

Aggregation- and Leaching-Resistant, Reusable, and Multifunctional Pd@CeO₂ as a Robust Nanocatalyst Achieved by a Hollow Core–Shell Strategy

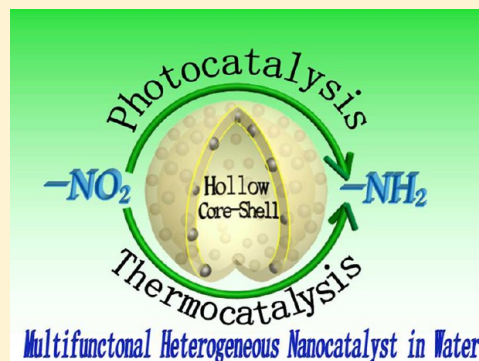
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S Supporting Information

ABSTRACT: To develop various strategies to prevent the aggregation, sintering, or leaching of noble metal nanoparticles (NPs) represents a crucial issue for efficient synthesis and utilization of supported noble metal NPs with highly active and stable catalytic performance. Here, we report a facile synthesis approach to obtain a Pd@hCeO₂ hollow core–shell nanocomposite that is composed of tiny Pd nanoparticles cores encapsulated within CeO₂ hollow shells. The core–shell strategy efficiently prevents the aggregation of Pd NPs in the high temperature calcination process and the leaching of Pd NPs for the catalytic reaction in a liquid phase. This anti-aggregation and anti-leaching behavior is not able to be achieved for traditional supported Pd/CeO₂ catalyst. Such a Pd@hCeO₂ composite can serve as an efficient multifunctional nanocatalyst in both heterogeneous thermocatalytic and photocatalytic selective reduction of aromatic nitro compounds in water under ambient conditions. Each component, namely Pd metal core or semiconductor CeO₂ shell, makes a necessary but totally dissimilar reactive contribution to achieving the same end product during these two different catalytic processes. Importantly, Pd@hCeO₂ exhibits an excellent reusable and much higher catalytic performance than supported Pd/CeO₂. This work provides a generic concept example on inhibiting aggregation of noble metal NPs during high temperature calcination and leaching of noble metal nanoparticles into solution via a hollow core–shell strategy and, more significantly, on sufficiently harnessing the specific metal core or semiconductor shell function integrated in a core–shell nanoarchitecture toward a multifunctional catalytic use in both thermocatalytic and photocatalytic selective green transformation in water.

KEYWORDS: hollow core–shell, anti-aggregation, leaching-resistance, thermocatalysis, photocatalysis, selective reduction



INTRODUCTION

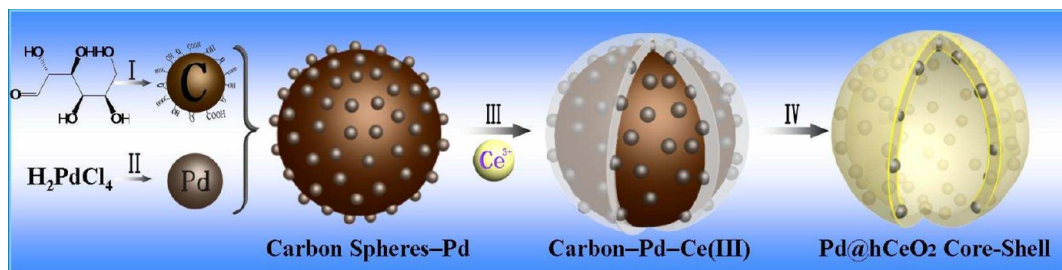
The development of high-performance and stable catalysts has been remaining a significant objective because of its paramount importance for energy conversion.^{1–3} In particular, great efforts are paid to the use of noble metal nanoparticles (NPs) in catalysis due to their versatile, tunable size-, shape- and composition-dependent properties.^{3–11} In the design and application of noble metal NPs catalysts, the sintering or aggregation of metal NPs is a main route leading to the decreased catalytic activity or deactivation.^{3–12} In addition, for the catalytic reaction in a liquid phase, the leaching of metal NPs is often the other detrimental factor inducing the significant loss of catalytic activity. Therefore, developing various strategies to prevent the aggregation, sintering, or leaching of metal NPs represents a technologically crucial but challenging issue for the effective synthesis and utilization of noble metal NPs catalysts with desirable dimension and improved catalytic performance.^{3,9–11} A few cases have been reported to prevent the aggregation of metal NPs through steric stabilization by an overlayer of inorganic oxide shells (e.g., silica, carbon, zirconia) with tens of nanometers thick via the

approach of chemical vapor deposition, dendrimer encapsulation or grafting.^{3,9,10,13–23} However, the shell thickness is often poorly controlled, thereby leading to a decrease in catalytic activity. Very recently, Peter's group has reported an elegant, powerful strategy, through a 45 layers alumina (Al₂O₃) overcoating of supported Pd NPs via an atomic layer deposition (ALD) process, to effectively and simultaneously prevent both the sintering/aggregation and coking of Pd NPs in a high-temperature oxidative dehydrogenation of ethane to ethylene.²⁴ Notably, in all the above thermocatalytic process, since the catalytic active sites are primarily associated with noble metal NPs, the potential use of shells in heterogeneous photocatalysis is often ignored or not harnessed.^{3,9,10,13,14,16,17,24–27} In other words, if the shell is composed of reactive semiconductors that can be band-gap-excited by visible-light irradiation, the nanoarchitectures, consisting of noble metal NPs coated with the visible-light-active semiconductor shell, could be potentially

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Scheme 1. Schematic Illustration for Fabrication of Pd@hCeO₂ Core–Shell Nanocomposite: (I) Synthesis of Carbon Sphere Template; (II) Preparation of Colloidal Pd Nanoparticles; (III) Fabrication of Carbon–Pd–Ce(III) Nanocomposites via a Hydrothermal Treatment; (IV) Preparation of Pd@hCeO₂ Core–Shell Nanocomposite with Inner Hollow Space by a Calcination Process



used as a multifunctional catalyst toward both thermocatalytic and photocatalytic processes. Furthermore, the robust shield of semiconductor shell could prevent the undesirable noble metal leaching during catalytic reactions in a liquid phase, thereby potentially offering the possibility of achieving a stable and reusable catalyst for both thermocatalytic and photocatalytic reactions.

