation process of 4-NPA.⁴⁴ For all the calculations, we have selected the generalized gradient

approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) to accurately describe the exchange-correlation energy.^{45,46} For all the geometry optimizations, we have set 380 eV as the cutoff energy of the plane-wave basis set based on the ultrasoft pseudopotentials. The Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm was chosen for this work.⁴⁷ For the valence states, we treated the (4d, 5s, and 5p) and (3s and 3p) for Pd and S, respectively. The coarse quality of *k*-points is applied for all the energy minimizations.

Based on the experimental characterizations, we constructed three different structures including h-mesoPdS, PdS, and Pd. We have cleaved (100) and (111) surfaces of PdS and Pd to represent the nanoparticle as the comparison samples as experiments. To accomplish the geometry optimizations the following convergence test requirements are as follows: (1) the Hellmann-Feynman forces should not exceed 0.001 eV/Å, (2) the total energy difference should be less than 5×10^{-5} eV/atom, and (3) the inter-ionic displacement should be less than 0.005 Å.

Results and Discussion

Binary h-mesoPdS alloy nanoparticles were synthesized by a novel solid-phase KEST strategy with mesoPd/KIT-6 hybrids as the synergistic template and solid sulfur powder as the S source (Figure 1a). Typically, mesoPd/KIT-6 hybrids, in which highly uniform mesoPd with an average nanoparticle size of 176 nm is solidly confined in KIT-6 (Supporting Information Figure S4), were first synthesized with a classic nanocasting method.^{21,48,49} Then, the KEST process was conducted by physically mixing mesoPd/KIT-6 and sulfur powder with a weight ratio of 1:1 and directly heat-treated at 150 °C under N₂ atmosphere for 10 h. No solvent or extra reactants are needed in this step. After that, binary h-mesoPdS alloy nanoparticles were collected by washing with water/ethanol and HF to remove unreacted S and KIT-6 template (see Materials and Methods in Supporting Information for more details).

Scanning electron microscopy (SEM) images show the products are monodispersed and uniform having a nearly polyhedral geometry with an average diameter of ~250 nm (Figure 1b). Under the high-magnification SEM images, the nanoparticles are observed to have abundant mesopores throughout the polyhedral nanoparticles (Figures 1c and 1d). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image discloses that the synthesized samples are structurally hollow with a nearly polyhedral interior cavity (Figure 1e). TEM and STEM images of a single nanoparticle further show a hollow and mesoporous geometry (Figures 1f and 1g). The interior hollow cavity diameter and shell framework thickness are 156 and 48 nm, respectively. Furthermore, high-magnification STEM images in

different mesoscopic facets disclose the highly ordered mesoporous structure of *1a-3d* (Figures 1h-1j). It confirms that h-mesoPd is completely nanocasted from the double gyroid KIT-6 template and preserves the same symmetry through the KEST strategy. STEM tomography recorded at different observation angles further illustrates the interior hollow cavity with a periodically ordered mesoporous framework (Supporting Information Figure S5 and Video S1). Moreover, STEM energy dispersive X-ray spectroscopy (EDS) reveals homogeneously dispersed Pd and S elements through the entire mesoporous shell framework of h-mesoPdS nanoparticles (Figure 1k). The compositional ratio of Pd/S is 61:39, which is consistent with the data observed from inductively coupled plasma-mass spectrometry (ICP-MS) (67:33). Additionally, the high-resolution TEM image of h-mesoPdS shows two distinct lattice spacings of 0.225 and 0.196 nm, which are assigned to (111) and (200) plane of face-centered cubic (*fcc*) PdS alloy nanoparticles, respectively (Figure 1l).

