

Core-Shell Nanoparticles

International Edition: DOI: 10.1002/anie.201600625
German Edition: DOI: 10.1002/ange.201600625 L-Arginine-Triggered Self-Assembly of CeO₂ Nanosheaths on Palladium Nanoparticles in WaterXiao Wang⁺, Yibo Zhang⁺, Shuyan Song,^{*} Xiangguang Yang, Zhuo Wang, Rongchao Jin,^{*} and Hongjie Zhang^{*}

Abstract: Pd@CeO₂ core-shell nanostructures with a tunable Pd core size, shape, and nanostructure as well as a tunable CeO₂ sheath thickness were obtained by a biomolecule-assisted method. The synthetic process is simple and green, as it involves only the heating of a mixture of Ce(NO₃)₃, L-arginine, and preformed Pd seeds in water without additives. Importantly, the synthesis is free of thiol groups and halide ions, thus providing a possible solution to the problem of secondary pollution by Pd nanoparticles in the sheath-coating process. The Pd/CeO₂ nanostructures can be composited well with γ -Al₂O₃ to create a heterogeneous catalyst. In subsequent tests of catalytic NO reduction by CO, Pd@CeO₂/Al₂O₃ samples based on Pd cubes (6, 10, and 18 nm), Pd octahedra (6 nm), and Pd cuboctahedra (9 nm) as well as a simply loaded Pd cube (6 nm)-CeO₂/Al₂O₃ sample were used as catalysts to investigate the effects of the Pd core size and shape and the hybrid nanostructure on the catalytic performance.

The use of biomolecules as capping agents to assist the formation of inorganic nanoparticles (NPs) has become a hot topic of research.^[1–5] DNA and other nucleic acids are the most commonly used. Since they contain functional groups capable of binding metallic NPs, nucleic acids have great impact on crystal growth, such as the stabilization of ultra-small noble metals (NMs),^[1] the induction of morphology evolution,^[2] and assistance in the formation of self-assembled superlattices.^[3] In principle, this control provides a means of constructing highly functional materials with designed optical, magnetic, electronic, and catalytic properties. However, the extremely high cost of DNA and nucleic acids have seriously limited the application of this approach. The

existence of similar functional groups in amino acids inspired us to develop a new synthesis by using a low-cost amino acid to control the crystal-growth process.

Our research group has continuously focused on the potential of ceria (CeO₂) owing to its numerous oxygen vacancy defects and high oxygen-storage capacity.^[6–10] Cerium is highly earth-abundant and can readily convert between the III and IV oxidation states.^[11] These properties have made CeO₂ the key oxygen-storage component of the three-way catalyst used in automotive catalytic converters for the elimination of engine-exhaust pollutants.^[12] The use of CeO₂ as an excellent support for NMs has emerged as an attractive alternative with the required high activity for low-temperature water-gas shift (WGS) reactions, oxygen sensors, oxygen-permeation membrane systems, and fuel cells.^[13] Furthermore, among various hybrid NM/CeO₂ materials, the NM@CeO₂ core@shell nanostructure has gained attention for its significantly increased catalytic activity and stability.^[14–18] After densely coating with a CeO₂ sheath, the noble-metal core can be protected physically to prevent mass transformation during both synthesis and long-term catalytic cycling, especially in a high-temperature environment. In the typical Pd@CeO₂ system, some important advances have been made. Gorte, Fornasiero, and co-workers have made a significant contribution towards the design and synthesis of Pd@CeO₂ core@shell nanostructures by the use of thiol-protected Pd NPs as cores, and the controlled hydrolysis of a cerium(IV) alkoxide self-assembled around the Pd NPs to form CeO₂.^[19–22] Our research group also found that uniform Pd@CeO₂ core-shell nanospheres can be fabricated through an autoredox reaction between Ce(OH)₃ and Na₂PdCl₄ with the help of a large amount of KBr as the salting-out agent.^[7] Furthermore, Zheng and co-workers showed that unique Pd@CeO₂ multicore-shell nanostructures can be produced by using oil-soluble Pd NPs as seeds in conjunction with a coating-assembling-etching process (SiO₂ is used as a hard template in during synthesis by this approach).^[23] However, the use of thiol groups and halide ions during the CeO₂ coating process can cause secondary pollution, which is very harmful for catalytic performance. Precise control is required, and the use of expensive and toxic organic surfactants and solvents should be avoided. Furthermore, the size and shape of Pd cores can still not be controlled well. Generally, the catalytic performance of Pd NPs can be optimized by tuning their particle size and the properties of exposed faces. However, no investigation of the effects of the size and shape of the Pd NPs in the core@shell nanostructures has been reported until now, as challenges still exist in the aqueous synthesis of high-quality monodisperse Pd@CeO₂

