

REVIEW

CeO₂-encapsulated noble metal nanocatalysts: enhanced activity and stability for catalytic application

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Encapsulation of small noble metal nanoparticles has received attention owing to the resulting highly increased stability and high catalytic activity and selectivity. Among the types of inert metal oxides, CeO₂ is unique. It is inexpensive and highly stable, and, more importantly, the unique electronic configuration gives it a strong capability to provide active oxygen. The method of fabricating CeO₂-encapsulated noble metal nanocatalysts is determined by the requirements of the application. In this review, we first describe the various types of encapsulated noble metals and then the current developments of synthesis in detail, including the types of hybrid nanostructures and successful synthetic strategies. The following section, concerning catalytic applications, is divided into three topics: anti-sintering capabilities, catalytic activities and selectivities. We hope that this review of the recent achievements and the proposed strategy for addressing the emerging challenges will inspire further developments in this research area.

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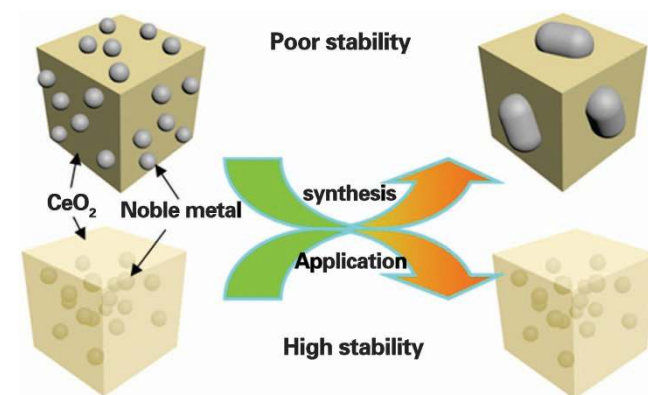
INTRODUCTION

Noble metal catalysts have received much attention in the past decade because of their unique chemical and physical properties, and they have been widely applied in industrial use.^{1–10} With the help of noble metal catalysts, environmental friendly catalysis resulting in the decreased production of pollutants, waste minimization and new synthetic routes that circumvent modern synthetic techniques such as Sonogashira–, Heck– and Miyaura–Suzuki-type reactions can be easily realized.^{11–15} However, for most technologically important chemical processes, noble metal catalysts spontaneously aggregate and grow to reduce the surface energy, which limits the catalysts' lifetime and efficiency. The ultra-high prices of noble metals have also seriously limited their further development. Because of the development of modern industry, there remains a critical need for robust, simple and readily controllable routes to fabricate highly active, stable and recyclable nanocatalysts.

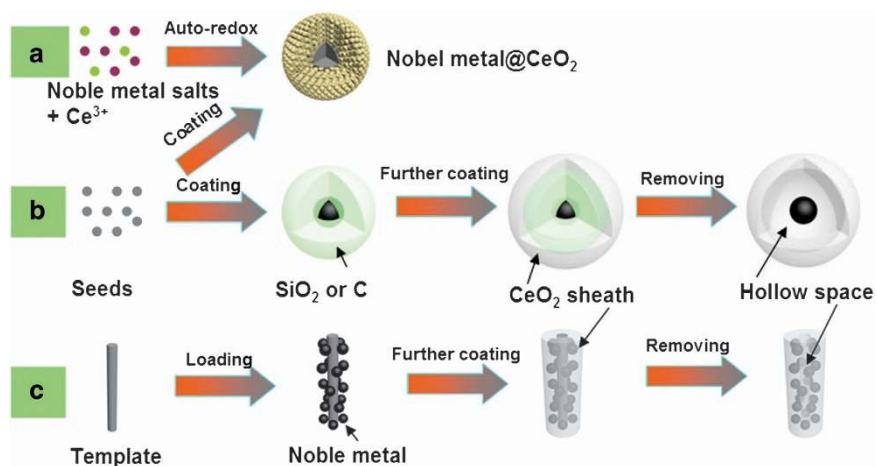
To maximize the catalytic performance of noble metals and reduce the quantity used, it is necessary to load the active centers on a substrate.^{16–20} A suitable substrate not only provides a high surface area to stabilize small nanoparticles (NPs) under long-term catalysis but also renders hybrid junctions with rich redox reactions on the two-phase interface. With the development of synthetic techniques in nanoscience, small noble metal NPs, especially atomically precise nanoclusters/metal oxide hybrid nanostructures, have been successfully fabricated very recently, and these materials exhibit remarkable enhanced catalytic activity and selectivity.^{21–23} However, this simple loading form cannot meet the growing demand for the stability, because the noble metal catalysts contain numerous exposed surfaces

and are always used in harsh environments, such as those with high temperatures and concentrated acid and alkali solutions. The lack of surface protection causes the noble metal NPs to easily aggregate to minimize the surface energy, which can cause a serious loss of the catalytic active sites, a reduction of the catalytic activity and even complete inactivation (as shown in Scheme 1). Therefore, determining how to improve the stability of the noble metal catalysts is one of the most important problems in current nanoscience.

The concept of 'encapsulation' emerged with the aim of substantially increasing the stability of noble metals. Embedding small noble



Scheme 1 Schematic representation of the different stabilities of noble metal-CeO₂ simple loading form and CeO₂ encapsulated noble metal nanostructures under long-term synthetic or catalytic processes.



Scheme 2 Schematic representation of the three methods for the synthesis of CeO₂-encapsulated noble metal nanostructures: (a) auto-redox reaction, (b) seeded growth method, and (c) hard template strategy.

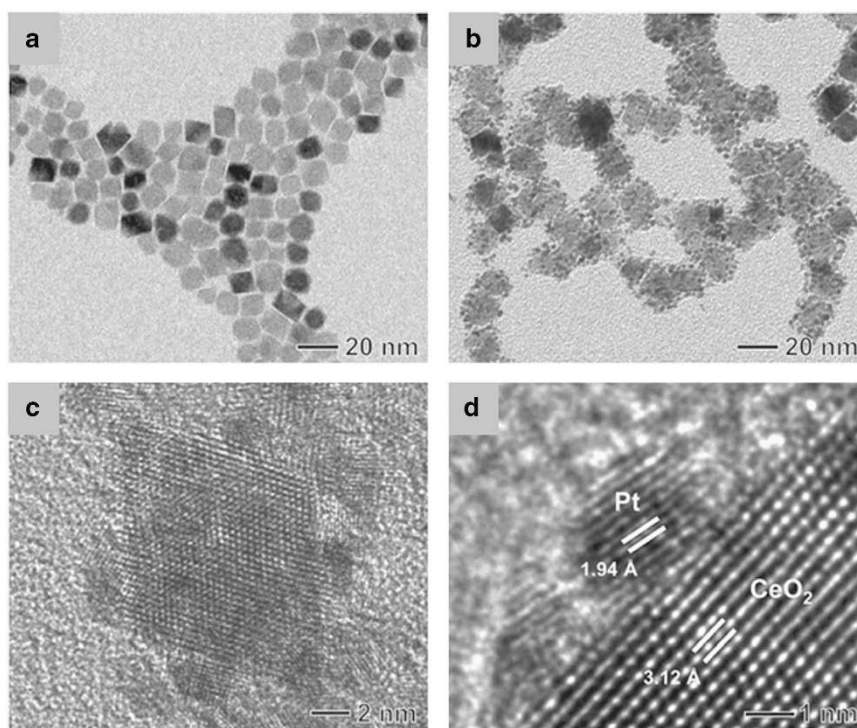


Table 1. Zeta potential values of AHA-stabilized CeO₂ octahedra, PVP-stabilized CeO₂ octahedra, Pt/CeO₂ hybrid nanostructures, and PVP-stabilized Pt nanocrystals at pH ≈ 5.5.

	Stabilizer	Zeta Potential [mV]
CeO ₂ octahedra	AHA	+48.4
	PVP	+0.6
Pt/CeO ₂ nanostructures	AHA and PVP	-1.1
Pt nanocrystals	PVP	-6.7

Figure 1 TEM images of CeO₂ octahedral stabilized by AHA (a) and Pt-CeO₂ hybrid nanostructures (b); HR TEM images of the Pt-CeO₂ (c) and (d). Reprinted with permission from Yu *et al.*⁷⁶ Copyright 2010 Wiley-VCH.

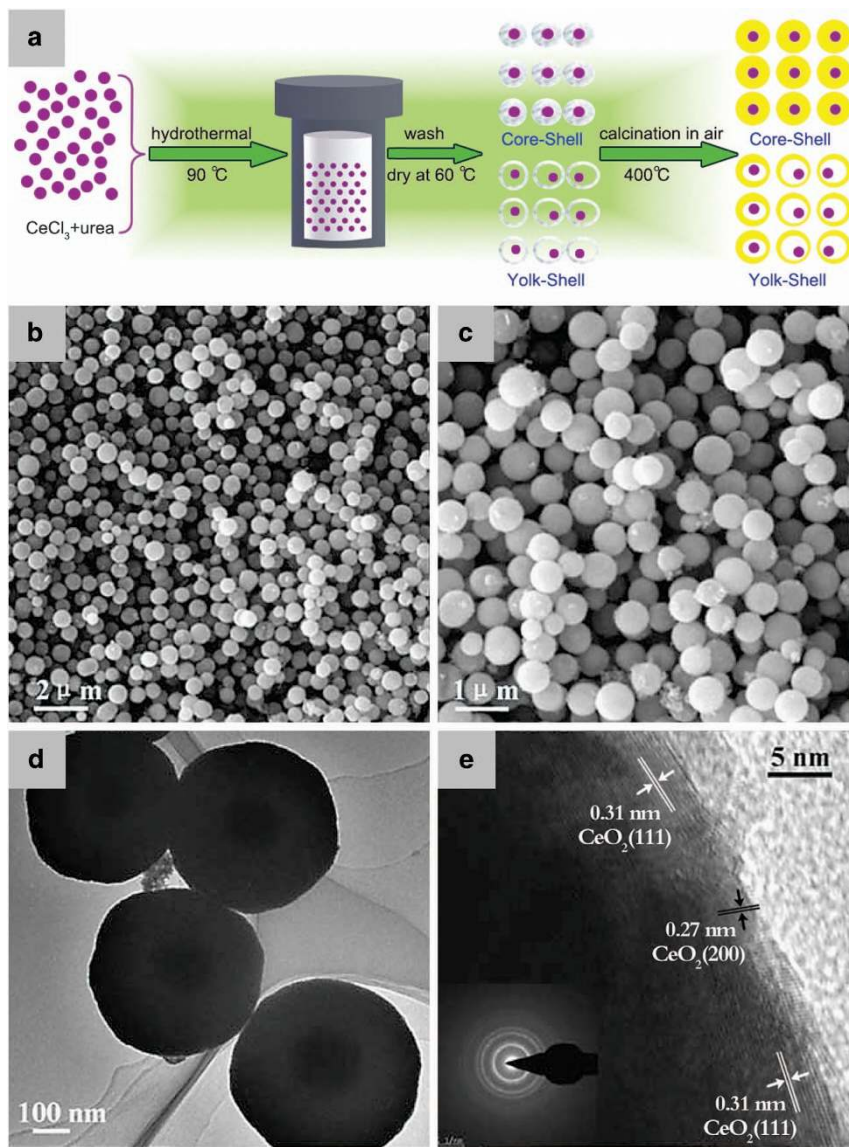


Figure 2 (a) Schematic representation of the synthesis of the Pt@CeO₂ core-shell or yolk-shell nanostructures via a hydrothermal method; (b and c) SEM images of Pt@CeO₂ core-shell NPs; (d) TEM image of Pt@CeO₂ core-shell NPs; and (e) high-resolution TEM image of Pt@CeO₂ core-shell NPs. Reprinted with permission from Zhang *et al.*⁷⁷ Copyright 2011 Royal Society of Chemistry.

metal NPs into highly stable porous inorganic nanostructures (for example, CeO₂,^{24–26} TiO₂,^{27–34} SiO₂,^{35–39} ZrO₂,^{40,41}) and encapsulating noble metal NPs within metal oxides to form core-shell or yolk-shell nanostructures are common strategies. Three requirements must be satisfied simultaneously: (1) the sheath must maintain its chemical inertness in the specific working environment; (2) mass transformation must be avoided during the long-term synthetic and catalytic process, especially under high-temperature treatment; (3) after heat treatment, the active sites should maintain their original particle size, shape and catalytic activities.