Physical and chemical parameters of binary h-mesoPdS alloy nanoparticles were further revealed by other advanced characterization techniques. First, small-angle X-ray scattering (SAXS) displays two main peaks located at 0.72 and 0.82 nm⁻¹ (Figure 2a), which correspond to the highly ordered *1a-3d* mesoporous structure with a uniform *d*-spacing of 8.7 nm for both mesoPd and h-mesoPdS nanoparticles. They are consistent with the data for KIT-6, mesoPd/KIT-6 hybrids, and h-mesoPdS/KIT-6 hybrids (Supporting Information Figure S6), further confirming that mesoporous nanoparticles are completely nanocasted from the initial KIT-6 templates. Second, wide-angle X-ray diffraction (XRD) patterns of mesoPd and h-mesoPdS display a single set of diffraction peaks assigned to (111), (200), (220), (311), and (222) planes of a *fcc* crystalline structure (Figure 2b). In comparison to monometallic mesoPd, all diffraction peaks of h-mesoPdS alloys slightly shift toward the higher angles (~0.12°), evidencing that S with a slightly smaller atomic size randomly substitutes Pd atoms and further forms binary PdS alloys. Well-alloyed PdS was revealed by the high-resolution X-ray photoelectron spectroscopy (XPS). Compared to monometallic mesoPd, the Pd 3d of binary h-mesoPdS positively shifts toward higher binding energy (~1.25 eV), indicating a remarkable electron transfer between Pd and S within binary alloys (Figure 2c and Supporting Information Figure S7a). Meanwhile, two pairs of S 2p peaks that can be assigned to the sulfides (Pd-S, major) and disulfides (S-S, minor) are clearly seen (Supporting Information Figure S7).

Surface electronic features of binary h-mesoPdS alloy nanoparticles were also revealed by DFT simulations. We first constructed a hollow and mesoporous structure of binary PdS alloys with a pore size of 3.6 nm and a