Core–shell structured materials with hollow space represent a unique class of complex hybrids, which provides an efficient solution to prevent the undesirable coalescence, sintering, aggregation or corrosion/dissolution of entrapped catalytic species, e.g., noble metal particles, by the shell protection.^{14,16,17,25,26,28,29} Meanwhile, the porous voids endowed by hollow space can promote diffusion and mass transfer of reactants.^{3,9,14,17,26,29–31} Such a concerted synergy interaction between the core and permeable shell make it very useful in a myriad of fields, including surface enhanced Raman scattering (SERS), drug/gene delivery systems, energy storage media, and nanospace confined catalytic reactor.^{3,9,10,14,17,25,26,29,30,32–35} However, for the thermocatalytic application of noble metal related core–shell materials (e.g., Au@ZrO₂, Pt@carbon, Pt@SiO₂) in hydrogenation, oxidation, reduction or reforming reactions, it should be noted that the outer shell often consists of unreactive silica, carbon and zirconia.^{3,9,10,13–17,24–27} From a viewpoint of photocatalysis, these inert shells can not be band gap-photoexcited by visible light irradiation. Thus, if the shell is composed of reactive semiconductor components, the hollow core–shell nanocomposites, consisting of noble metal particles core and visible-light-active semiconductor shell, would find their multifunctional use in both thermocatalytic and photocatalytic redox processes, although fundamentally the respective underlying catalytic reaction mechanisms between these two different catalytic processes are remarkably different.

Toward this end, we herein report the synthesis of Pd@CeO₂ core–shell nanocomposite with inner hollow space (denoted as Pd@hCeO₂) via a facile aqueous-phase method followed by a high temperature calcination in air to remove the template. The aggregation of Pd nanoparticles during high temperature treatment process can be significantly inhibited by such a core–shell strategy whereas, in contrast, the obvious aggregation of Pd nanoparticles is observed during preparation of supported Pd/commercial CeO₂ nanocomposite without a core–shell structure. The as-synthesized Pd@hCeO₂ nanocomposite is able to be highly active in two different processes, heterogeneous thermocatalytic and photocatalytic selective reduction of a variety of substituted aromatic nitro compounds in water under ambient conditions. Each component of the Pd@hCeO₂ nanocomposite makes a necessary but totally

dissimilar reactive contribution to achieving the same end product though with distinctly different catalytic mechanism. In particular, Pd@hCeO₂ exhibits an excellent reusable and higher catalytic performance than supported Pd/CeO₂ in both thermocatalytic and photocatalytic selective reduction of aromatic nitro compounds in water, which is because of the efficient anti-leaching of Pd into solution and anti-aggregation of Pd during a high temperature calcination process, resulting from the confined robust shield of the semiconductor CeO₂ shell.

RESULTS AND DISCUSSION

The fabrication procedure for Pd@hCeO₂ core–shell nanocomposite is illustrated in Scheme 1. The Pd colloidal nanoparticles with the diameter ranging from 1 to 5 nm (see Figure S1 in the Supporting Information) prepared in the presence of polyvinylpyrrolidone (PVP) as stabilizer are preferentially loaded onto the surface of carbon sphere template in virtue of the π – π interactions between PVP and carbon spheres.^{36–38} Because of the plentiful functional groups of carbon spheres inherited from glucose polymerization and carbonization in the hydrothermal process,^{39,40} the carbon spheres–Pd composite is still negatively charged, as evidenced by the results of zeta potential (ξ) measurements (see Figure S2 in the Supporting Information). Then, CeCl₃ as the precursor of CeO₂ gives positively charged Ce³⁺ ions that interact with the negatively charged carbon spheres–Pd composite via electrostatic interaction. Followed by a hydrothermal treatment and a calcination process in air, the carbon sphere template and PVP stabilizer are removed and, simultaneously, the shell of CeO₂ is formed, thus resulting in the formation of Pd@hCeO₂ core–shell nanocomposite with inner hollow space.

As evidenced by the field-emission scanning electron microscope (FESEM) image in Figure 1A, structurally well-defined hollow spheres with the diameter around 200 nm are distributed. The inner hollow structure can be observed more clearly from the broken spheres in Figure 1B as pointed out by the arrows, which is further confirmed by the transmission electron microscope (TEM) image (Figure 1C). The high-resolution TEM (HRTEM) result for the edge of the Pd@hCeO₂ nanoparticles as displayed in Figure 1D reveals that there is neither Pd nanoparticles deposited on the outer surface of CeO₂ shell nor the obvious aggregation of Pd colloids occurred, indicating the effective prevention of Pd nanoparticles from significant coalescence or aggregation in such a configuration even during the high-temperature calcination process. The thickness of the CeO₂ shell in the Pd@hCeO₂

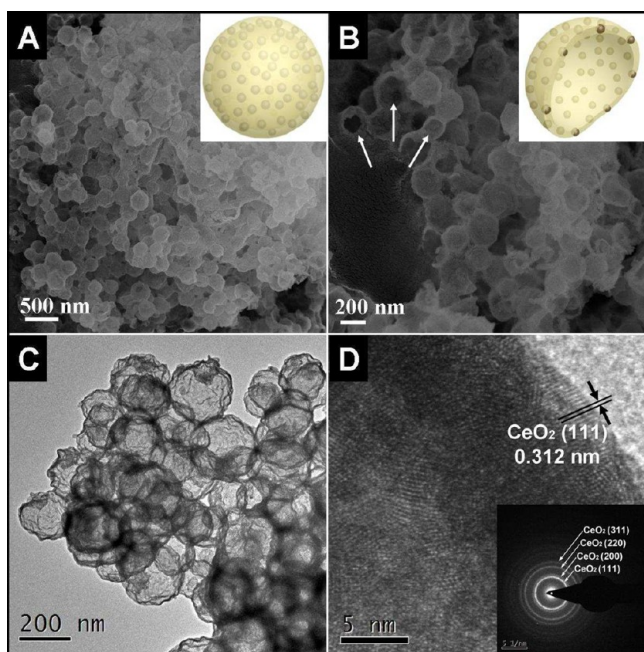


Figure 1. Typical (A, B) SEM, (C) TEM, and (D) HRTEM images of Pd@hCeO₂ core-shell nanocomposite (the insets of A and B are the corresponding model illustrations; the inset of D is the SAED pattern).

hollow core-shell nanocomposite is ca. 10 nm. The identified lattice spacing of 0.312 nm in the outer edge in HRTEM image (Figure 1D) corresponds to the (111) facet of CeO₂. In contrast, no signal of noble metal Pd is distinguished in the edge region, suggesting that Pd is located in the core region of Pd@hCeO₂ nanocomposite. Because of the high electron density of polycrystalline CeO₂,^{11,41} the small size of Pd nanoparticles and the specific core-shell architecture, it is difficult to resolve the interface between Pd and CeO₂; therefore, the encapsulated Pd nanoparticles can not be