Of the various shell materials, including SiO₂, TiO₂, SnO₂, ZrO₂ and CeO₂, CeO₂ clearly has the broadest spectrum of applicability. Cerium (Ce) is one of the most abundant elements and is much more abundant in the Earth's crust (66.5 p.p.m.) than even copper (60 p.p.m.) or tin (2.3 p.p.m.). Because of its unique electronic configuration ([Xe] 4f²6s²), Ce has two common valence states—Ce³⁺ and Ce⁴⁺—which give CeO₂ excellent chemical and physical properties: 1/4 O₂, at

most, can be released from each CeO₂ unit cell.⁴² It serves as an active oxygen donor in many reactions, such as three-way catalytic reactions to eliminate toxic automobile exhaust,⁴³ the low-temperature water-gas shift reaction,^{44,45} oxygen sensors,^{46–48} oxygen permeation membrane systems⁴⁹ and fuel cells.^{50–56} Furthermore, the growth process of CeO₂ NPs is easily controlled such that they can maintain their small particle sizes and uniform morphologies, key features in the coating process. Many types of CeO₂-encapsulated noble metal superstructures have been successfully prepared. There are five types of typical hybrid nanostructures: (1) core-shell hybrid nanostructures, composed of one or more cores uniformly coated with a dense CeO₂ layer; (2) yolk-shell or rattle-type hybrid nanostructures, that is, a single movable noble metal core inside a hollow CeO₂ sheath; (3) hollow multi-core-shell structures, composed of many noble metal NPs encapsulated within a CeO₂ hollow sheath; (4) sandwich structures, so-called for their interlayers composed of multiple noble metal NPs embedded in a CeO₂ film; and (5) multiple noble metal NPs

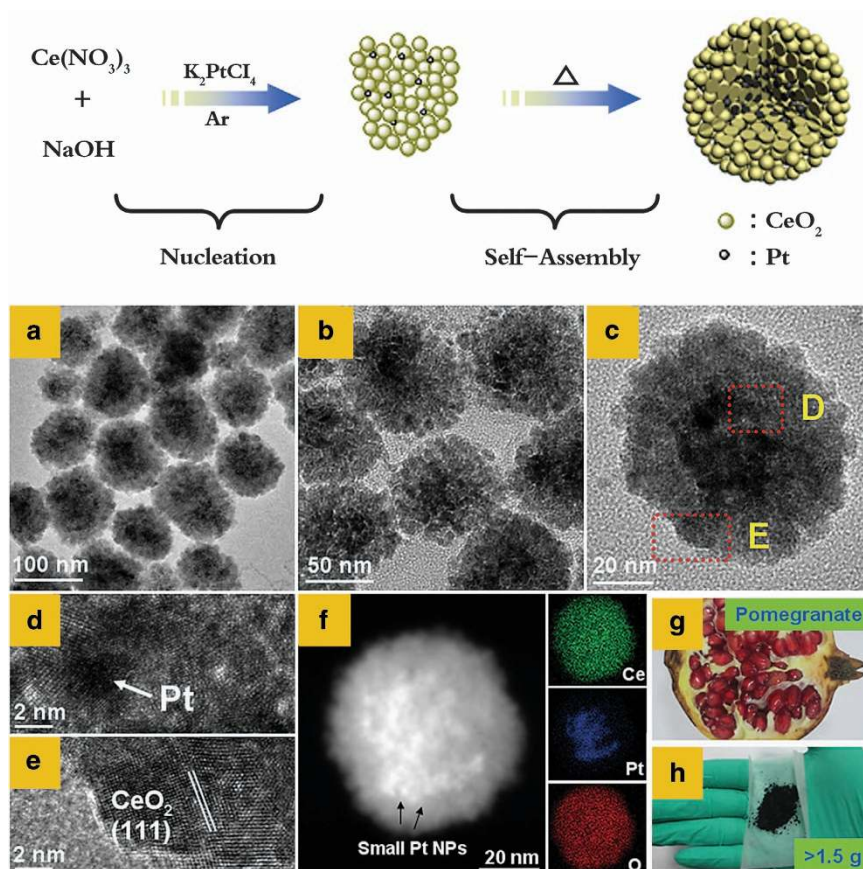


Figure 3 (a) Schematic representation of the synthesis of the Pt@CeO₂ multi-core-shell nanostructures via an auto-redox reaction; (b–d) TEM, (e and f) HR-TEM and STEM images of the as-prepared Pt@CeO₂ multi-core-shell hybrid nanostructures; (g) interior of a real pomegranate; (h) products obtained in one pot. Reprinted with permission from Wang *et al.*⁷⁸ Copyright 2013 American Chemical Society.

embedded within a porous CeO₂ matrix. However, it is not possible to cover all aspects of these categories and cite the relevant references in one article. In this review, we first summarize the preparation of CeO₂-encapsulated noble metal nanocatalysts. The following section, on catalytic applications, is divided into three topics: anti-sintering capabilities, catalytic activities and selectivity. In this section, we discuss the influence of the hybrid nanostructure on the catalytic performance. Finally, we describe the emerging challenges and future developments of CeO₂-based noble metal nanocatalysts.

SYNTHESIS OF CeO₂-ENCAPSULATED NOBLE METAL NANOCATALYSTS WITH VARIOUS MORPHOLOGIES

Very recently, many synthetic strategies have been successfully developed to prepare noble metal–CeO₂ hybrid nanocatalysts.^{57–63} Generally, the methods used for the synthesis of CeO₂-encapsulated noble metal nanocatalysts can be divided into three categories (as shown in Scheme 2): one-pot synthesis, multi-step layer-by-layer coating processes and hard-template methods. Unlike other common shell components with continuous phases, including SiO₂,^{35–39} TiO₂,^{27–34} SnO₂,^{64–66} Cu₂O,^{67–72} ZnO⁷³ and ZrO₂,^{40,41} the CeO₂ layer is composed of hundreds of tiny CeO₂ NPs assembled together instead of a single continuous crystal. Therefore, it is believed that, of the various experimental parameters, including reaction temperature, time, surface state of the noble metal seeds and solvent pH value, the most important characteristic is how the independent nucleation of the CeO₂ NPs is controlled. Many types of CeO₂-encapsulated

noble metal superstructures, such as Pt@CeO₂, Pd@CeO₂, Au@CeO₂ and Ag@CeO₂, have been successfully synthesized. However, for other noble metals, such as Ru, Ir, Rh and multi-component noble metal alloys, a similar hybrid nanostructure has yet to be reported.

CeO₂-encapsulated Pt nanostructures

Pt-based catalysts exhibit much higher catalytic activities and stabilities in many catalytic reactions. Most importantly, ultrafine Pt NPs with small particle sizes can be easily obtained as the seeds, which is beneficial for further enhancement of the catalytic activities and the coating process. Additionally, there is a strong synergistic effect between Pt and CeO₂, which could be attributed to the abundant oxygen vacancy defects, peerless oxygen storing/releasing capabilities and easy shuttling between the III–IV oxidation states of CeO₂. Consequently, CeO₂-encapsulated Pt nanostructures have been widely investigated.

Pt@CeO₂ core-shell hybrid nanostructures. Fabrication of the Pt@CeO₂ core-shell hybrid nanostructure is difficult because of the large lattice mismatch between Pt and CeO₂. To counterbalance the interfacial energy between Pt and CeO₂, embedding a layer of ligands and/or surfactant molecules between the core and sheath has been shown to be an effective method and is widely used.^{74,75} The surface of the noble metal should be densely functionalized, and specific groups should be attached outside to promote the proximal growth of the metal oxide layer. In an example of successful surface modification of CeO₂, Xia's group used 6-aminohexanoic acid as a

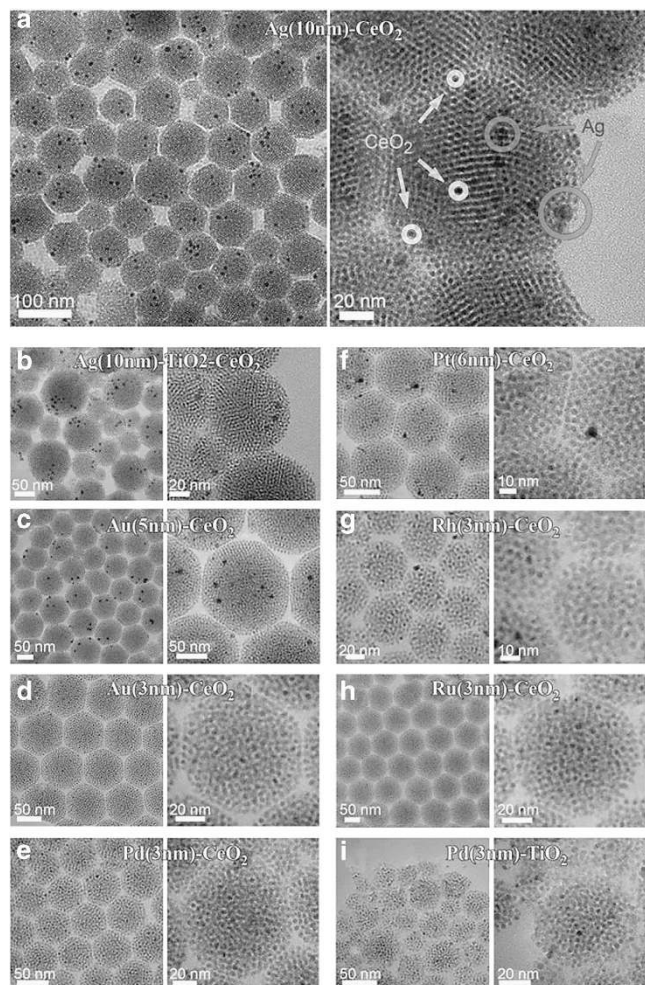


Figure 4 TEM images of mesoporous colloidal spheres built up by multiple components: (a) 10-nm Ag in porous CeO₂; (b) 10-nm Ag in porous TiO₂/CeO₂; (c) 5-nm Au in porous CeO₂; (d) 3-nm Au in porous CeO₂; (e) 3-nm Pd in porous CeO₂; (f) 6-nm Pt in CeO₂; (g) 3-nm Rh in porous CeO₂; (h) 3-nm Ru in porous CeO₂; and (i) 3-nm Pd in porous TiO₂. Reprinted with permission from Chen *et al.*⁸³ Copyright 2011 Wiley-VCH.

capping molecule to limit the growth of CeO₂ and to maintain a positively charged particle surface such that the NPs can easily hybridize to Pt, which has a negative surface (Figure 1).⁷⁶ However, such a surface modification approach is yet to be successful in the fabrication of Pt@CeO₂ core-shell hybrid nanostructures.