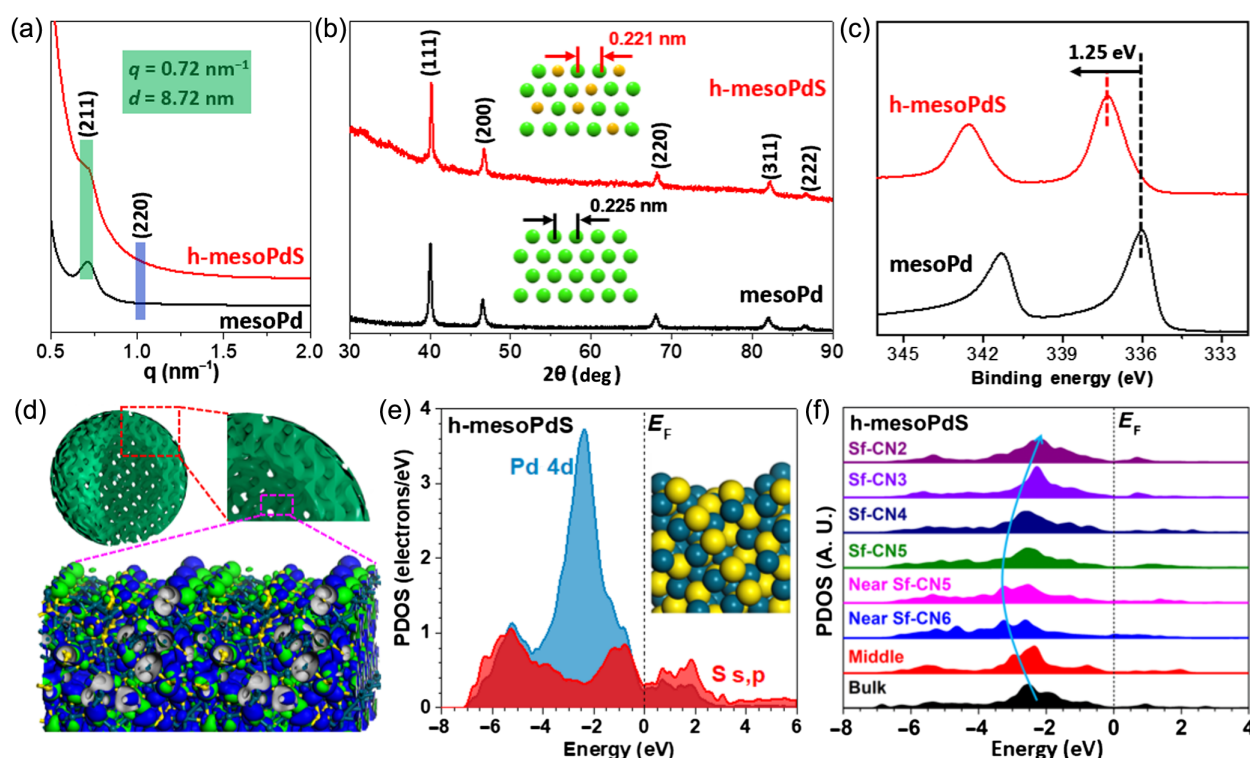


Figure 2 | Physical and chemical properties. (a) SAXS and (b) XRD patterns, and (c) high-resolution XPS Pd 3d spectra of mesoPd and h-mesoPdS nanoparticles. (d) The 3D contour plot of electronic distribution of the h-mesoPdS alloy nanoparticles. (e) The PDOS and (inset) the surface configuration of the h-mesoPdS nanoparticles. (f) Site-dependent PDOS of Pd in h-mesoPdS.

framework thickness of 4.5 nm. Figure 2d shows the electronic distributions near the Fermi level (E_F) of the highly curved framework of h-mesoPdS. There are abundant low-coordinated sites along the surfaces of the mesoporous framework, resulting in strongly perturbed electronic structures. In comparison, PdS(100) and Pd(111) surfaces of nanoparticles display a more ordered electronic distribution (Supporting Information Figure S8). The detailed electronic structures in different surfaces are demonstrated through the projected partial density of states (PDOSs). The h-mesoPdS has an evident curvature feature of the mesoporous surface with many low-coordination sites (Figure 2e). The Pd 4d orbitals show a sharp peak near the maximum of valence band (E_V) -2.7 eV ($E_V = 0$ eV). Meanwhile, the S s,p orbitals cover a broad range and cross the E_F , which guarantees the efficient electron transfer within the h-mesoPdS. This distinguishes the PdS(100) and Pd(111) surfaces (Supporting Information Figures S9 and S10). The site-dependent PDOSs of Pd 4d orbitals for h-mesoPdS are also shown (Figure 2f). Notably, from the bulk structure to the surface, the Pd 4d orbital positions display a remarkable curve evolution trend along the mesoporous framework. Obviously, the low-coordinated Pd sites show a closer position to E_F , which could change the adsorption nature of the reactants and meanwhile alter

the reaction trends for catalysis. These results confirm that geometric and compositional effects synergistically optimize the surface electronic structures of binary h-mesoPdS alloy nanoparticles.

We further explored how the KEST strategy drives the desired formation of binary h-mesoPdS alloy nanoparticles by carefully investigating its reaction intervals (Figure 3). The mesoPd nanoparticles with a uniform diameter and polyhedral morphology that are homogeneously confined in the mesoPd/KIT-6 were first synthesized and used as the parent synergistic template (Figures 3a–3c). When the reaction proceeded for 2 h, internal mesoPd gradually diffused outward and atomically recrystallized with evaporated sulfur within the KIT-6 template (Figures 3d–3f). Nanocasting nucleation and growth of binary PdS alloys within confined mesoporous KIT-6 result in the targeted synthesis of the mesoporous shell. Structural characterizations reveal a typical yolk-shell geometry with distinct vacancy voids between the external mesoPdS shell and internal mesoPd, confirming a KEST growth mechanism. With a longer reaction time of 5 h, the vacancies diffused inward and the mesoporous shell re-crystallized outward, causing a smaller interior mesoPd core and a thicker mesoPdS shell (Figures 3g–3i). Finally, the internal mesoPd diffused completely, resulting in the formation of h-mesoPdS

alloy nanoparticles with a complete hollow cavity and mesoporous shell (Figures 3j–3l). During the synthesis, both the hollow interior cavity and mesoporous framework gradually increased (Supporting Information Figure S11). Meanwhile, ICP-MS showed S gradually diffused into Pd nanocrystals during the synthesis (Supporting Information Figure S12). More interestingly, bowl-like half nanoparticles with an asymmetric geometry are seen around the edges of mesoporous KIT-6 templates (arrows in Figure 3j), further suggesting that the interdiffusions of Pd and S favorably occur within the confined mesoporous framework (rather than outside) based on a capillary phenomenon.^{21,50}