visualized very evidently in the TEM image of Pd@hCeO₂ core-shell nanocomposite. However, as shown in Figure 2A and 2B, the energy-dispersive X-ray (EDX) analysis on selected different areas of an individual Pd@hCeO₂ sphere demonstrates clearly that the hollow spheres contain Ce, O and Pd elements. Additionally, the elemental mapping has also been performed to reveal the element distribution in the Pd@hCeO₂ spheres. The mapping results (Figure 2C–F) indicate that the elements Ce, O and Pd spread evenly in the whole spheres and the Pd nanoparticles are not located on the outermost surface of the hollow spheres, which confirms the Pd core@CeO₂ shell structure of Pd@hCeO₂ as obtained by the step-by-step assembly procedures illustrated in Scheme 1. The selected area electron diffraction pattern (SAED) shown in the inset of Figure 1D indicates the polycrystalline structure of the Pd@hCeO₂ core-shell nanocomposite, which is consistent with the XRD pattern (see Figure S3 in the Supporting Information). There is no diffraction peak belonging to Pd in the XRD pattern of the Pd@hCeO₂ hollow core-shell nanocomposite, which should result from the relatively low content and uniform distribution of Pd nanoparticles.^{42,43} The valence state of Ce, O and Pd in the Pd@hCeO₂ core-shell nanocomposite is determined by X-ray photoelectron spectra (XPS). As shown in Figure 3A, the Ce 3d_{5/2} and Ce 3d_{3/2} peaks located at ca. 881.7 and 900.0 eV, respectively, along with four satellite peaks indicated by asterisks, signify that the Ce element is in the +4 oxidation state.^{44,45} In the O 1s XPS spectra (Figure 3B), the peaks at around 528.6 and 531.8 eV are ascribed to the lattice oxygen in CeO₂ and the chemisorbed oxygen caused by the absorption of H₂O or/and CO₂ molecule to the surface, respectively.^{46,47} Pd(3d_{5/2} 3/2) peaks at about 335.1 and 340.3 eV can be assigned to metallic Pd.⁴⁸ There is no detectable N signal in the XPS spectra (see Figure S4 in the Supporting Information), confirming the complete removal of the PVP stabilizer due to the calcination treatment. Given that the chemisorbed carbon species, i.e., CO₂, inevitably give carbon

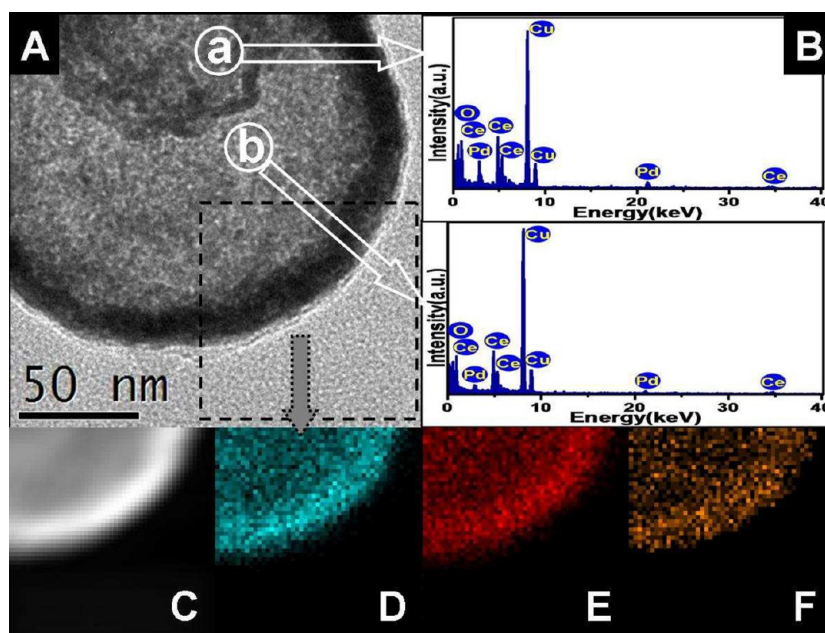


Figure 2. (A) Typical TEM image, (B) the corresponding EDX spectra for different areas of Pd@hCeO₂ core-shell spheres, (C) the high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image, and mapping results of the elements (D) Ce, (E) O, and (F) Pd for the boxed area of A.

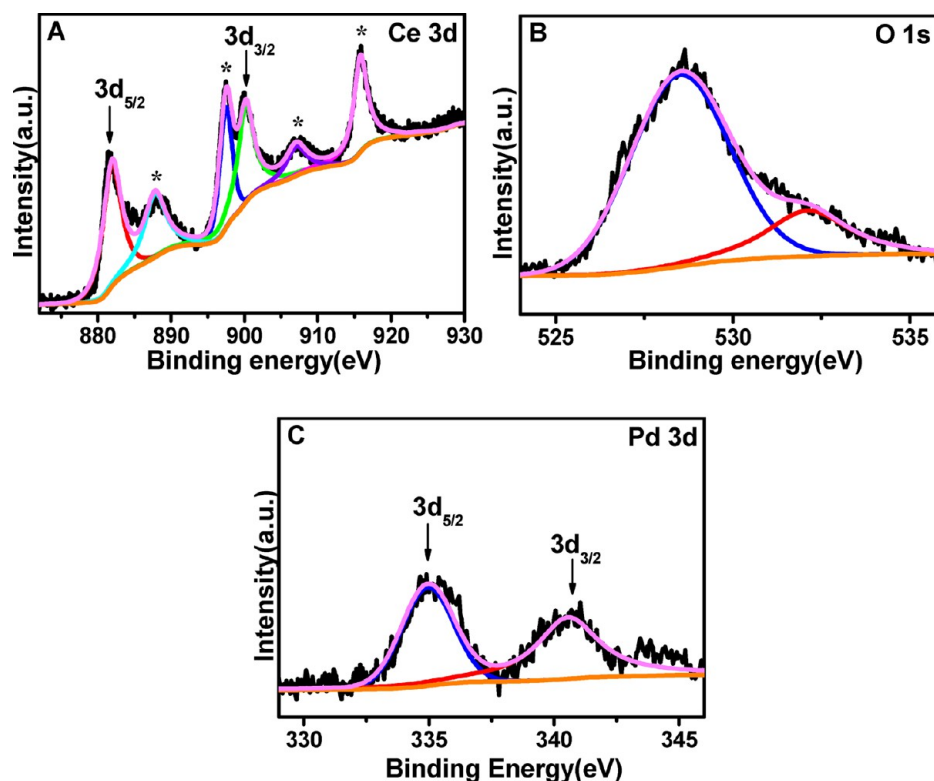


Figure 3. XPS spectra and the peak deconvolution for (A) Ce 3d, (B) O 1s, and (C) Pd 3d in the Pd@hCeO₂ hollow core-shell nanocomposite.

signal in XPS spectra, thermogravimetric analysis of the Pd@hCeO₂ core-shell nanocomposite has been carried out. It can be seen from Figure S5 (see the Supporting Information) that the weight change curve of Pd@hCeO₂ core-shell nanocomposite does not exhibit apparent weight loss in the temperature range of 323–973 K, which sufficiently demonstrates the total elimination of the carbon spheres. The weight ratio of Pd in the Pd@hCeO₂ hollow core-shell nanocomposite is found to be ca. 3.6% according to the quantification of XPS results, which is similar to the theoretical feedstock value of Pd content (3.0%). Notably, in contrast to SiO₂-based core-shell nanocomposites, the use of carbon spheres with abundant functional groups as template not only dismisses the requirement of coupling agents and surface modification steps, but also facilitates the interaction of metal or oxide nanoparticles with the template.^{39,40} In addition, because the nanoparticles with various sizes, shapes, and compositions can be loaded onto the carbon sphere surface along with the less limitation on the selection of the oxide shell precursor compared to using SiO₂ as template, this approach could represent a facile process for the synthesis of core-shell nanocomposites with inner hollow space.