Single core-shell Pt@CeO₂ nanospheres have also been successfully produced by Xu and coworkers via a heterogeneous seeded growth mechanism.⁷⁷ The seeded growth strategy is used to synthesize multicomponent core-shell hybrid nanostructures. Typically, this synthetic strategy can be divided into two separate steps: first, synthesis of uniform noble metal NPs with controllable morphologies, compositions and particle sizes, and second, by using the layer-by-layer coating technology to grow a dense layer of metal oxide on the core's surface. Uniform single core-shell Pt@CeO₂ hybrid nanostructures are obtained by using the data shown in Figure 2. Control of the growth rate of the shell component is the key factor that determines whether the synthesis will be successful. Notably, as reported in Xu's paper, the core-shell nanostructure can be finely tuned by simply changing the feeding amount of CeCl₃ added to an aqueous Pt colloid solution. Our understanding is that the hydrothermal approach and the usage of

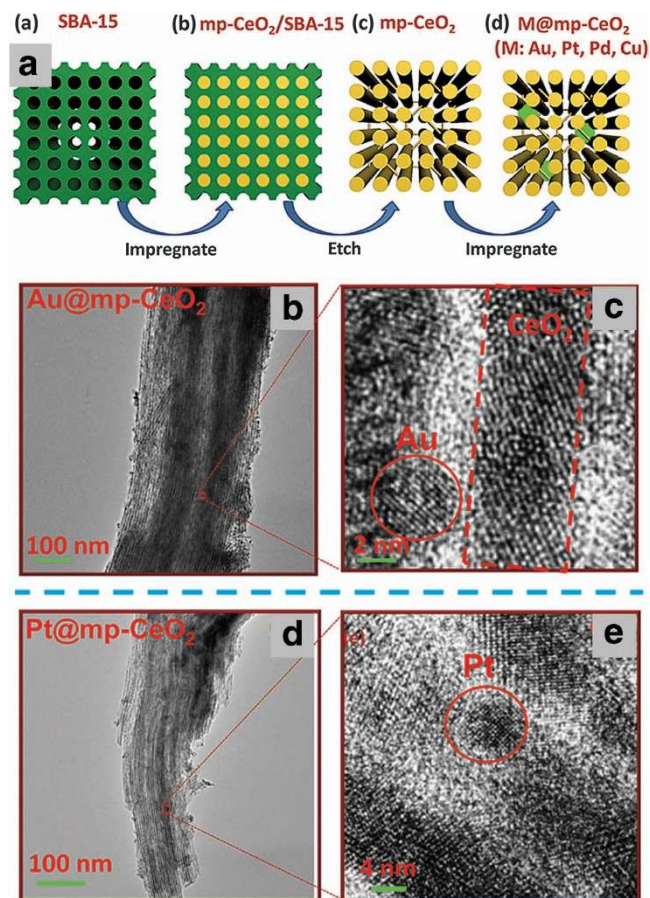


Figure 5 (a) Schematic representation of the synthesis of the noble metals@CeO₂ nanostructures; (b) large-scale image of Au@CeO₂; (c) HRTEM image of Au@CeO₂ showing the encapsulation of Au nanoclusters; (d) low-magnification TEM image of Pt@CeO₂; (e) HRTEM image showing the encapsulation of Pt nanoclusters. Reprinted with permission from Wen *et al.*²⁶ Copyright 2012 American Chemical Society.

urea are very suitable for the formation of single core-shell nanostructures seeded by noble metals for the following reasons: (1) water is the most inexpensive, nontoxic and environment friendly solvent; (2) many inorganic salts have high solubility in water, which is very important for the homogeneous nucleation of shell components; and (3) such growth conditions could ensure that the rate of OH⁻ released is slow enough to efficiently avoid the independent nucleation of the shell component.⁷⁴

In addition to the single core-shell sample, preparation of the Pt@CeO₂ multi-core-shell hybrid nanostructure has been reported via one-pot methods that are driven by special forces. Our previous report⁷⁸ noted that Ce³⁺ exhibits greater reducing capability in alkaline conditions than in neutral ones. A redox reaction can be easily triggered on the two-face interface between Pt metal salt with high oxidation potential and Ce(OH)₃ precursor. Uniform and monodisperse sphere-like Pt@CeO₂ multi-core-shell hybrid nanostructures are prepared on a large scale. The transmission electron microscopic (TEM) images are shown in Figure 3; in each sphere-like nanostructure, thousands of small CeO₂ NPs (6.2 nm in average) assembled to form a dense shell outside. Because their deeper contrast compared with CeO₂, the Pt NPs beneath the shell can be clearly distinguished. It is believed that the formation process of such superstructures involves two separate steps: first, the nucleation and growth of Pt and CeO₂

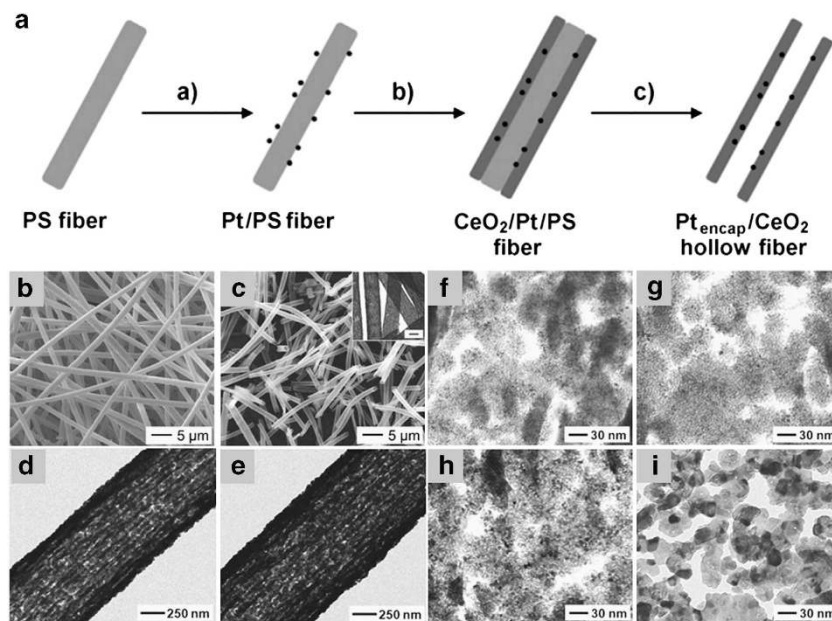


Figure 6 (a) Schematic representation of the synthesis of the Pt–CeO₂ hollow fiber nanostructures; (b and c) SEM images of PS/Pt/CeO₂ core-shell fibers (b) before and (c) after calcination; (d and e) low-magnification TEM images of Pt/CeO₂ hollow fibers after calcinations at 400 °C (d) and 800 °C (e) for two hours in air; (f–i) high-magnification TEM images of Pt/CeO₂ hollow fibers after calcinations at 400 °C (f), 500 °C (g), 600 °C (h) and 800 °C (i). Reprinted with permission from Yoon *et al.*⁸⁵ Copyright 2012 Wiley-VCH.

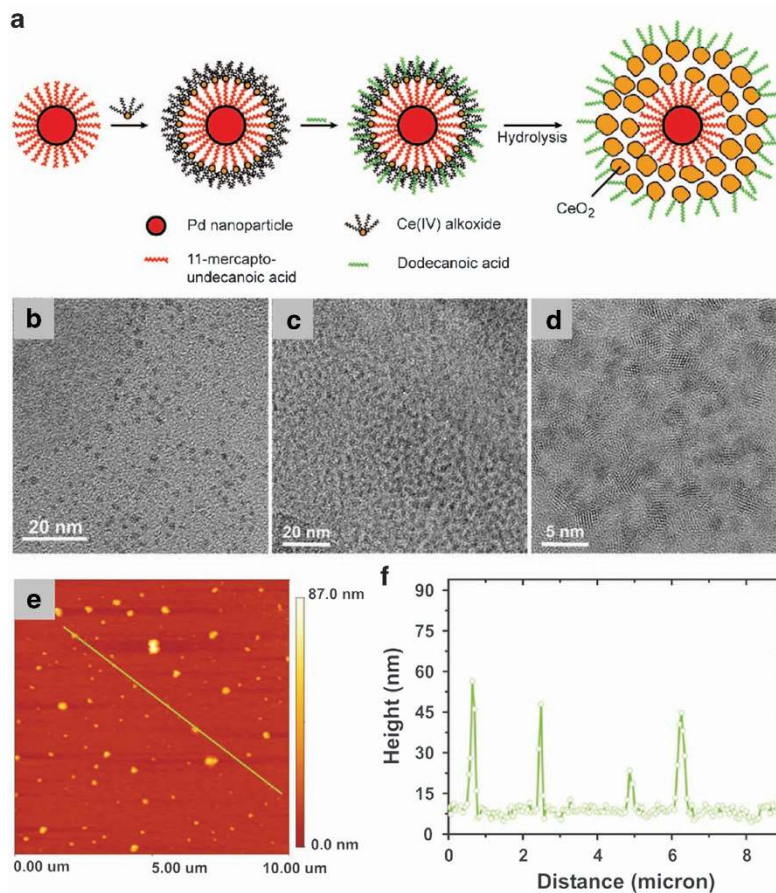


Figure 7 (a) Schematic representation of the synthesis of the Pd@CeO₂ core-shell nanostructure; (b) TEM image of MUA-protected Pd NPs; (c and d) HRTEM images of Pd@CeO₂ core-shell NPs; (e and f) AFM image and line-height measurement of Pd@CeO₂ NPs. Reprinted with permission from Cargnello *et al.*⁸⁷ Copyright 2012 American Chemical Society.

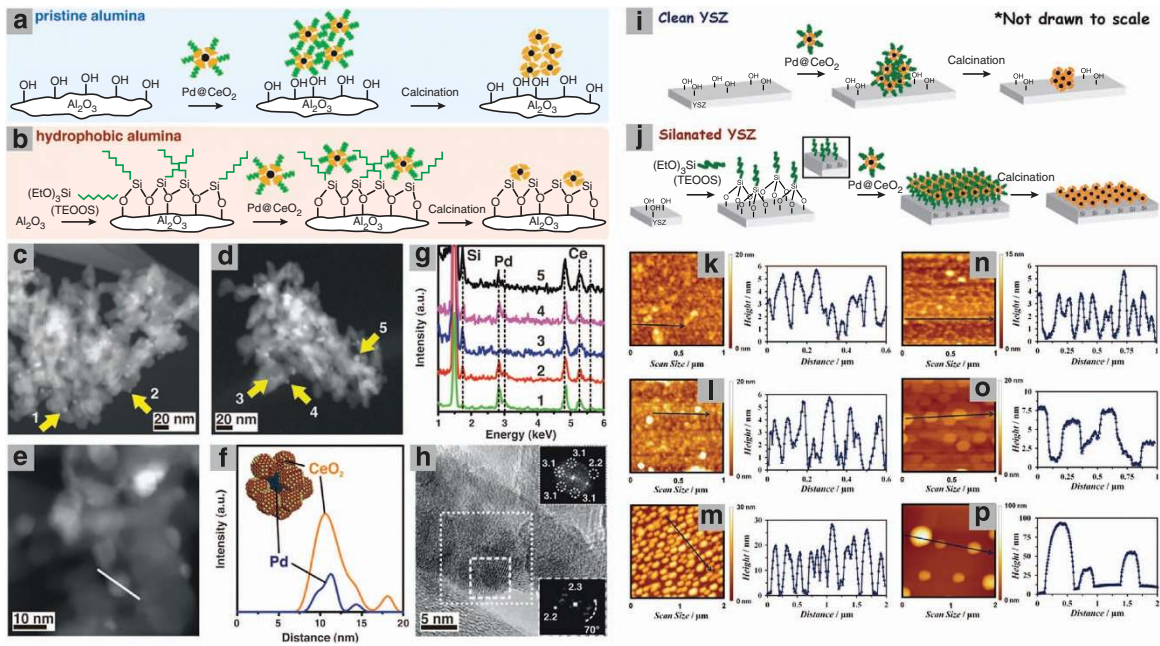


Figure 8 Schematic representation of the agglomeration of Pd@CeO₂ structures by using pristine alumina (a) and their deposition as single units after treatment of the same support with triethoxy(octyl)silane (TEOS) (b); HAADF-STEM images of Pd@CeO₂ core-shell nanostructures dispersed on hydrophobic Al₂O₃ after calcining at 500 °C (c) and 850 °C for 5 h (d); EDS spot analysis (g); high-magnification HAADF-STEM images of Pd@CeO₂/Al₂O₃ products after being calcined at 500 °C (e); the corresponding EDS line profile (f); HRTEM image of a single Pd@CeO₂ structure on the Pd@CeO₂/H-Al₂O₃ catalysts calcined at 500 °C (h). Reprinted with permission from Cargnello *et al.*⁸⁶ Copyright 2012 Science. Overview of the deposition of Pd@CeO₂ nanostructures on (i) clean YSZ (100) and (j) alkyloxane functionalized YSZ (100); AFM topography images with representative line scans for Pd@CeO₂ deposited on alkyloxane functionalized YSZ (100) after calcination in air at 723 K (k), 973 K (l), 1373 K (m); and Pd@CeO₂ deposited on clean YSZ (100) after calcination in air at 723 K (n), 973 K (o), 1373 K (p). Reprinted with permission from Adjianto *et al.*⁹⁰ Copyright 2013 American Chemical Society.