Our observations corroborated the successful formation of binary h-mesoPdS alloy nanoparticles with highly ordered mesoporous channels and polyhedral interior cavity by a newly developed KEST strategy. We deduce that, at the proper temperature, sulfur powder gradually evaporates and then inserts into mesoporous channels of the mesoPd/KIT-6 template. Then, the Kirkendall cavitation between diffused Pd and evaporated S drives the re-crystallization growth of h-mesoPdS polyhedral nanoparticles. Meanwhile, the interior hollow cavity of h-mesoPdS alloy nanoparticles is slightly smaller than the diameter of the initial mesoPd, suggesting that binary PdS alloys crystallize partially inward. It is likely

due to the different interdiffusion rates between Pd and S.⁵¹ In sharp contrast, with a lower or higher treatment temperature (120 and 200 °C), h-mesoPdS alloy nanoparticles with a smaller or larger size (hollow cavity) are obtained accordingly (Supporting Information Figure S13).

The utilization of mesoPd/KIT-6 hybrids as the synergistic template is the key for the solid-phase synthesis of h-mesoPdS alloy nanoparticles through a KEST strategy. On the one hand, it endows a spatial circumstance that separates mesoPd nanoparticles and sulfur powder, enabling the solid-phase Kirkendall cavitation of hollow PdS (h-PdS) alloys. On the other hand, it behaves as a mesoporous hard-template that directs the nanocasting crystallization of mesoporous PdS alloys inside the confined KIT-6 template. Such a synergistic template thus produces h-mesoPdS alloy nanoparticles. In contrast, when both mesoPd (after the removal of KIT-6 from mesoPd/KIT-6 hybrids) and commercial Pd nanoparticles were used as the parent templates in reference experiments, only solid or hollow nanoparticles without any mesoporous channels were obtained by the above synthetic procedures (Supporting Information Figures S14). Meanwhile, due to direct physical contact of Pd and S powder, the hollow cavity was also remarkably destroyed. Moreover, the traditional nanocasting method by the direct