The catalytic activity of the Pd@hCeO₂ core-shell nanocomposite is initially evaluated by the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with excess of NaBH₄ under ambient conditions, i.e., room temperature and atmospheric pressure, which is one of the typical model reactions for investigating the catalytic activity of noble metal nanoparticles.^{9,10,49–53} The reaction does not proceed for a couple of days even with a large excess of NaBH₄ in the absence of the catalyst.^{9,10,51–53} As shown in Figure S6 (Supporting Information), when a trace amount of the Pd@hCeO₂ core-shell nanocatalyst (2 mg) is introduced into the solution, the absorption peak at 400 nm decreases and, concomitantly, a new

absorption peak at 300 nm appears and increases which can be ascribed to the reduction of 4-NP and the formation of 4-AP, respectively.^{9,50,53–55} The UV-vis spectra exhibit an isosbestic point between two absorption bands, demonstrating that there are only two principal species, 4-NP and 4-AP.⁹ Indeed, we have also used the high performance liquid chromatograph (HPLC) to quantify the distribution of reactant and product, which confirms that the product is primarily dominated by 4-AP with a high selectivity of ca. 99%. For comparison, the catalytic activities of supported Pd/CeO₂ and commercial CeO₂ as reference catalysts for reduction of 4-NP have also been investigated under identical experimental conditions. The conversion can be directly read off from the curves composed of the ratios of the concentration of 4-NP at a certain time to its initial concentration value, as displayed in Figure 4A. It is obvious that commercial CeO₂ exhibits negligible catalytic reduction activity, suggesting that the reduction is mainly catalyzed by the Pd nanoparticles; whereas the supported Pd/CeO₂ possesses inferior catalytic performance as compared to Pd@hCeO₂ core-shell nanocomposite. Such a similar trend of catalytic activity can also be observed in the case of selective reduction of other substituted aromatic nitro compounds, such as 3-nitrophenol, 2-nitrophenol, 4-nitroaniline, 3-nitroaniline, 2-nitroaniline, 4-nitrotoluene, 4-nitroanisole, 1-chloro-4-nitrobenzene, and 1-bromo-4-nitrobenzene, as clearly reflected in Figure 4B–J.

It is known that, in the thermocatalytic reduction process of aromatic nitro compounds with excess NaBH₄, metal nanoparticles act as the primary active component to catalyze the reactions by facilitating the transfer of electrons from BH₄[−] to the reactants, thus leading to the effective reduction of the nitro group.⁵³ Therefore, the size of the metal nanoparticles plays a significant role in affecting the catalytic activity.^{6,55} Accordingly, the difference in the catalytic activities of Pd@hCeO₂ core-

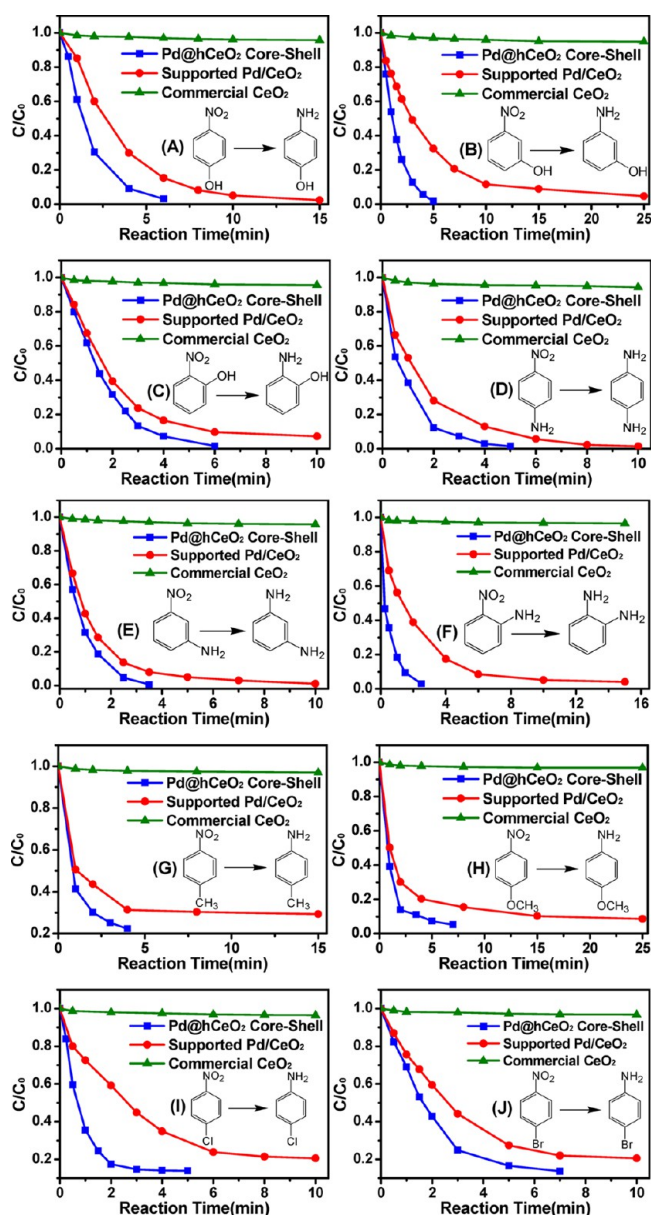


Figure 4. Performances of commercial CeO_2 , supported Pd/CeO_2 , and Pd@hCeO_2 core-shell nanocomposites for thermocatalytic reduction of substituted aromatic nitro compounds under ambient conditions: (A) 4-nitrophenol; (B) 3-nitrophenol; (C) 2-nitrophenol; (D) 4-nitroaniline; (E) 3-nitroaniline; (F) 2-nitroaniline; (G) 4-nitrotoluene; (H) 4-nitroanisole; (I) 1-chloro-4-nitrobenzene; (J) 1-bromo-4-nitrobenzene.

shell nanocomposite and supported Pd/CeO_2 should mainly result from the disparity of Pd nanoparticles size. As verified by the TEM results in Figure 5, severe agglomeration of the Pd nanoparticles in supported Pd/CeO_2 irreversibly occurred due to the calcination process at high temperature, which greatly decreases the surface area of Pd metal available for the electron transfer, resulting in the loss of the catalytic activity. In sharp contrast, the Pd@hCeO_2 core-shell nanocomposite can effectively retard the undesirable aggregation of the Pd nanoparticles because of the robust protection of CeO_2 shells, thereby preserving the high catalytic activity of the Pd nanoparticles. The other more significant advantage of Pd@hCeO_2 as compared to supported Pd/CeO_2 for catalytic reaction in solution is that the core-shell structure can