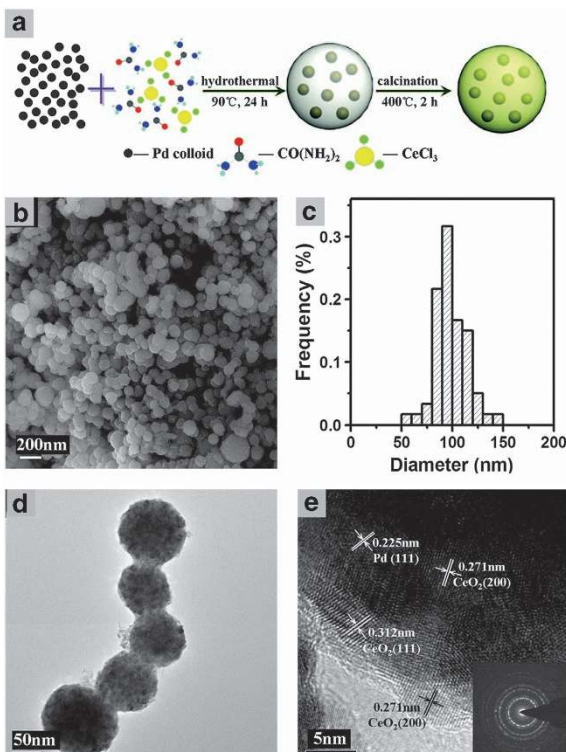


Figure 9 (a) Schematic representation of the synthesis of the Pd@CeO₂ nanospheres; (b) SEM image of Pd@CeO₂ nanospheres; (c) particle-size distribution of Pd@CeO₂; (d and e) TEM and HRTEM images of Pd@CeO₂. Reprinted with permission from Zhang *et al.*⁹¹ Copyright 2011 American Chemical Society.

NPs, followed by the self-assembly of the two components. In the nucleation – growth stage, the zeta potential of the Ce(OH)₃ surface has been reported to be +25.9 mV. The positive surface has a strong attractive force for the negative PtCl₄²⁻ anions. These anions could be strongly attracted to the Ce(OH)₃ surface via electrostatic interactions. Then, an auto-redox reaction occurs on the surface of the CeO₂ NPs. When the ultra-small Pt NPs are formed, the Ce(OH)₃ precursors are oxidized to CeO₂ at the same time. Thus, the original strongly coupled Pt–CeO₂ self-assembled hybrid structures are formed.

Embedded Pt NPs in porous CeO₂ nanostructures. Another efficient way to encapsulate Pt NPs in CeO₂ is to embed them into a porous nanostructure. Sticky's group has published a series of reports of the successful fabrication of mesostructured silica or other metal oxides.^{79–82} The pores provide enough space for noble metal growth; however, the limited space of the channel can limit the overgrowth of noble metals, and the hard framework of CeO₂ can separate the Pt NPs far away from one another even during long-term high-temperature treatment or catalytic application. The porous CeO₂ can be either a single crystal or a closely packed 3D structure composed of tiny CeO₂ NPs. A representative protocol was reported by Li and coworkers.⁸³ They used the van der Waals' force as the driving force to trigger the self-assembly of oleic acid-modified noble metals and CeO₂ NPs to form a multicomponent porous structure (Figure 4). For both the hard template and wet chemistry methods, the aims are the same: to stop the mass transformation process of the unstable noble metals by fixing them in CeO₂ cages.

Mesostructured metal oxides are among the most important types of catalysts and have attracted great interest because of their ultra-large specific surface area and uniform channel interconnectivity for gas

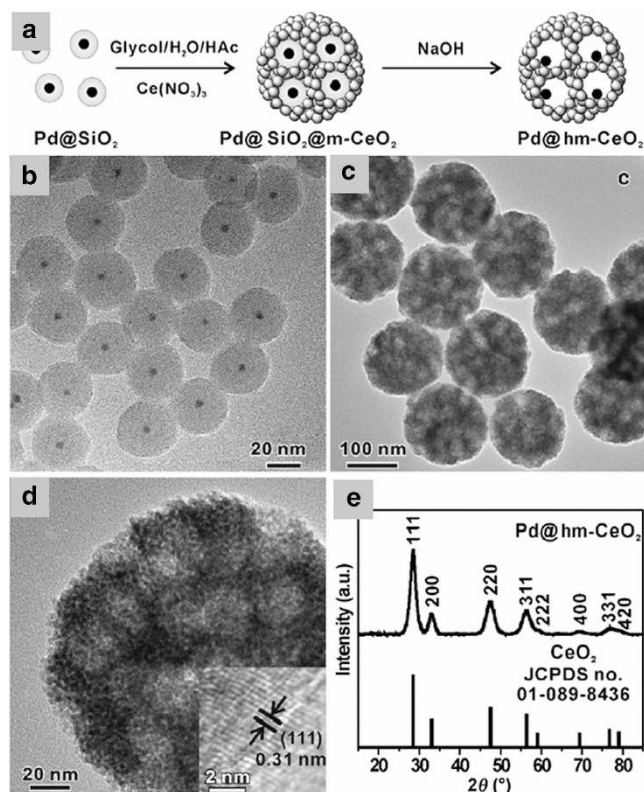


Figure 10 (a) Schematic representation of the synthesis of the Pd@CeO₂ multi-yolk-shell nanostructures; (b) TEM image of Pd@SiO₂; (c) TEM image of Pd@CeO₂; (d) HRTEM image of Pd@CeO₂; (e) XRD data of Pd@CeO₂ nanostructures. Reprinted with permission from Chen *et al.*⁹² Copyright 2012 Wiley-VCH.

diffusion and host-guest interactions. Various techniques, including conventional sol-gel synthesis procedures, template growth, chemical vapor deposition and spray pyrolysis, have been developed for the synthesis of mesoporous metal oxides for new applications. Corma and coworkers used the block copolymer (EO₂₀PO₇₀EO₂₀, Pluronic P123) as a template to produce mesostructured CeO₂ and CeO₂-SiO₂ materials with high thermal stability.⁸⁴ The assembly process is controlled by adjusting the interactions of a copolymer template with the CeO₂ NPs and SiO₂. Subsequently, 2–3-nm Pt nanocrystals are embedded within ultrathin layers of highly structured SiO₂ binder via wet impregnation of the CeO₂-SiO₂ support and CeO₂ support in a Pt salt solution. Catalysis of the chemoselective hydrogenation of an α , β -unsaturated aldehyde such as crotonaldehyde is performed, and the resulting catalyst is satisfactorily active and selective. Recently, Tao and coworkers encapsulated Pt and other noble metals in channels of mesoporous CeO₂, in which SBA-15 silica is used as a hard template to synthesize mesoporous CeO₂, and metal nanoclusters are formed on the internal surface of the wall of channels via a conventional impregnation method (Figure 5).²⁶

Encapsulated Pt NPs in the inner walls of hollow CeO₂ nanostructures. Loading the Pt NPs on the surfaces or the inner walls of CeO₂ could yield vastly different stabilities. Simply loading the Pt NPs makes it difficult to prevent their secondary growth because of strong Brownian motion. If a collision occurred between different CeO₂ NPs, the surface-loaded Pt NPs have a better chance to further their growth, but such a situation could not occur for the Pt NPs encapsulated by

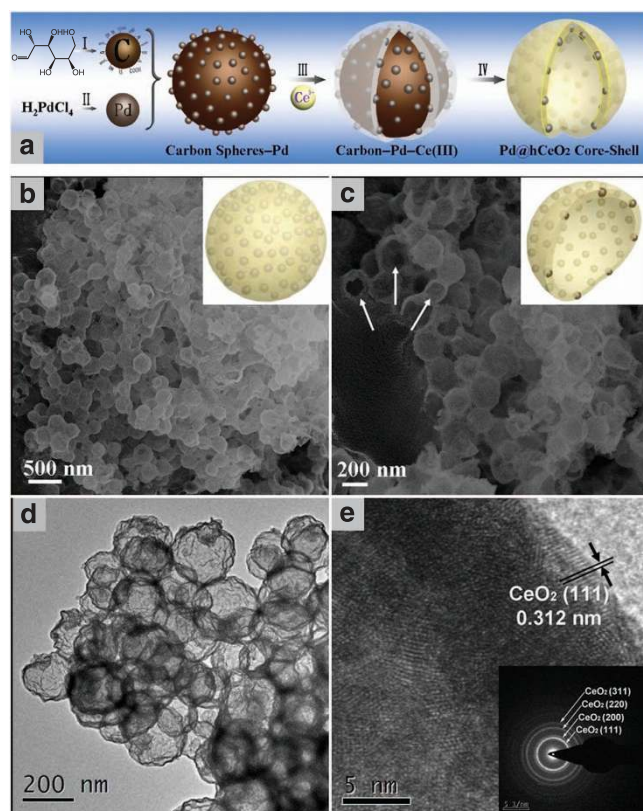


Figure 11 (a) Schematic representation of the synthesis of the Pd@CeO₂ core-shell hollow nanospheres; (b) and (c) SEM images of the as-prepared Pd@CeO₂; (d) TEM image of Pd@CeO₂; and (e) HRTEM image of Pd@CeO₂. Reprinted with permission from Zhang *et al.*⁹³ Copyright 2013 American Chemical Society.

the inner walls of the hollow CeO₂ nanostructure. Xia and coworkers reported a hard template method for embedding Pt NPs in the inner surfaces of CeO₂ hollow fibers with open ends to generate a new catalytic system.⁸⁵ As shown in Figure 6a, polystyrene fibers are first used as the hard template to guide the growth of the 1D nanostructure. After the selective deposition of Pt NPs on the surface of the polystyrene fibers, a dense CeO₂ layer is placed outside and sintered at high temperature such that the small Pt NPs have been strongly encapsulated by the inner walls of the hollow CeO₂ fibers. The as-prepared Pt/CeO₂ nanostructures exhibit satisfactory thermal stability against sintering of as high as 700 °C and catalytic activity with CO oxidation (2–3 orders of magnitude higher than those of other systems).