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core-shell nanostructures with controllable Pd cores and clean surface states.

Herein, we describe the use of the biomolecule L-arginine (Arg) as a capping agent to induce the self-assembly of CeO₂ nanosheaths on a variety of Pd NPs as cores. The whole synthetic process is carried out by mixing Ce(NO₃)₃, L-arginine, and presynthesized Pd NPs as seeds without additives of any kind (Figure 1). The choice of L-arginine resulted from the following considerations: 1) L-arginine is rich in functional groups capable of binding both Pd and CeO₂ NPs; 2) the guanidine group exists at the end of L-arginine and provides the excellent solubility in water; more importantly, the guanidine group can generate a large number of OH[−] ions under aqueous conditions.

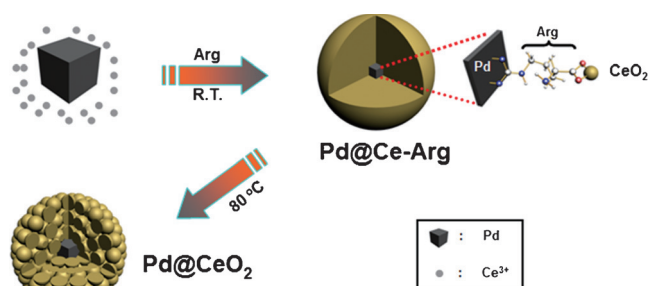


Figure 1. Synthesis of Pd@CeO₂ core-shell nanostructures.

As shown by a low-magnification TEM image (Figure 2A), uniform and monodisperse nanospheres with a narrow size distribution ((25 ± 3) nm) were formed by this method. No scattered CeO₂ NPs or uncoated Pd NPs were found. From Figure 2B, it is clear that these nanospheres have

a typical core@shell superstructure. In each hybrid nanosphere, the shell is built up by numerous tiny CeO₂ NPs, which together form a complete sheath. The Pd cubes beneath the shell can be distinguished by their deeper contrast from CeO₂ (see Figure S1 in the Supporting Information for corresponding TEM images of 6 nm Pd cubes). Careful observation of the Pd cubes after the seeded growth process detected no obvious change in their size or shape. This result confirms that L-arginine is mild enough to maintain the original size and shape of the Pd cores.

High-resolution TEM (HRTEM) showed that the lattice spacing of the shells (0.27 nm) corresponds well with the (200) planes of fluorite phase CeO₂ (Figure 2C). However, the dense CeO₂ coating makes it hard to observe any clear crystal planes of Pd in the core position; therefore, HAADF-STEM technology was used to further analyze the distribution of Pd and Ce components in the nanospheres. It was observed that the element Ce is spread everywhere and that Pd only exists in the center of the nanosphere (see Figure S2), thus confirming the synthesis of Pd@CeO₂ core-shell nanostructures. The peaks at $2\theta = 28.5, 33.0, 47.4,$ and 56.3° in the XRD pattern of the 6 nm Pd cube@CeO₂ hybrid samples (Figure 2D) can be indexed to (111), (200), (220), and (311) CeO₂ fluorite-phase reflections (JCPDS No. 34-0394), respectively. The other strong peak at $2\theta = 40.1^\circ$ corresponds to the pure (111) Pd reflections (JCPDS No. 46-1043). The two peaks at 881.9 and 900.2 eV observed by X-ray photoelectron spectroscopy (XPS; without any surface-etching treatment; see Figure S3) can be assigned as Ce 3d_{5/2} and 3d_{3/2} spin-orbit peaks, respectively. However, there was no clear peak observed between 350 and 330 eV (typical peaks of Pd), which is indirect evidence of core-shell nanostructures. Furthermore, the Pd content of the as-obtained Pd@CeO₂ core-shell nanospheres was 15.4 wt %, as determined by elemental analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES). The specific surface area of the as-obtained Pd@CeO₂ sample, as calculated from the BET curve (see Figure S4), was approximately $74.2 \text{ m}^2 \text{ g}^{-1}$. Such a large BET surface is possibly caused by the smaller size of whole hybrids with a porous sheath.