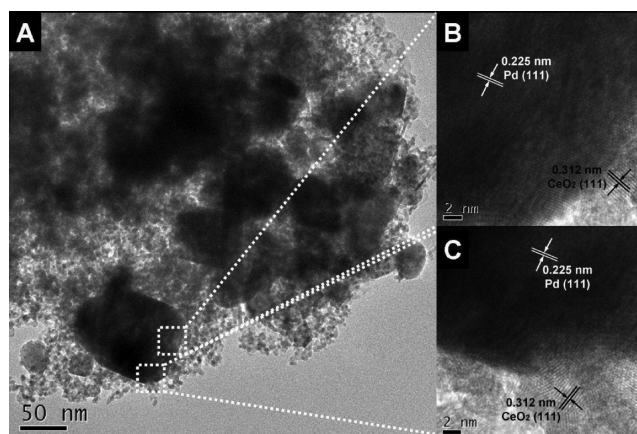


Figure 5. Typical (A) TEM and (B, C) HRTEM images of supported Pd/CeO_2 nanocomposite.

effectively prevent the leaching of Pd metal, thus making Pd@hCeO_2 be a reusable catalyst with antideactivation capability. This prominent feature can be corroborated by the very stable recycling catalytic activity test on Pd@hCeO_2 (Figure 6A) and its steady nanostructure. Through comparing the morphology of the fresh and used Pd@hCeO_2 hollow core-shell catalyst (see Figure S7 in the Supporting Information), it can be found that there is no obvious change in the morphology after the catalytic process which is in line with its excellent repeated catalytic activity. However, the obvious activity loss is clearly observed for supported Pd/CeO_2 , as shown in Figure 6B. The inductively coupled plasma mass spectrometry (ICP-MS) analysis on the supernatant after catalytic reduction of 4-NP over supported Pd/CeO_2 faithfully evidence the leaching of Pd metal particles into solution (see Figure S8 in the Supporting Information). Compared to deionized (DI) water as a reference sample, it is apparent that the obvious leaching of Pd nanoparticles is found for supported Pd/CeO_2 after the catalytic reduction reaction, whereas such undesirable phenomenon is not observed for the Pd@hCeO_2 core-shell nanocomposite. The color of the supernatants, as displayed in Figure S9 (Supporting Information), also provides the direct proof of Pd leaching into solution for the case over supported Pd/CeO_2 catalyst, i.e., a brown color appears for the supernatant after catalytic reduction of 4-NP over supported Pd/CeO_2 , which indicates the leaching of Pd nanoparticles being consistent with the ICP-MS analysis. In addition, X-ray photoelectron spectroscopy (XPS) measurements have also been carried out for fresh and used supported Pd/CeO_2 nanocomposite to analyze the content of Pd on the surface of the samples. It is easy to see from Figure S10 (see the Supporting Information) that the normalized intensity of Pd 3d X-ray photoelectron spectra (XPS) for the used supported Pd/CeO_2 is much weaker than that of its fresh counterpart, indicating that the content of Pd on the surface of the used supported Pd/CeO_2 is obviously decreased after the catalytic process in solution. Therefore, all of these results provide sufficient proof for the leaching of Pd nanoparticles in supported Pd/CeO_2 , which thus leads to the significant deactivation of catalytic activity. In sharp contrast, because of the anti-leaching feature of the Pd@hCeO_2 core-shell nanocomposite, it is able to serve as a stable, reusable catalyst without activity loss for selective reduction of aromatic nitro compounds in water.

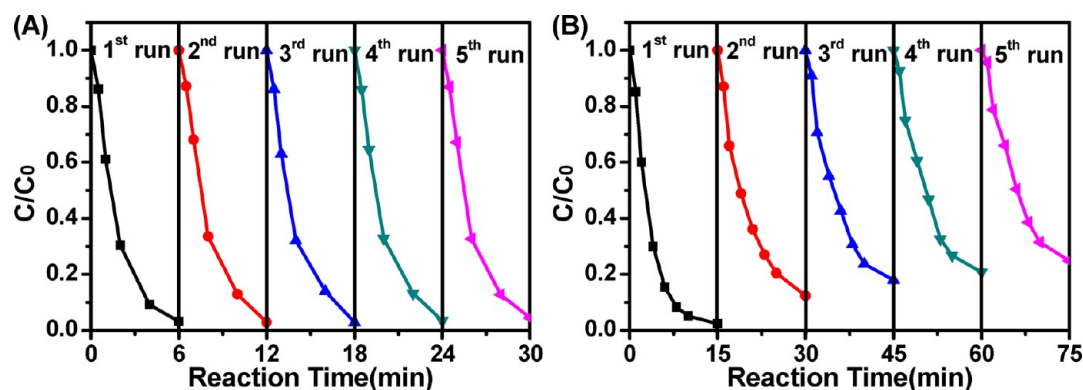
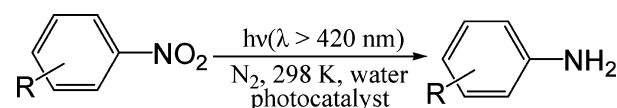


Figure 6. Stability testing of thermocatalytic activity of (A) Pd@hCeO₂ core-shell and (B) supported Pd/CeO₂ nanocomposites for reduction of 4-nitrophenol under ambient conditions.

Unlike the metal core@inactive shell (e.g., SiO₂, ZrO₂, carbon shell) nanocomposites,^{3,9,10,14,16,17,19,25–27} the visible-light photoactive CeO₂ shell in Pd@hCeO₂ can bestow the additional function for its photocatalytic applications. The photocatalytic performance of core-shell Pd@hCeO₂ and the reference samples, i.e., supported Pd/CeO₂ and commercial CeO₂, toward selective reduction of aromatic nitro compounds in water has been studied under visible-light irradiation. It is seen clearly from Table 1 that Pd@hCeO₂ demonstrates improved photoactivity as compared to supported Pd/CeO₂ and commercial CeO₂. There is no evidence for ring reduction in the photocatalytic processes which is in agreement with the previous reports.⁵⁶ The order in the photoactivity for reduction of aromatic nitro compounds is Pd@hCeO₂ > supported Pd/CeO₂ > commercial CeO₂, which is similar to that reflected in the thermocatalytic process as discussed above. Importantly, Pd@hCeO₂ shows very stable photoactivity during the test on reused Pd@hCeO₂ sample, whereas significant deactivation of photoactivity occurs for supported Pd/CeO₂ as will be discussed later.