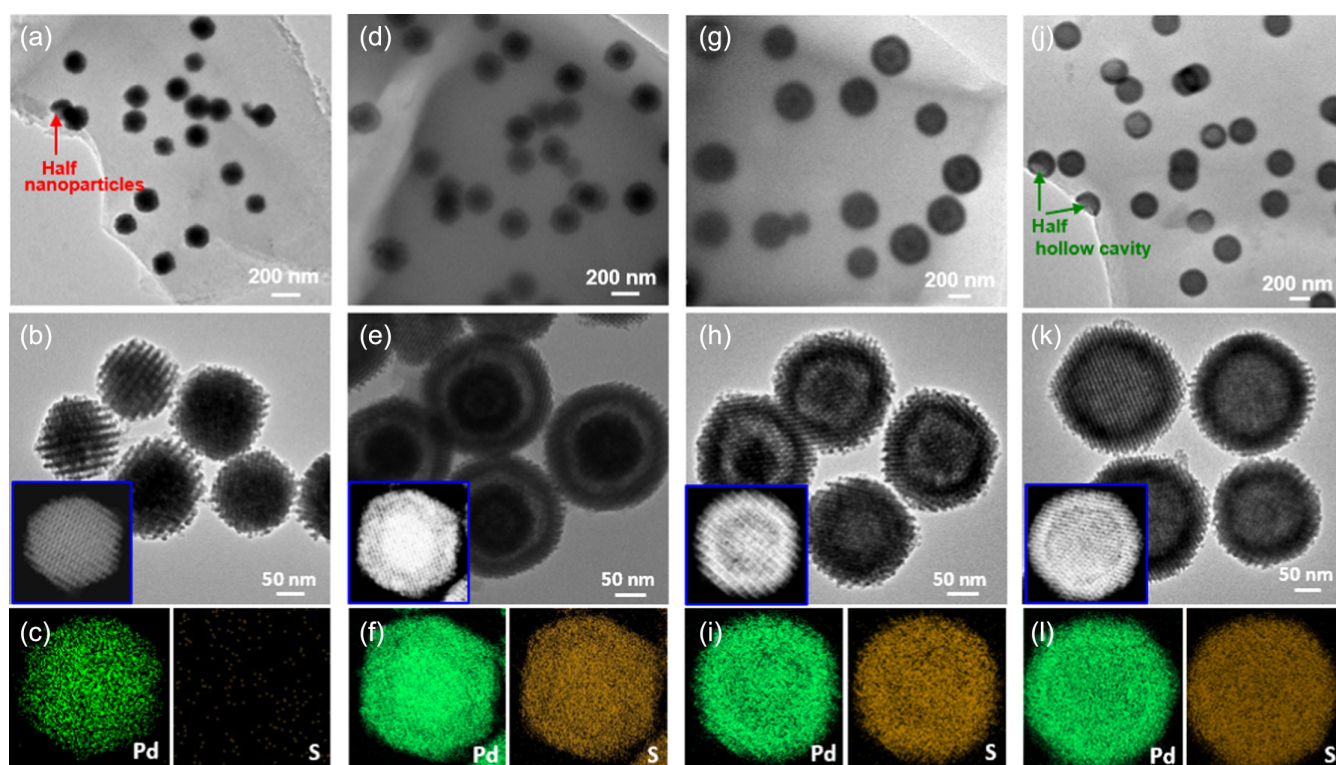


Figure 3 | Formation mechanism. TEM images of mesoPd/KIT-6 (or h-mesoPdS/KIT-6) with a reaction time of (a) 0 h, (d) 2 h, (g) 5 h, and (j) 10 h. (b, e, h, and k) TEM and STEM images and (c, f, i, and l) corresponding EDS maps of mesoPd (or h-mesoPdS) with a reaction time of (b and c) 0 h, (e and f) 2 h, (h and i) 5 h, and (k and l) 10 h.