CeO₂-encapsulated Pd nanostructures

The growth in demand and the ultrahigh price level have seriously limited a broader application of Pt nanocatalysts. Therefore, the development of 'Pt-free' CeO₂-based noble metal catalysts has generated much interest in recent years. Compared with Au and Ag, Pd has the closest catalytic performance to Pt in many catalytic reactions. In fact, for several such reactions, the Pd catalyst exhibits higher activity than Pt. For example, in organic chemistry, numerous carbon-carbon bond forming reactions, such as Suzuki, Heck and Stille couplings, depend on catalysts based on Pd or its compounds. Moreover, supported PdO_x is recognized as one of the best catalysts for catalytic CH₄ combustion. Unfortunately, Pd has poor stability; it is difficult for Pd to maintain its size and shape under

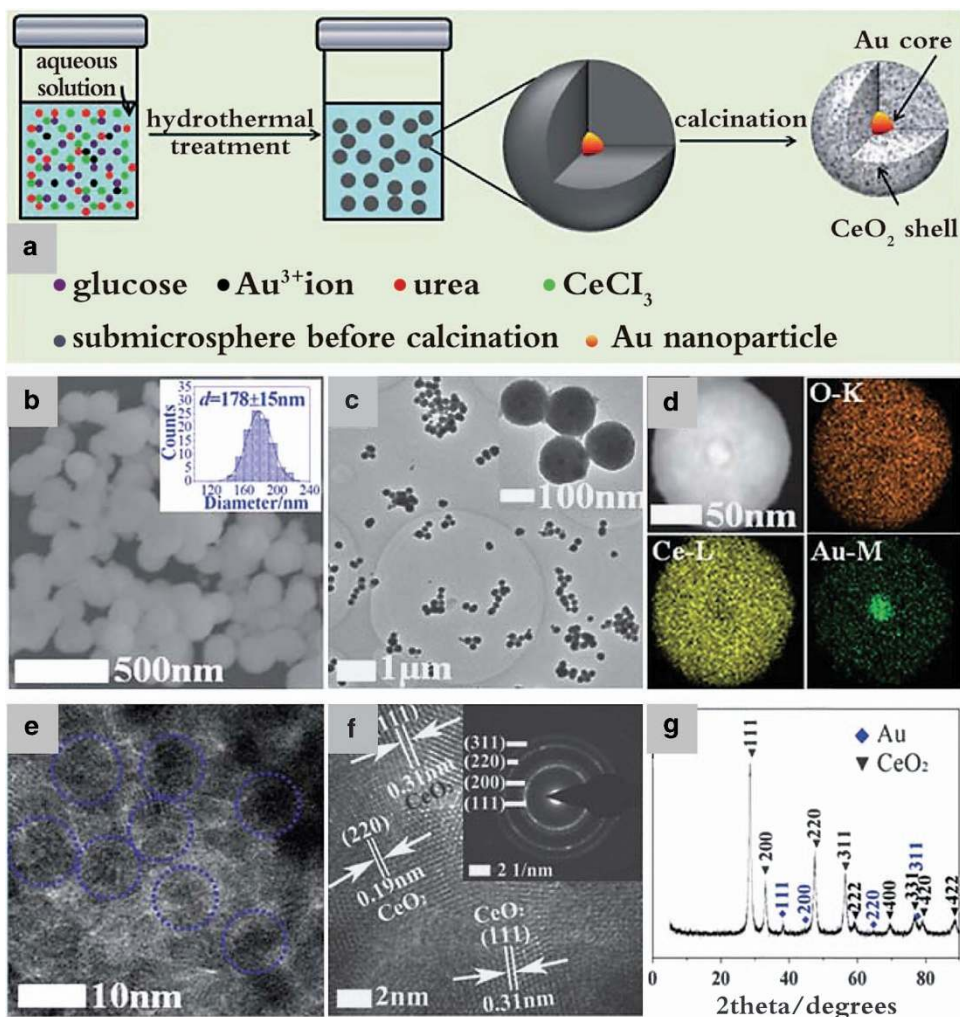


Figure 12 (a) Schematic representation of the synthesis of the Au@CeO₂ core-shell nanostructures; (b) SEM images and (c) TEM images of the as-obtained Au@CeO₂; (d) Mapping analysis of Pd@CeO₂; (e and f) HRTEM images of Au@CeO₂; (g) XRD data of Au@CeO₂. Reprinted with permission from Qi *et al.*⁹⁴ Copyright 2013 Royal Society of Chemistry.

high-temperature conditions. Thus, the formation of CeO₂ encapsulated by Pd nanostructures is required for actual industrial processes.

Pd@CeO₂ core-shell hybrid nanostructures. The core-shell hybrid nanostructure is another important Pd/CeO₂ hybrid structure. A typical Pd@CeO₂ core-shell nanostructure was constructed by Gorte and coworkers via a supramolecular self-assembly process.⁸⁶ The synthesized procedure consists of the following three steps: (1) the use of difunctional 11-mercaptopundecanoic acid as the capping molecular to protect ultra-small Pd NPs; (2) a self-assembly process triggered by adding a Ce precursor (cerium(IV) tetrakis(decyloxyde)) to the solution; and (3) controlled hydrolysis to obtain dispersible Pd@CeO₂ nanostructures. The corresponding TEM and atomic force microscopic images clearly demonstrated the effectiveness of these three steps (Figures 7b–e).

The as-produced core-shell sample is functionalized with dodecanoic acid, and the hydrophobic alkyl surface state is repelled by the hydrophilic surface of most oxide supports, such as Al₂O₃ and yttria-stabilized zirconia (YSZ). As a result, when they are dropped onto planar supports, the hydrophilic Pd@CeO₂ NPs have a strong tendency to aggregate, which makes them unsuitable for their catalytic applications. Gorte and coworkers conducted a further surface

modification process on the second supports to make the hydrophobic functional groups remain on their surface such that the Pd@CeO₂ sample can be uniformly dispersed on the substrate's surface. As shown in Figures 8c–f and K to P, a series of supported Pd@CeO₂ catalysts have been successfully fabricated, including Pd@CeO₂/Al₂O₃^{87–89} and Pd@CeO₂/YSZ,⁹⁰ owing to the presence of a strong interaction driven by Van der Waals forces between the Pd@CeO₂ sample and modified Al₂O₃ or YSZ. Additional atomic force microscopic images have further confirmed the uniformity of the Pd@CeO₂ samples.

In addition to this supramolecular chemistry strategy, seeded growth methods have been successful in the synthesis of the Pd@CeO₂ core-shell nanostructure. Xu's group reported a facile, low-temperature hydrothermal synthesis of 'plum pudding'-structured Pd@CeO₂, which is similar to the previously reported Pt@CeO₂ (Figure 9).⁹⁰ In their work, polyvinylpyrrolidone-stabilized Pd NPs are used as seeds, and the CeO₂ coating process is finished via a hydrothermal treatment.

Pd@CeO₂ yolk-shell hybrid nanostructures. In contrast to core-shell structures, which have solid cores, yolk-shell structures have a mobile core inside and fixed sheath outside, which gives such hybrid

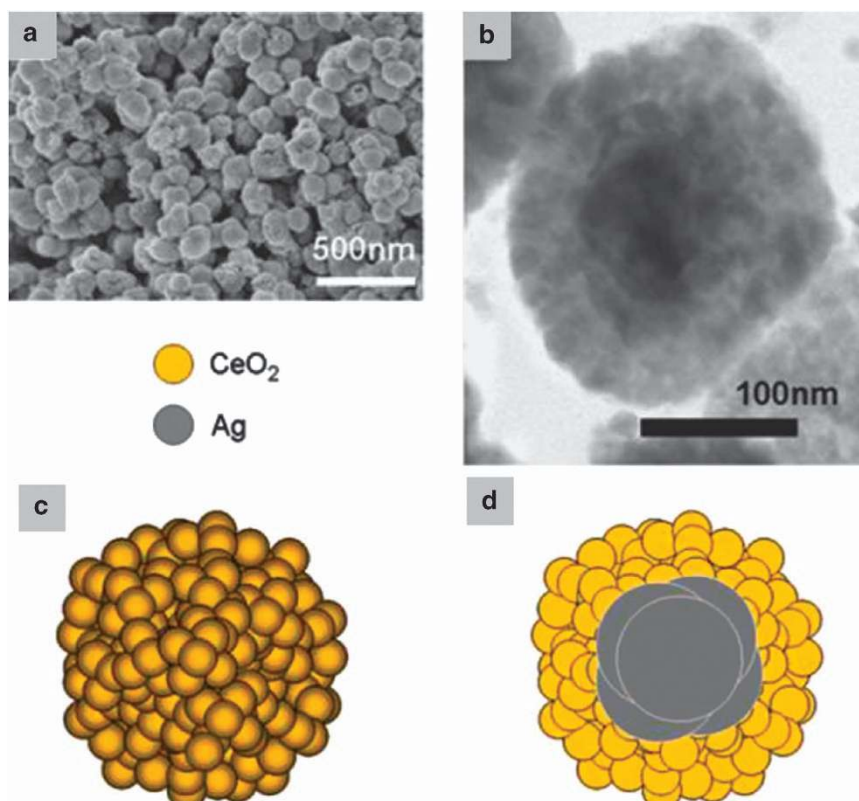


Figure 13 (a) Low-magnification SEM image of Ag@CeO₂ and (b) high-magnification TEM image of single Ag@CeO₂ nanospheres; (c and d) schematic illustrations of Ag@CeO₂. Reprinted with permission from Kayama *et al.*⁹⁵ Copyright 2010 American Chemical Society.

structures special properties, including low density, high surface area and interstitial hollow spaces. The void between the core and shell is very important because the space ensures that the active cores are infiltrated in the reaction solution, which is helpful in enhancing catalytic performance in a liquid-phase catalytic reaction. Typically, one of three synthetic strategies is used to produce a yolk-shell nanostructure. (1) The hard-templating method, the most common strategy, in which the presynthesis of noble metal cores is followed by further coating them with a transitional layer (for example, SiO₂, C or polymer). The template for this layer should be easy to remove after the synthesis, and the target shell materials are deposited onto the surface of the template to form a sandwiched nanostructure, followed by the selective removal of the template layer by using dissolution with a solvent or calcination with heating. (2) The soft-templating method, in which the synthetic mechanism is similar to that of the hard-templating method, with the only significant difference being that it uses the organic long-chain molecules to occupy the space between the core and shell instead of a crystal layer. (3) The template-free method, in which, for some conditions, the original core-shell structure can be translated into a yolk-shell structure, which is driven by the Ostwald ripening force.

Zheng and coworkers successfully synthesized multi-yolk-shell Pd@CeO₂ nanocatalysts via the hard-templating method, by using the data shown in Figure 10.⁹¹ First, uniform and monodisperse Pd-Fe₂O₃@SiO₂ core-shell nanospheres are prepared in a reverse micelle system with the help of Brij 56 molecules. After acid has been used to etch the part of Fe₂O₃, Ce(NO₃)₃ is added in a mixture of water, ethylene glycol, acetic acid and the as-obtained Pd@SiO₂ core-shell sample in a solvothermal process to form a Pd@SiO₂@CeO₂ multi-shell superstructure. Further selective removal of silica with a NaOH

solution causes the multi-core-shell sample to transform into a multi-yolk-shell nanostructure.

Encapsulated Pd NPs in the inner walls of hollow CeO₂ nanospheres. Hollow structures have attracted great interest because of their promising applications in various areas, including catalysis, drug delivery, gas sensors, energy conversion and storage systems. Xu's group developed a new method for fixing the unstable Pd NPs into a hollow CeO₂ nanostructure (Figure 11).⁹² They use carbon nanospheres as the hard templates to deposit 1–5-nm Pd NPs on the surface. Subsequently, a dense layer of CeO₂ is coated on the Pd/C hybrid nanospheres. Finally, the inside carbon nanospheres can be easily removed via a simple heating process. Unlike the multi-yolk-shell sample, the Pd is immobile, but there is still a large space inside the nanospheres. The core-shell strategy efficiently prevents the aggregation of Pd NPs during the high-temperature calcination process and the leaching of Pd NPs for the catalytic reaction in a liquid phase.