It should be stressed that the reaction mechanism for photocatalytic reduction of aromatic nitro compounds is totally different from that in the thermocatalytic process. During the photocatalytic reduction, the CeO₂ shell acts as the primary active component, which is excited to give photogenerated electron-hole pairs under visible light irradiation while the Pd nanoparticles cores with low lying Fermi level serve as an electron reservoir to prolong the lifetime of the charge carriers.^{43,57} In particular, the three-dimensional interfacial contact between Pd cores and hollow CeO₂ shells facilitates the efficient charge carrier transfer, thereby leading to the enhanced fate of photogenerated electron-hole pairs from CeO₂ under visible-light irradiation. This is faithfully supported by the photoluminescence (PL) analysis (Figure 7), which is a well-known technique to study surface process involving the electron-hole fate of semiconductors.⁵⁸ The PL intensity of the core-shell Pd@hCeO₂ is much weaker than that of supported Pd/CeO₂ and commercial CeO₂, thus indicating the efficiently prolonged lifetime of electron-hole pairs, which is in line with the photocurrent-voltage plots as displayed in Figure 8. The photocurrent density obtained on Pd@hCeO₂ under visible light irradiation is enhanced as compared to that of supported Pd/CeO₂ and commercial CeO₂, which suggests the longer life span achieved on the Pd@hCeO₂ core-shell nanocomposite.^{59–61} On the other hand, the photogenerated holes are scavenged by the quenching agent of ammonium

Table 1. Photocatalytic Reduction of Substituted Aromatic Nitro Compounds over Pd@hCeO₂ Core-Shell Nanocomposite, Supported Pd/CeO₂, and Commercial CeO₂ Aqueous Suspension under Visible-Light Irradiation ($\lambda > 420$ nm) with the Addition of Ammonium Oxalate As Quencher for Photogenerated Holes and N₂ Purge at Room Temperature



	Substrate	t/[h]	Conversion (%)		
			Pd@hCeO ₂	Pd/CeO ₂	CeO ₂
1		6	93	77	19
2		6	87	69	16
3		6	99	81	22
4		6	64	44	13
5		6	50	35	8
6		6	43	22	6
7		4	96	75	14
8		6	84	55	11
9		4	92	75	17
10		4	94	73	15

oxalate. Thus, the improved lifetime of photogenerated electrons for Pd@hCeO₂ can effectively lead to the enhanced photoactivity toward the sequential reduction of the nitro group.^{56,62} Furthermore, the electrochemical impedance spectroscopy (EIS) Nyquist plots reveal another advantage of Pd@hCeO₂ core-shell nanocomposite. As shown in Figure 9, the Pd@hCeO₂ electrode exhibits decreased arc at high frequency

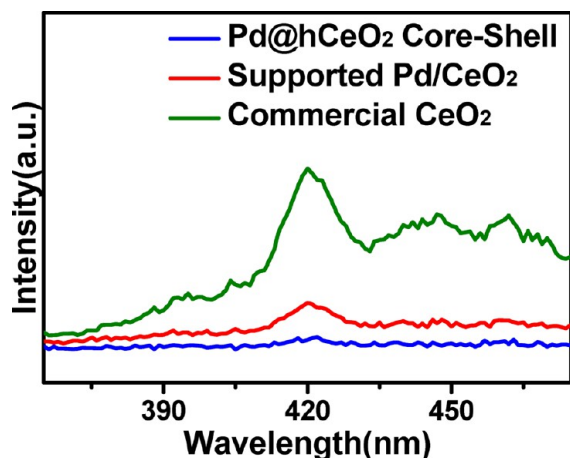


Figure 7. Photoluminescence (PL) spectra of commercial CeO_2 , supported Pd/CeO_2 , and Pd@hCeO_2 core-shell nanocomposites.

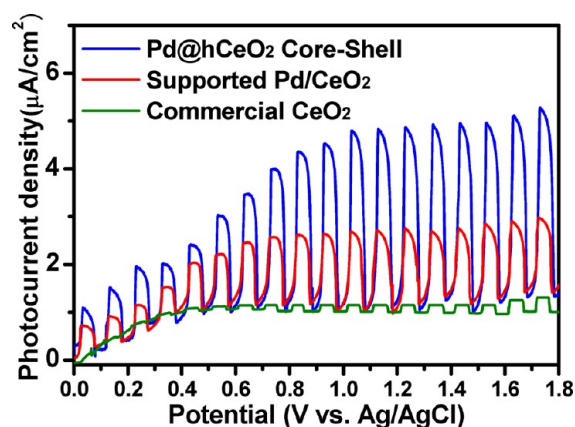


Figure 8. Chopping visible-light photocurrent-voltage curves of commercial CeO_2 , supported Pd/CeO_2 and Pd@hCeO_2 core-shell nanocomposites in 0.2 M Na_2SO_4 (pH 6.8) aqueous solution versus Ag/AgCl .

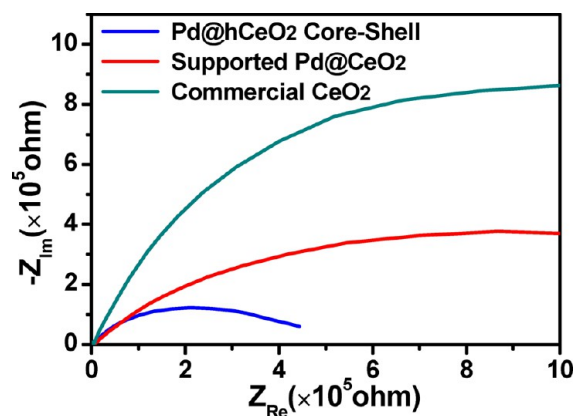


Figure 9. Electrochemical impedance spectroscopy (EIS) Nyquist plots of commercial CeO_2 , supported Pd/CeO_2 and Pd@hCeO_2 core-shell nanocomposites under visible-light irradiation ($\lambda > 420$ nm) in 0.2 M Na_2SO_4 aqueous solution (pH 6.8).

under visible light irradiation compared to supported Pd/CeO_2 and commercial CeO_2 electrodes, manifesting that the more efficient transfer of charge carriers is obtained over Pd@hCeO_2 than supported Pd/CeO_2 and commercial CeO_2 .^{63,64}

The optical properties measurement by UV-vis diffuse reflectance spectra (DRS) (see Figure S11 in the Supporting Information) shows that the introduction of Pd nanoparticles increases the absorption intensity of the samples in the visible light region. In particular, Pd@hCeO_2 has a much better absorption capability than supported Pd/CeO_2 ; this may be ascribed to its specific hollow core-shell structure with tiny Pd nanoparticles, which allows more efficient, permeable absorption and scattering of visible light, thereby contributing to the photoactivity enhancement. More significantly, as reflected in Figure 10, similar to the excellent catalyst reusability for

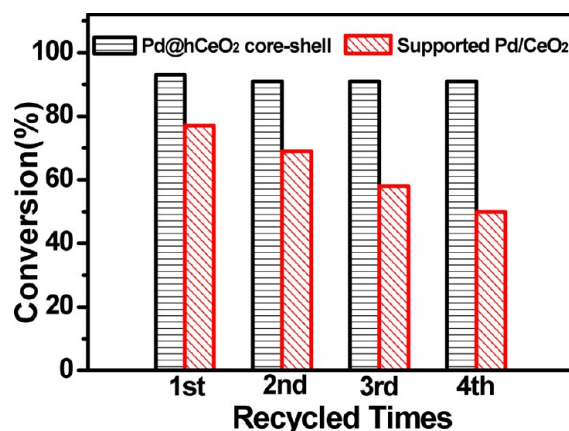


Figure 10. Stability testing of photocatalytic activity of supported Pd/CeO_2 and Pd@hCeO_2 core-shell nanocomposites for reduction of 4-nitrophenol under visible light irradiation ($\lambda > 420$ nm) for 6 h.