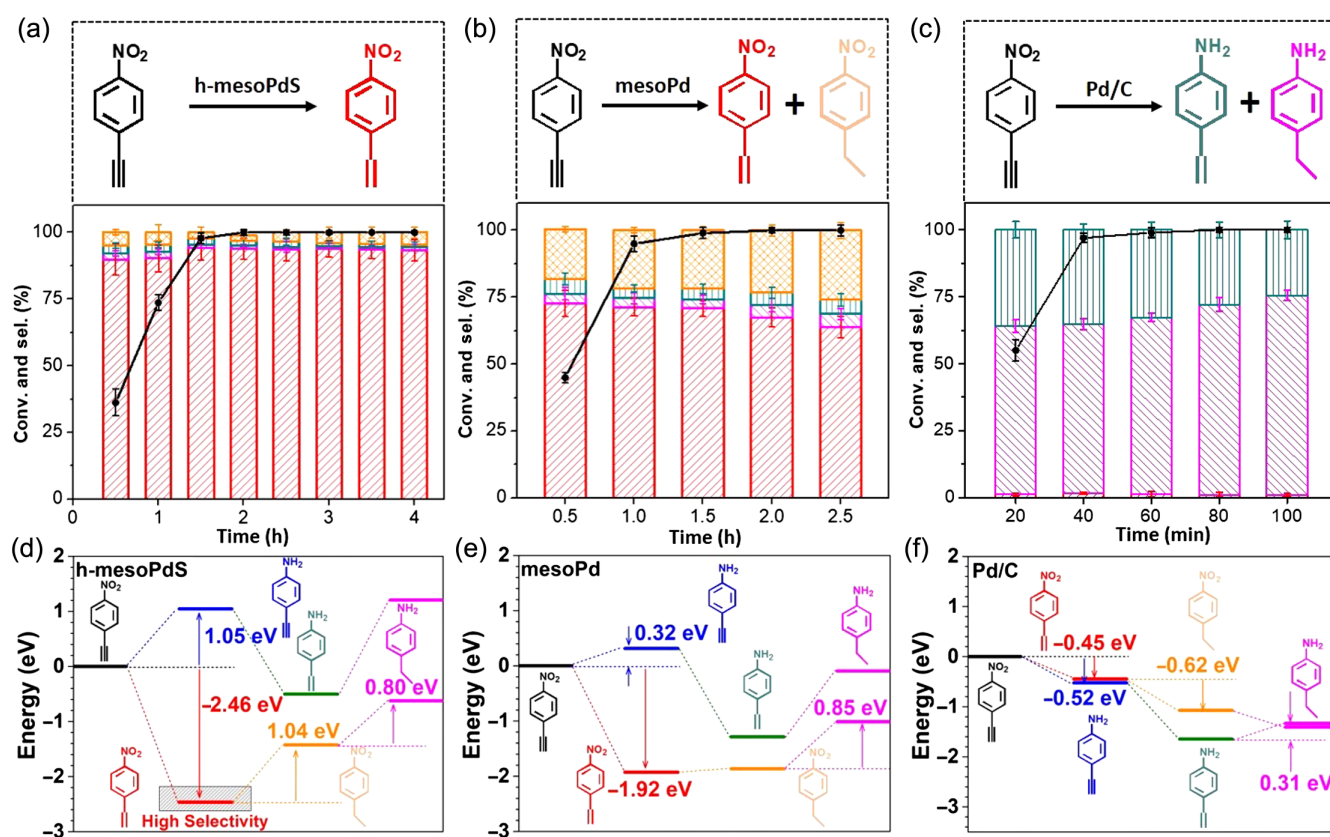


Figure 4 | Catalytic performance and mechanism. (a–c) 4-NPA conversion and product selectivity and (d–f) corresponding overall hydrogenation reaction trends over (a and d) h-mesoPdS, (b and e) mesoPd, and (c and f) commercial Pd/C.

reduction of PdCl_4^{2-} /KIT-6 with S source was also investigated. MesoPdS alloys with a disordered geometry and remarkably destroyed hollow cavities are obtained due to a larger volume contraction of PdCl_4^{2-} .^{52,53} Meanwhile, the direct formation of PdS alloys from PdCl_4^{2-} disables the Kirkendall cavitation process, resulting in solid pieces without any hollow cavity (Supporting Information Figure S15).

With multiple geometric and compositional synergies in one material that remarkably optimize the surface electronic structure, binary h-mesoPdS alloy nanoparticles are expected to perform well as a highly efficient heterogeneous catalyst. Selective hydrogenation of 4-NPA was evaluated as the model for catalysis because it is an important catalytic reaction for obtaining high-value products that still requires better control of product selectivity (Supporting Information Figure S16).^{5,9,54} Monometallic mesoPd, commercial Pd/C (3–5 nm, imitating the wall thickness of h-mesoPdS), Pd black (30–50 nm, imitating the shell thickness of h-mesoPdS), and h-PdS were also tested for comparison (Supporting Information Figure S17). As shown in Figure 4a, 4-NPA was completely converted over h-mesoPdS alloy nanoparticles at 2 h with an impressive high-selectivity of 94%

and a conversion of 100% toward 4-NS. Meanwhile, the selectivity was retained without an obvious decrease until 4 h. It needs to be noted that 4-NS is one of the most industrially important nitro compounds.⁴ Our catalyst material thus provides a new opportunity to obtain 4-NS under a mild condition. Meanwhile, the high selectivity is also comparable to the state-of-the-art catalysts for the hydrogenation reactions (Supporting Information Table S1). In comparison, by using the mesoPd catalyst, the main product for selective hydrogenation of 4-NPA is still 4-NS, but its selectivity decreases to 64% (Figure 4b). Meanwhile, 26% of 4-NPA was also over-hydrogenated into 4-nitroethylbenzene (4-NE). Interestingly, the nitro group of 4-NPA was almost not hydrogenated over both h-mesoPdS and mesoPd. Similarly, ~60% of 4-NPA was selectively hydrogenated into 4-NS over h-PdS alloy nanoparticles (Supporting Information Figure S18a). These results confirm the geometric and compositional synergies for the selectivity enhancement in the hydrogenation of 4-NPA. As a control, commercial Pd/C favors converting 4-NPA toward 4-aminoethylbenzene (4-AE) and 4-aminostyrene (4-AS) with the selectivity of 63% and 35%, respectively (Figure 4c). Similarly, Pd black shows a low catalytic activity and selectivity (Supporting