CeO₂-encapsulated Au and Ag nanostructures

The catalytic activities of Au and Ag NPs should not be overlooked. These materials also have an important role in certain applications. Although Au/SiO₂, Au/ZrO₂, Au/ZnO and Au/TiO₂ have been widely synthesized and studied in depth, very little such research has been conducted on Au/CeO₂ and Ag/CeO₂.

Au@CeO₂ and Ag@CeO₂ core-shell hybrid nanostructures. As a typical example, Tang and coworkers have described a 'self-templating' technique to synthesize uniform Au@CeO₂ core-shell sub-microspheres.⁹³ In the initial reaction, HAuCl₄, CeCl₃, glucose and

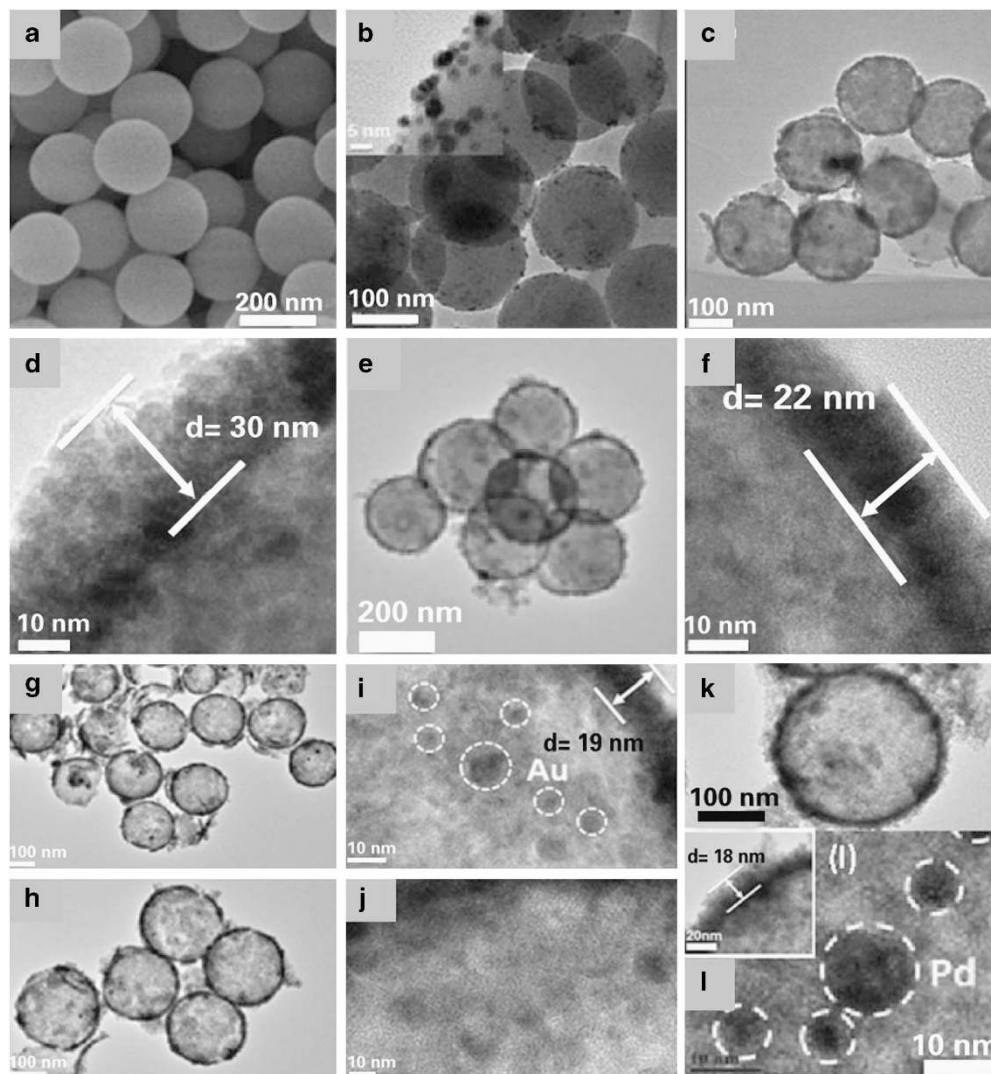


Figure 14 (a) SEM image of SiO₂ and TEM images of (b) Au/SiO₂; (c and d) SiO₂/Au@CeO₂; (e and f) SiO₂/Pd@CeO₂; (g–j) @Au/CeO₂; and (k,l) @Pd/CeO₂ nanospheres. Reprinted with permission from Liu *et al.*⁹⁸ Copyright 2013 Royal Society of Chemistry.

urea are mixed in water, followed by a hydrothermal treatment to produce a sphere-like precursor. As shown in Figure 12, the magnified TEM images confirmed that the submicrospheres have a core-shell nanostructure with sub-17-nm Au NPs inside. Analysis of the TEM results indicates that two separate steps occur during this hydrothermal process. First, the redox reaction between HAuCl₄ and glucose is induced by increasing the reaction temperature. Then, the condensation of glucose in solution under hydrothermal conditions leads to the formation of amorphous carbon submicrospheres with Au as cores inside, and the adsorption of Ce ions simultaneously occurs with the growth of the carbon matrix. To transfer the noncrystal Ce/C mixture into the CeO₂ crystal, the as-obtained precursors are calcined in air. The corresponding TEM, scanning transmission electron microscopic and mapping images reveal that the final products maintain their core-shell structure, and the X-ray diffraction spectra indicate that both the Au and CeO₂ structures maintained high crystallinities.

Ag has the poorest stability of the noble metals. Because of the high K_{sp} (solubility product) values of the types of Ag-based compounds,

such as AgCl, AgBr, AgI, Ag(NH₃)₂⁺ and Ag₂S, Ag NPs can be etched by many types of ions, including Cl⁻, Br⁻, I⁻, S²⁻, NH₃ and O²⁻. As a result, it is very difficult to synthesize CeO₂-encapsulated Ag nanostructures via the seeded growth method. The most successful work has been reported by Kayama and coworkers (Figure 13). They established a new mechanism, 'autocatalyzed redox reaction,' to synthesize riceball-like Ag@CeO₂ core-shell nanostructures.^{94–96} Typically, a mixed aqueous solution of Ce(NO₃)₃ and AgNO₃ is added to stirred aqueous ammonia, causing an auto-redox reaction and yielding a precipitate. There are four steps involved in this reaction: (1) the nucleation of Ce(OH)₃ and Ag(OH); (2) the dissolution of Ag(OH) and formation of [Ag(NH₄)₂]⁺ driven by thermodynamics (K_{sp}([Ag(NH₄)₂]⁺) ≫ K_{sp}(Ag(OH))); (3) the auto-redox reaction between Ce(OH)₃ and [Ag(NH₄)₂]⁺ on the surface of crystallized Ce(OH)₃; and (4) an additional self-assembled process to form the final Ag@CeO₂ riceball-like core-shell hybrid NPs. This facile one-pot aqueous method enables large-scale synthesis.

Encapsulated Au NPs on the inner walls of hollow CeO₂ nanospheres. Figure 14 shows the TEM images of encapsulated Au NPs on the inner

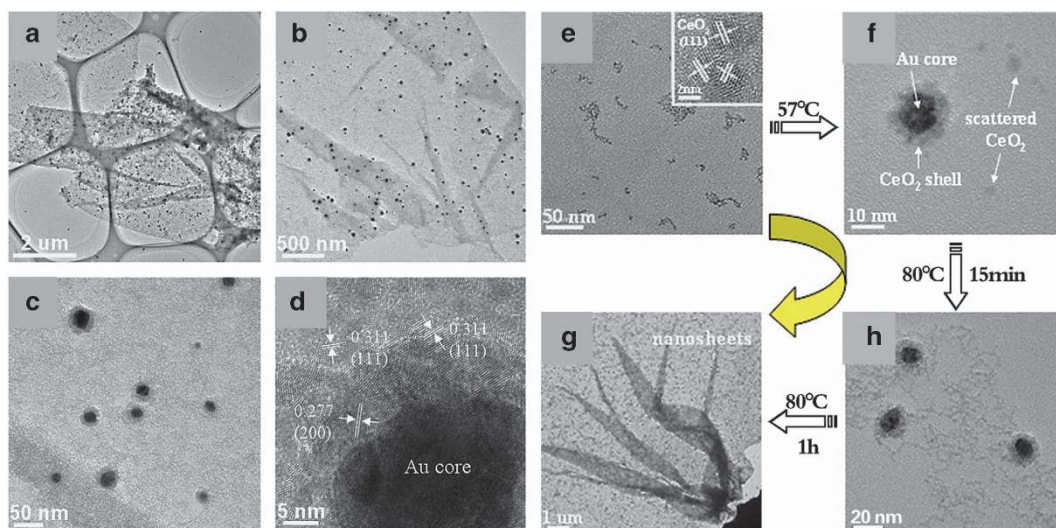


Figure 15 (a–c) Low-magnification TEM images of Au–CeO₂ hybrid nanosheets; (d) high-magnification TEM image of Au–CeO₂ hybrid nanosheet; (e–h) structural evolution, TEM images acquired at different reaction times: (e) after addition of butylamine; (f) after the solution was heated to 57 °C; (g) after the solution reached 80 °C and was kept there for 15 min; and (h) after the solution was maintained at 80 °C for 1 h. Reprinted with permission from Wang *et al.*⁹⁹ Copyright 2012 Royal Society of Chemistry.

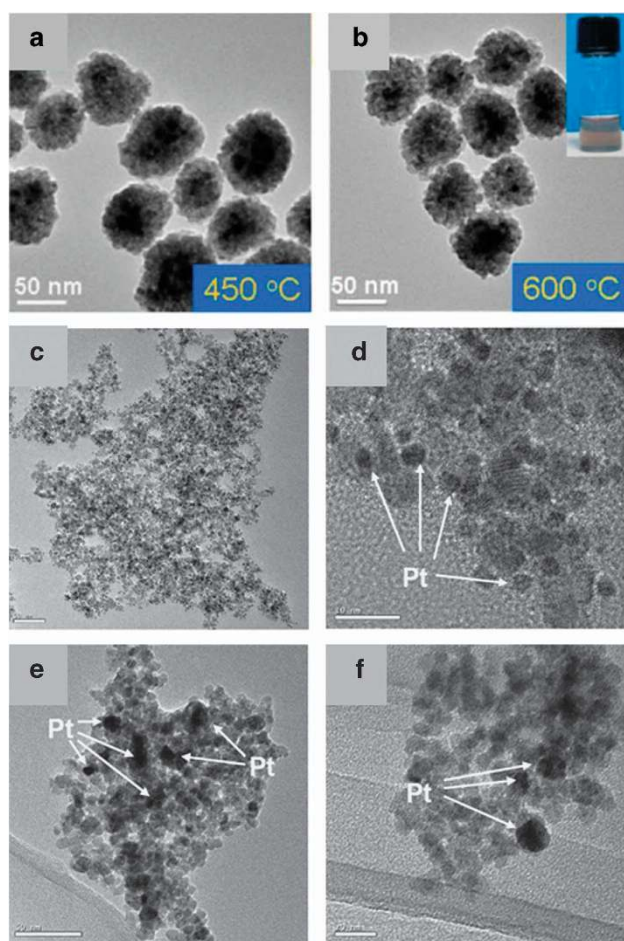


Figure 16 Low-magnification TEM images of Pt@CeO₂ multi-core-shell nanospheres after calcinations at 450 °C (a) and 600 °C (b) for 5 h; (c and d) TEM images of directly mixed Pt–CeO₂ sample; (e and f) TEM images of directly mixed Pt–CeO₂ sample after calcinations at 600 °C for 5 h. Reprinted with permission from Wang *et al.*⁷⁸ Copyright 2013 American Chemical Society.