thermocatalytic reduction, the core-shell Pd@hCeO_2 does not have the loss of photoactivity neither during the recycled activity testing on reused samples whereas the significant loss of photoactivity is also clearly observed for supported Pd/CeO_2 . As mentioned above on the remarkable decrease of supported Pd/CeO_2 activity in heterogeneous thermocatalytic reduction of aromatic nitro compounds in water, the significant leaching of Pd nanoparticles in supported Pd/CeO_2 is also the main reason accounting for the decline in its recycling photocatalytic performance. The loss of noble metal Pd for supported Pd/CeO_2 markedly decreases the optical absorption in the visible light region (see Figure S12 in the Supporting Information), as clearly evidenced by the DRS comparison for the fresh and used supported Pd/CeO_2 samples. In distinct contrast, there is no significant change in the visible light absorption for the fresh and used Pd@hCeO_2 core-shell nanocomposite. The variation in the optical properties can also be well-reflected by the color change of the fresh and used samples as shown in Figure S12 in the Supporting Information. Therefore, it is reasonable to understand that the core-shell Pd@hCeO_2 can function as a stable, robust and reusable catalyst for both thermocatalytic and photocatalytic reduction of aromatic nitro compounds in a solution phase, whereas the case is not for traditional supported Pd/CeO_2 .

In addition, the surface area and porosity of the Pd@hCeO_2 core-shell and supported Pd/CeO_2 nanocomposites have been characterized. It is easy to see from Figure 11 that both of the nitrogen adsorption-desorption isotherms are ascribed to type IV isotherm according to the IUPAC classification.⁶⁵ The isotherm of Pd@hCeO_2 core-shell nanocomposite shows typical H3 hysteresis loop characteristic of mesoporous solids.⁶⁵ The BET surface area of the Pd@hCeO_2 core-shell composite

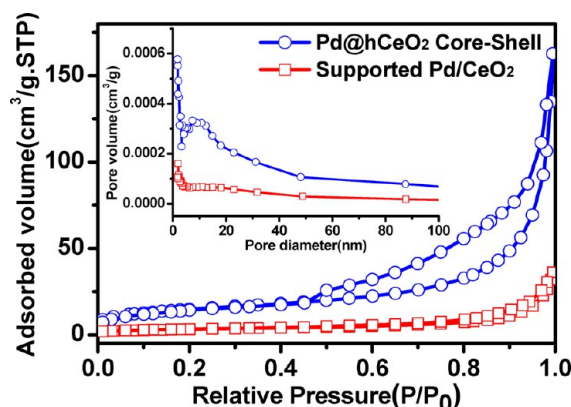


Figure 11. Nitrogen adsorption–desorption isotherm of the Pd@hCeO₂ core–shell and supported Pd/CeO₂ composites; the inset is the corresponding pore diameter distribution.

is measured to be $53 \text{ m}^2 \text{ g}^{-1}$, which is almost five times as large as that of supported Pd/CeO₂ ($11 \text{ m}^2 \text{ g}^{-1}$), suggesting that the Pd@hCeO₂ core–shell nanocatalyst could provide more active sites for catalytic reactions to proceed. The pore volume of the core–shell Pd@hCeO₂ and supported Pd/CeO₂ composites is $0.21 \text{ cm}^3 \text{ g}^{-1}$ and $0.05 \text{ cm}^3 \text{ g}^{-1}$, respectively. These results indicate that the Pd@hCeO₂ with a specific core–shell structure has higher specific surface area and pore volume than the supported Pd/CeO₂ counterpart, which is able to enhance the adsorption capability of nitro compounds over Pd@hCeO₂ thereby contributing to the improvement of catalytic activity. However, the catalyst stability behavior can not be attributed to the difference of surface area and porosity of the two samples Pd@hCeO₂ and supported Pd/CeO₂. On the contrary, it should be ascribed to the fact if there is the leaching of Pd metal particles into the solution, as discussed above. Thus, it is clear that the specific core–shell structure endows Pd@hCeO₂ with an enhanced and very stable catalytic activity toward both thermocatalytic and photocatalytic reduction of nitro compounds in an aqueous phase.

CONCLUSION

In summary, we have prepared a Pd@hCeO₂ hollow core–shell nanocomposite featuring tiny Pd multicore encapsulated in the hollow CeO₂ shell. The confined robust shield of CeO₂ shell efficiently prevents the undesirable aggregation of Pd nanoparticles during a high-temperature calcination process whereas the significant aggregation of Pd nanoparticles occurs for traditional supported Pd/CeO₂ catalyst. The Pd nanoparticles as multicore located inside the CeO₂ shell with three-dimensional interfacial contact allows for the more sufficient use of the metal-oxide interface while inhibiting the leaching of Pd metal for the catalytic reaction in solution. Thus, Pd@hCeO₂ shows an improved activity and excellent reusability toward both thermocatalytic and photocatalytic selective reduction of aromatic nitro compounds in water under ambient conditions. This work provides a generic concept example to perform the same catalytic reaction via two different catalytic processes, i.e., thermocatalysis and visible light photocatalysis, which is afforded by harnessing the interactive function of metal core and reactive semiconductor shell that are integrated by such a hollow core–shell strategy. The promising results herein suggest that the metal core@reactive semiconductor shell

nanocomposite can offer a class of nanospace confined reactor for multifunctional catalytic applications.

EXPERIMENTAL SECTION

Materials. Glucose (C₆H₁₂O₆), palladium chloride (PdCl₂), cerium chloride heptahydrate (CeCl₃·7H₂O), polyvinylpyrrolidone (PVP), commercial cerium oxide (CeO₂) powder, hydrochloric acid (HCl), and ethanol (C₂H₅O) were supplied by Sinopharm chemical reagent Co., Ltd. (Shanghai, China). All materials were used as received without further purification. Deionized (DI) water used in the synthesis was obtained from local sources.