Information Figure S18b). Moreover, h-mesoPdS alloy nanoparticles attain a remarkable catalytic stability even under full conversion of 4-NPA. The selectivity to 4-NS is retained at 92% (with full conversion of 4-NPA) for five successive recycling experiments (Supporting Information Figure S19a). STEM and EDS maps also display the integral hollow and mesoporous geometry and binary PdS composition after the catalysis (Supporting Information Figure S19b).

DFT calculations are used to further understand why binary h-mesoPdS alloy nanoparticles selectively hydrogenate 4-NPA to 4-NS. Based on different geometric and compositional features, the hydrogenation reaction trends of three catalysts are proposed and compared. For the h-mesoPdS, the hollow channel environment delivers a much stronger reaction trend toward the initial hydrogenation on the alkyl chain (Figure 4d). Because of the large barriers of the nitro-to-amino group (1.05 eV) and further hydrogenation of C=C group (1.04 eV), the high selectivity occurs toward the formation of 4-NS. Similarly, we also noticed the strong reaction trend for the hydrogenation on the alkyl chain in mesoPd (Figure 4e). However, the stronger reduction capability of Pd sites also promotes significant further hydrogenation, which lowers the selectivity for 4-NS and increases the selectivity for 4-NE. For the Pd/C surface, in contrast, the initial hydrogenation reactions are energetically favorable on both nitro group and alkyl chain, causing a low selectivity (Figure 4f). The reaction trends of both pathways are supported by the strong reduction capability of Pd/C, leading to the high yield of complete reduction of 4-NPA to 4-AE on Pd/C.

Conclusion

A newly developed KEST strategy is reported, for the first time, as a general route to precisely prepare binary h-mesoPdS alloy nanoparticles, which subtly combine a highly ordered mesoporous shell framework with an interior hollow cavity into one geometry. Such a hierarchical geometry is achieved by Kirkendall cavitation of PdS alloys inside a confined mesoPd/KIT-6 synergistic template that precisely controls the interdiffusion and recrystallization growth of mesoporous shell at the mesoscopic level. The concurrent realization of the geometric and compositional synergies remarkably optimizes the electronic structures of h-mesoPdS nanoparticles. When investigated as a heterogeneous catalyst for the hydrogenation of 4-NPA, h-mesoPdS alloy nanoparticles exhibit a remarkably high catalytic selectivity and stability toward 4-NS (one of the most important intermediates in industry), which are superior to mesoPd, commercial Pd/C and Pd black, and h-PdS. Comparison experiments and DFT calculations reveal that the hollow and mesoporous geometry and binary Pd-S composition of

h-mesoPdS endow the varied coordination environments and the optimized electronic structures on the catalyst surfaces, resulting in the evident reaction preference and high selectivity toward the formation of 4-NS. We believe that the reported synthetic strategy represents a new advance in the precise fabrication of hollow and mesoporous nanomaterials with multiple geometric and compositional synergies, which significantly impacts their potential applications in catalysis, fine chemical productions, and energy storage and conversions.

Supporting Information

Supporting Information is available and includes the details of the synthesis, characterizations, and catalytic measurements, and more SEM and TEM images as well as the evaluation of catalytic performances.

Author Contributions

B.L. supervised and directed the project. H.L., W.L., and B. L. proposed and designed the project. H.L. synthesized the samples and carried out the characterizations and catalysis. L.S. assisted the experiments. D.X. assisted the high-resolution TEM characterizations. B.H. carried out the DFT calculations. All the authors analyzed the results and wrote the manuscript.

Conflict of Interest

The authors declare no competing financial interests.

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