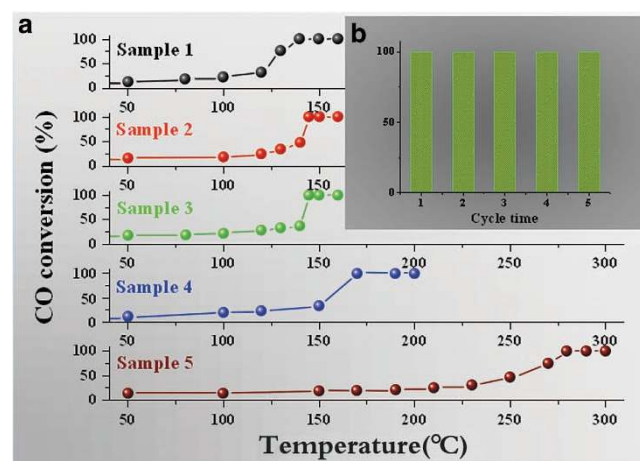


Figure 17 (a) CO conversion curves of Pt@CeO₂ and Pt–CeO₂ sample; (b) cycling test (150 °C) of Pt@CeO₂ sample after calcinations at 600 °C for 5 h. Every 8 mg of catalysts is mixed with 20 mg of SiO₂ (the SiO₂ powder was purchased from Aladdin Company (Shanghai, China) with a particle size of 15 nm ± 5 nm). Reprinted with permission from Wang *et al.*⁷⁸ Copyright 2013 American Chemical Society.

walls of hollow CeO₂ nanospheres, which were reported by Zhang and coworkers.⁹⁷ The ‘hard-templating’ method used is similar to that for the aforementioned Pt@CeO₂ hollow nanofiber and Pd@CeO₂ hollow nanospheres. The difference is that Zhang’s group used a SiO₂ layer as the hard template. Compared with other carbon materials, such as carbon nanofibers and amorphous carbon nanospheres, SiO₂ has two unparalleled advantages. First, the Stöber sol-gel method is very mature. Uniform SiO₂ spheres with different particle sizes can be synthesized very simply on a large scale. Second, the removal of SiO₂ is straightforward in alkali solutions at room temperature; it is unnecessary to use a high-temperature calcination process. However, an obvious disadvantage remains: compared with a carbon template, a SiO₂ template requires surface modifications to allow further hybridization with noble metals. In the authors’ study, 3-amino

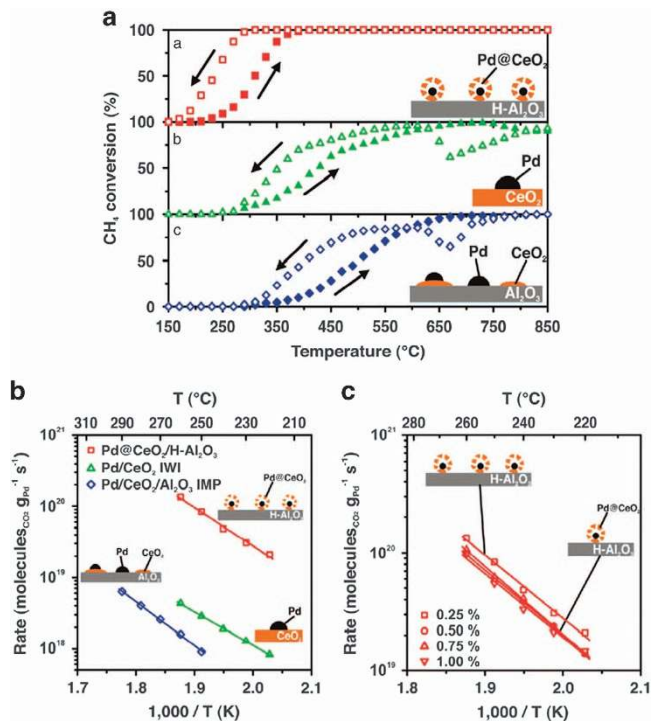


Figure 18 (a) Heating and cooling (10 °Cmin⁻¹) light-off curves of CH₄ conversion as a function of temperature for the three catalyst formulations used. Kinetic rate data for CH₄ oxidation on (b) Pd@CeO₂/Al₂O₃ core-shell catalyst, Pd/CeO₂, and Pd/CeO₂/Al₂O₃. (c) Pd@CeO₂/Al₂O₃ core-shell catalysts at different loadings of the structures (the Pd/CeO₂ weight ratio is maintained at 1/9): Pd loading of 0.25, 0.50, 0.75 and 1.00%. Reprinted with permission from Cargnello *et al.*⁸⁶ Copyright 2012 Science.

propyl-3-methyl silane was used to modify the SiO₂ surface to embed a mass of amino groups on the surfaces, which favors the anchoring of noble metal NPs.

Encapsulated Au NPs into CeO₂ nanosheets. Our group has also focused on a Au–CeO₂ hybrid system.⁹⁸ We observed that a one-pot self-assembly synthesis could be induced by the addition of HAuCl₄, Ce(NO₃)₃, L-lysine, polyvinylpyrrolidone and butylamine in water at 80 °C for 1 h. Figure 15 shows the corresponding TEM images of the as-obtained Au–CeO₂ hybrids with graphene-like nanostructures. Many drapes were observed in the final products, which could be attributed to the self-folding behavior of the 2D nanostructure. In Figure 15c, uniform Au NPs with an average diameter of 20 nm can clearly be seen because of their greater contrast compared with CeO₂ NPs, and the high-resolution TEM image in Figure 15d distinctly shows the components of both the core and shell. To determine the growth mechanism of such a unique hybrid nanostructure, the TEM images acquired at different reaction times were tested carefully. As shown in Figures 15e–h, after butylamine was added to the solution, only 4-nm CeO₂ NPs exhibited no Au NPs. The reaction solution appeared dark green when the temperature reached 57 °C. The corresponding TEM image in Figure 15f confirms that the Au NPs grew to as much as 20 nm and that the original core–shell nanostructure was formed. The solution turned purple after the temperature reached 80 °C. Finally, the self-assembled sheet-like nanostructure is shown in Figure 15g, which indicates that the L-lysine molecules increased the reduction potential of Au³⁺, and, after the formation

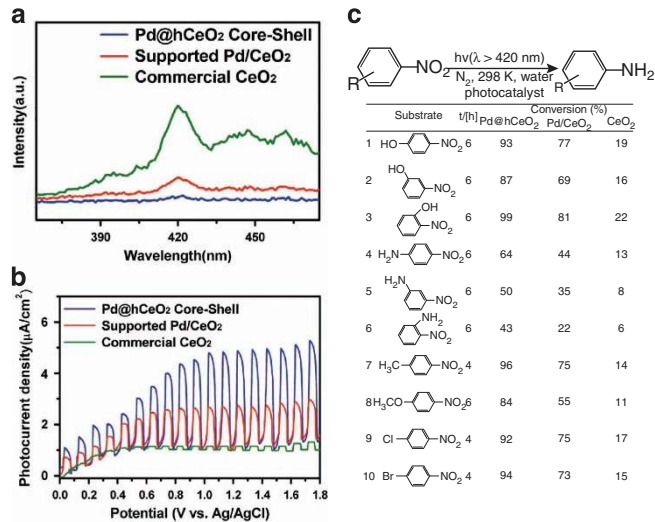


Figure 19 (a) Photoluminescence spectra of commercial CeO₂, supported Pd/CeO₂, and Pd@CeO₂ core-shell sample; (b) chopping visible-light photocurrent–voltage curves of commercial CeO₂, supported Pd/CeO₂ and Pd@hCeO₂ core-shell nanocomposites in 0.2 M Na₂SO₄ (pH 6.8) aqueous solution versus Ag/AgCl; (c) 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 (λ > 420 nm) with the addition of ammonium oxalate as a quencher for photogenerated holes and N₂ purge at room temperature. Reprinted with permission from Zhang *et al.*⁹³ Copyright 2013 American Chemical Society.

of the Au³⁺–L-lysine complex, Au³⁺ could be reduced only at a temperature higher than 57 °C.

CATALYTIC APPLICATIONS

The interface between the noble metal and CeO₂ has been considered an excellent site for many catalytic reactions. For example, CeO₂-based noble metal hybrid catalysts have great efficacy with the CO oxidation reaction, water–gas shift reaction, methanol steam reforming reaction, carbon oxidation reaction, methane combustion reaction, selective oxidation and reduction reaction in the organic liquid phase, and even with some electrochemical catalytic reactions. The hybrid nanostructure has a considerable effect on its catalytic performance. Compared with the traditional catalysts with surface loading, the CeO₂-encapsulated noble metal catalysts exhibited much higher activity, stability and selectivity. The reasons for their superior properties are as follows: (1) the encapsulated nanostructure can provide an excellent opportunity for controlling the interaction among different components; (2) the core–shell and yolk–shell nanostructures can maximize the interface area, and the noble metal centers are closely surrounded by metal oxide supports, which is very beneficial in providing more active centers and novel synergistic effects to increase the reaction speed; and (3) the noble metals are fixed strongly within the CeO₂ nanostructures, in which the individual noble metal NP is isolated and separated by a layer of metal oxide supports, which can efficiently stop the mass transformation process during the thermal treatment or catalytic process.

Anti-sintering capabilities

Anti-sintering capability is required for applications. For example, three-way catalysts should work above 400 °C, and in the methane combustion reaction, the high stability of methane hinders the catalytic reaction; hence, the complete conversion temperature is