Preparation. (I) Fabrication of carbon sphere template. The monodisperse carbon particles as template are generated by the hydrothermal treatment of glucose aqueous solution (0.5 M) at 453 K for 6 h.^{39,40} (II) Preparation of PVP-capped noble metal Pd nanoparticles. Palladium colloid nanoparticles were synthesized via the alcohol reduction method.^{36,43,66} Typically, H₂PdCl₄ aqueous solution (2.0 mM) was prepared by dissolving PdCl₂ in HCl aqueous solution. A mixture containing 15 mL of 2.0 mM H₂PdCl₄ solution, 21 mL of H₂O, 14 mL of ethanol, and 0.0667 g of PVP (average MW of PVP 40 000) was refluxed at 363 K for 3 h. The resulting brown product is PVP-capped palladium colloidal solution. (III) Synthesis of Pd@hCeO₂ core–shell nanocomposite. The as-prepared carbon spheres (21.2 mg) was dispersed in 10 mL of DI water by ultrasonication to achieve homogeneous dispersion into which 10 μmol of the as-prepared Pd colloids solution was added. This mixture was stirred for 10 min to allow Pd nanoparticles to be adsorbed onto the surface of carbon spheres. Then, a solution obtained by dissolving 0.2 mmol CeCl₃·7H₂O in 14 mL of DI water was poured into the above mixture. The resulting intermixture was stirred continuously for 20 min and then transferred to 50 mL of Teflon-lined stainless steel autoclave to conduct hydrothermal treatment at 453 K for 6 h. After that, the products were cooled at room temperature, separated by centrifugation and rinsed with deionized water. Followed by a dry process at 333 K and calcination at 773 K for 2 h in air, the Pd@hCeO₂ core–shell nanocomposite was obtained. (IV) Preparation of supported Pd/CeO₂ composite. The supported 5 wt % Pd/CeO₂ catalyst was prepared by the rotary evaporation of commercial CeO₂ powder with an appropriate amount of colloid Pd nanoparticles solution followed by a calcination process at 773 K for 2 h.

Characterization. Zeta potentials (ξ) measurements were recorded on dynamic light scattering analysis (Zeta sizer 3000HSA) at room temperature of 298 K. The phase composition of the samples was determined on a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu K α radiation at 40 kV and 40 mA in the 2θ ranging from 20 to 80° with a scan rate of 0.02° per second. Field-emission scanning electron microscopy (FESEM) was used to characterize the morphology and elemental distribution of the samples on a FEI Nova NANOSEM 230 spectrophotometer. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The optical properties of the samples were analyzed by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary 500, Varian Co.), in which BaSO₄ was employed as the internal reflectance standard. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a Thermo Scientific ESCA Lab250 spectrometer which consists of a monochromatic Al K α as the X-ray source, a hemispherical analyzer and sample stage with multiaxial adjustability to obtain the surface composition of the sample. All of the binding energies were calibrated by the C 1s peak at 284.6 eV. Thermogravimetric analysis was conducted on a Perkin-Elmer TGA7 analyzer under 10 mL min^{−1} flowing air and at a heating rate of 10 K min^{−1}. The photoluminescence spectra (PL) for solid samples were investigated with an excitation wavelength of 250 nm on an Edinburgh FL/FS900 spectrophotometer. The electrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference

electrode, respectively. The electrolyte was 0.2 M Na₂SO₄ aqueous solution without additive (pH 6.8). The working electrode was prepared on indium–tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5 mg sample was dispersed in 0.5 mL of DMF by sonication to get slurry. The slurry was spread onto the pretreated ITO glass. After air drying, the working electrode was further dried at 393 K for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The exposed area of the working electrode was 0.25 cm². The chopping photocurrent–voltage curves were measured on a BAS Epsilon workstation with applied potentials of 0 to +1.8 V. The electrochemical impedance spectroscopy (EIS) experiments were conducted on a Precision PARC workstation. After thermocatalytic reduction of 4-NP over the Pd@hCeO₂ core–shell and supported Pd/CeO₂ nanocomposites under ambient conditions, the mixture was centrifuged to remove the catalyst particles. The supernatant was treated by aqua regia and diluted 10000 times with DI water. Then, the obtained sample was analyzed using an Agilent 7500 Series Inductively Coupled Plasma–Mass Spectrometer (ICP–MS) to detect the signal of element Pd in the supernatant. The parameters for the ICP–MS spectrometer were as follows: radio frequency (RF) power = 1400 W, RF matching = 1.77 V, nebulizer pump rate = 0.10 rps, carrier gas flow = 0.80 L min^{−1}, makeup gas flow = 0.20 L min^{−1}, spray chamber temperature = 275 K.

Thermocatalytic Activity. The thermocatalytic reactions were carried out in a breaker. 10 mg of NaBH₄ was dissolved into 50 mL of aromatic nitro compounds aqueous solution (20 mg L^{−1}). The use of a high excess of NaBH₄ aims to ensure that its concentration remains essentially constant during the whole reaction.^{50–52} This mixture was stirred vigorously at room temperature for 5 min to generate uniform aqueous solution. Afterward, 2 mg of the catalyst was added into the above solution. During the process of the reaction, 3 mL of solution was withdrawn by a syringe and filtered by 0.45 μm Millipore film at each time interval for UV–vis spectroscopy analysis.

Photocatalytic Activity. In a typical photocatalytic reaction, a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co., Ltd.) with a UV–CUT filter to cut off light of wavelength <420 nm was used as the irradiation source. 10 mg of the sample and 20 mg of ammonium oxalate (AO) were added into 30 mL of the aromatic nitro compounds solution (10 mg L^{−1}) in a quartz vial. Before visible light illumination, the above suspension was stirred in the dark for 1 h to ensure the establishment of adsorption–desorption equilibrium between the sample and reactant. During the process of the reaction, 3 mL of sample solution was collected at a certain time interval and centrifuged to remove the catalyst completely at 12000 rpm. Afterward, the solution was analyzed on a Varian UV–vis spectrophotometer (Cary–50, Varian Co.). The whole experimental process was conducted under N₂ bubbling at the flow rate of 80 mL min^{−1}.

■ ASSOCIATED CONTENT

■ Supporting Information

TEM image and size distribution of Pd nanoparticles, TEM image of used Pd@hCeO₂ core–shell nanocomposite, zeta potentials (ξ) of carbon spheres and carbon spheres–Pd composite in deionized water, N 1s XPS spectra and thermogravimetric analysis of the Pd@hCeO₂ hollow core–shell nanocomposite, XRD, DRS results and the corresponding photographs of commercial CeO₂, supported Pd/CeO₂ and Pd@hCeO₂ core–shell nanocomposites, time-dependent UV–vis spectral changes of the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-NA) catalyzed by Pd@hCeO₂ core–shell nanocomposite in the presence of NaBH₄ solution under ambient conditions, ICP–MS spectra of element Pd in the DI water and the supernatant after thermocatalytic reduction of 4-NP over Pd@hCeO₂ core–shell and supported Pd/CeO₂ nanocomposite and the corresponding bar chart comparison, photographs of the supernatant before and after thermocata-

lytic reduction of 4-NP over the Pd@hCeO₂ core–shell nanocomposite and supported Pd/CeO₂ nanocomposite under ambient conditions, the normalized intensity of Pd (3d) XPS spectra of fresh and used supported Pd/CeO₂ nanocomposite, DRS and photographs of the supported Pd/CeO₂ and Pd@hCeO₂ core–shell nanocomposites before and after the photocatalytic reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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