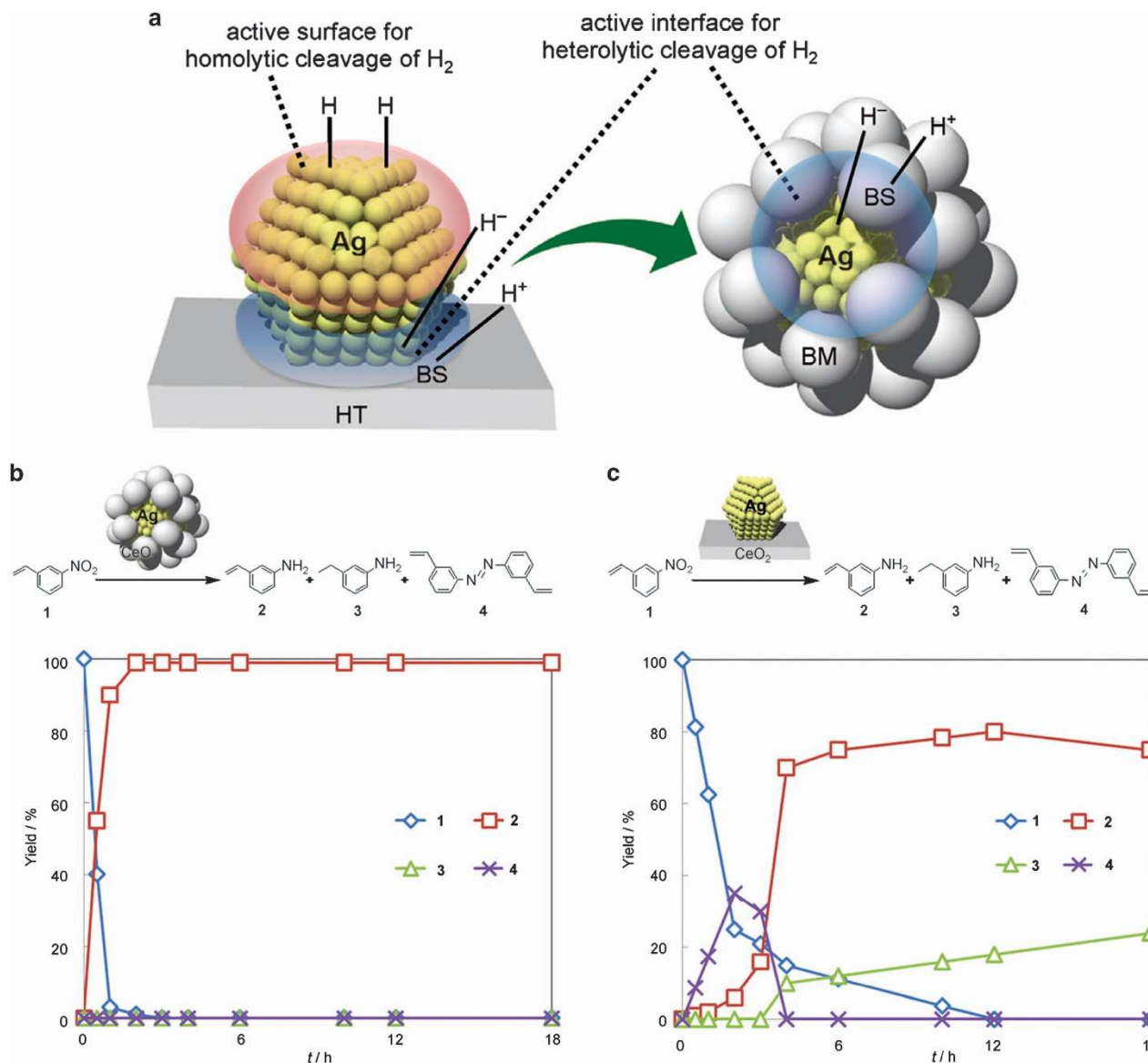


Figure 20 (a) Catalyst design of core-shell nanocomposite for chemoselective reductions with H₂. Representation of Ag/HT reacting with H₂; both polar and nonpolar hydrogen species are formed. The Ag NPs are covered with a basic material (BM), which reacted with H₂ to result in the exclusive formation of a polar hydrogen species. A basic site of HT and BM is represented by BS. Time course of the reduction of nitrostyrene with H₂ using (b) Ag@CeO₂ and (c) Ag/CeO₂. Reprinted with permission from Mitsudome *et al.*⁹⁷ Copyright 2012 Wiley-VCH.

always higher than 600 °C.⁸⁷ With such high working temperatures, the noble metals tend to deactivate through the loss of active surface. The CeO₂-encapsulated noble metal nanocrystal approach offers a powerful tool for minimizing deactivation of the catalyst during the sintering processes.

For instance, in the Pt@CeO₂ multi-core-shell system reported by Zhang and coworker,⁷⁵ it was observed that the core-shell nanostructure has much higher thermal stability compared with the simply loaded samples. As shown in Figure 16, after calcinations at 600 °C for 5 h in air, Pt@CeO₂ multi-core-shell hybrid nanospheres maintained their particle size and shape. No obvious growth or aggregation can be observed in the corresponding TEM images. For comparison, the simply mixed Pt-CeO₂ sample exhibited much poorer stability. After the heating treatment, the particles aggregated heavily, and the Pt NPs increased in size from 4 nm to over 20 nm. This result indicates that

the core-shell nanostructure can efficiently prevent the mass transformation process at high temperature.

Other types of noble metal@CeO₂ core-shell or yolk-shell hybrid structures also exhibited high thermal stabilities. Moreover, the hybrid nanostructure prepared by fixing the noble metal NPs on the inner walls of hollow CeO₂ supports has been proven to still be effective. As shown in Figures 6d-i, Xia and coworker performed a thermal analysis of the hollow CeO₂ fiber with Pt NPs embedded in the inner faces.⁷⁸ The products obtained at 400 and 800 °C still maintained a tubular structure without collapsing, demonstrating a rather high thermal stability for the relatively thin CeO₂ sheath. In addition, the Pt NPs were effectively prevented from aggregating, even with sintering up to 700 °C. However, further increasing the sintering temperature can cause the aggregation of both Pt NPs and CeO₂ sheath.

This result is consistent with our experiment that demonstrated that pure CeO₂ could withstand only calcining temperatures below 700 °C. Higher temperatures could cause an irreversible secondary growth process for CeO₂. Thus, elimination of the protection by CeO₂ could make the noble metals agglomerate. Gorte and coworkers developed a solution to solve the problem: load the monodisperse Pd@CeO₂ core-shell samples onto the secondary supports, including Al₂O₃ and YSZ. The anti-sintering temperature is increased to 850 °C.^{89,99}

Activity

Catalytic CO oxidation has been widely investigated as a typical model reaction. Being much different from the previously reported surface-loaded noble metal/metal oxide nanocatalysts with low-temperature CO oxidation capability,¹⁰⁰ the CeO₂-encapsulated noble metal nanocatalysts exhibit much poorer catalytic activities but with markedly increased high-temperature stabilities. For example, Zhang and coworkers developed Pt@CeO₂ multi-core-shell nanostructures for catalytic CO oxidation and compared them with simply mixed Pt-CeO₂ catalysts and pure CeO₂ samples.⁷⁵ Their catalytic CO conversion curves are shown in Figure 17. *T*₁₀₀, the 100% conversion temperature, has been selected as an important index to evaluate the catalysts' activities. The unheated Pt@CeO₂ sample has the lowest *T*₁₀₀, ~140 °C. After calcinations, *T*₁₀₀ increased slightly, to 145 °C. Simply mixed Pt-CeO₂ has a much higher *T*₁₀₀, 170 °C, and after the heat treatment, inactivation was obvious and *T*₁₀₀ increased to 300 °C. The better catalytic performance of the Pt@CeO₂ sample could be attributed to two factors: the stronger synergistic effect between Pt and CeO₂ caused by the two-face interface redox reaction and the protection of CeO₂ for tiny Pt NPs.

The catalytic methane combustion reaction of Pd@CeO₂/Al₂O₃ nanocatalysts, as compared with Pd/CeO₂ and Pd/CeO₂/Al₂O₃ samples, was studied by Prof. Gorte and demonstrated outstanding catalytic performance.⁸⁷ Complete conversion of CH₄ was observed at ~400 °C (Figure 18a). All other reference samples achieved the complete CH₄ conversion above 700 °C. Such an excellent catalytic performance can be attributed to the following three factors: (1) the presence of CeO₂ shifting the temperature window in which the reaction occurs; (2) the protection of the Pd core by the core-shell structure and good contact between Pd and CeO₂ during the high-temperature catalytic reaction; and (3) the effect of the support to enhance the catalytic performance of Pd@CeO₂.

Intriguingly, an energy transfer process is also observed in noble metal@CeO₂ nanostructures, which provides the hybrid sample with high catalytic activity in visible-light photocatalytic reactions. Xu and coworkers compared the visible-light photoactivity with that of traditional Pd/CeO₂ and commercial CeO₂.⁸⁷ The peaks in the photoluminescent spectra of the Pd@CeO₂ core-shell nanostructure are much lower than those in the other two samples, indicating the efficiently prolonged lifetime of electron-hole pairs, which is in line with the photocurrent-voltage plots displayed in Figure 19b. Compared with traditional Pd/CeO₂ and commercial CeO₂, the photocurrent density of Pd@CeO₂ is significantly greater, which may be the main reason for the longer life span achieved for the Pd@CeO₂ core-shell sample. Consequently, the photocatalytic activity in the reduction of aromatic nitro compounds follows the order Pd@CeO₂ > supported Pd/CeO₂ > commercial CeO₂.

Selectivity

Selectivity is another important parameter in measuring the quality of a catalyst. Kaneda and coworkers studied the Ag@CeO₂ core-shell

nanospheres composed of 10-nm Ag NPs as cores and 3–5-nm CeO₂ assembled outside to form a dense sheath for chemoselective hydrogenation.⁹⁶ The nanogaps among the adjacent CeO₂ NPs in the shell permitted the access of reactants to the active Ag sites in the core (Figure 20). Maximizing the interaction between Ag NPs and the basic sites of CeO₂ successfully induced the heterolytic cleavage of H₂ to Ag-hydride and proton species rather than hemolytic cleavage of H₂ on the bare Ag surface of the supported Ag/CeO₂ samples (Figure 13a). Correspondingly, the core-shell nanostructures exhibited an excellent chemoselective reduction of nitrostyrenes, epoxides and unsaturated aldehydes while maintaining the C–C bonds. For instance, the core-shell nanostructures showed high chemoselective conversion (>99%) of 3-nitrostyrene to 3-aminostyrene under high pressure H₂ at 110 °C (Figure 20), excellent activity (98%) and selectivity (>99%) for the catalytic deoxygenation of epoxides to alkenes, and enhanced chemoselective reduction (>99%) of unsaturated aldehydes to the corresponding allylic alcohols. Furthermore, Ag@CeO₂ could be highly dispersed on the CeO₂ matrix, exhibiting catalytic activity six times higher than that of the original Ag@CeO₂ as well as wide applicability for various substrates in the chemoselective reductions of unsaturated aldehydes.

CONCLUSION AND OUTLOOK

Although some encouraging results have been achieved, there remain many challenges. (1) The development of simple and cost-effective synthetic and fabrication processes for CeO₂-encapsulated noble metal nanomaterials is still desirable. (2) To date, besides that for the Pd@CeO₂ system, there has been no report of the successful encapsulation of ultra-small noble metal NPs, especially noble metal nanoclusters (<1 nm) with CeO₂. In general, the catalytic activities of noble metals are highly dependent on their particle sizes. Optimizing the particle sizes of noble metals is an efficient way to increase their catalytic performances.¹⁰¹ However, the ultra-small particles increase the surface energy, causing the small noble metals to aggregate seriously and thereby interfere with the formation of such core-shell structures. Hence, there is an urgent need to develop new methods to fabricate CeO₂-encapsulated noble metals with controllable particle sizes on the nanoscale. (3) The core materials are still limited to a few noble metals, including Pt, Pd, Au and Ag. The use of other types of noble metals, such as Ir, Ru, Rh and the corresponding noble metal alloys, has yet to be reported. (4) Control of the morphology of both the noble metals and CeO₂ has rarely been reported. It can be predicted that the selectively of special faces of both the noble metals and CeO₂ could greatly increase the hybrids' catalytic activity and selectivity. (5) The hybrid structure, especially the shell thickness in the core-shell or yolk-shell hybrid nanostructures, should be well controlled. It is difficult for some types of substrate molecules to penetrate the thick CeO₂ shell to reach the surface of noble metal cores; however, if the CeO₂ shell is too thin, its protection of the noble metal cores is very limited. The question of how to balance activity and stability is complicated. In our opinion, there are three directions worthy of attention in the future to address this question: (1) vigorously developing seeded growth methods because such a synthetic strategy could ensure control of the size, shape and composition of noble metal cores; (2) introducing an appropriate hard template in the synthesis to produce hollow space in the hybrid nanostructure, which is believed to be an efficient way to optimize the diffusion rate of substrate molecules; (3) quantitatively analyzing the effect of exposed crystal faces of noble metals on CeO₂, which is very helpful for the design of highly active CeO₂-encapsulated noble metal nanocatalysts for special catalytic reactions.

In conclusion, CeO₂-encapsulated noble metal hybrid nanomaterials have exhibited much higher catalytic performance than traditional catalysts. It is believed that in the future, such hybrid nanomaterials will assume a more important role in catalysis, energy conversion, environmental protection and remediation, as well as in the new field of biomedical applications.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

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