Interestingly, it was found that the hybrid structure is highly sensitive to the reaction temperature. A decrease in the reaction temperature from 80 to 60 °C can make the CeO₂ shell more branched (see Figure S5). To elucidate the growth mechanism, we also investigated the morphology evolution by following the addition of a solution of L-arginine at room temperature, without any heat treatment (Pd@Ce-Arg). In this case, no clear core@shell nanostructure was formed (see Figure S6A). Some parts have an approximate core-shell structure with Pd cubes in the core position, but a large number of tiny CeO₂ NPs are scattered everywhere. Furthermore, the corresponding XRD spectrum confirmed the formation of CeO₂ nanocrystals in the precursors (see Figure S6B). Thermogravimetric analysis (TGA) of Pd@Ce-Arg and 6 nm Pd cube@CeO₂ showed that 50 wt % of Pd@Ce-Arg was lost when the temperature increased to 800 °C (see Figure S6C); the weight loss of Pd@CeO₂ was approximately 7 wt %. The main inflection point in the two TGA spectra

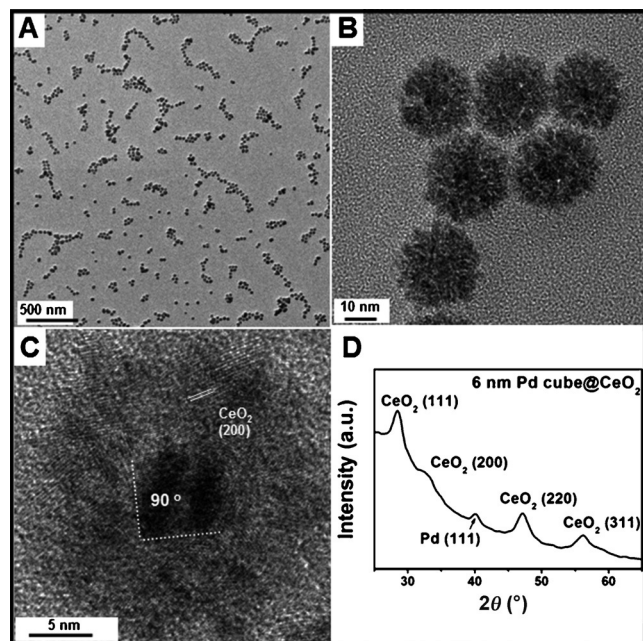


Figure 2. A,B) TEM images, C) HRTEM image, and D) XRD pattern of 6 nm Pd@CeO₂ core-shell nanostructures.

appeared at the same temperature, approximately 250 °C (i.e. the decomposition temperature of L-arginine).

These results indicate that some amount of L-arginine molecules adsorbed on the surface of CeO₂ NPs, as well as free L-arginine molecules, play an important role in the formation of the original sheath. Subsequently, heat treatment is necessary to provide enough OH[−] ions to slowly induce the complete hydrolysis of Ce³⁺ to build up a densely coated sheath. Therefore, the mechanism of formation of the Pd@CeO₂ core-shell nanostructures can be understood as follows: First, after the addition of L-arginine to the reaction solution, the guanidine group binds to the outer electro-negative surface of the Pd cube, and the −COOH group at the other end of the bound L-arginine molecule can bind a Ce³⁺ ion. In this way, L-arginine molecules can readily bind large amounts of Ce³⁺ ions around the Pd cubes. When the amount of L-arginine molecules is increased, Ce³⁺ ions are hydrolyzed partially, and L-arginine functions as an adhesive to make CeO₂ assemble to form a sheath instead of participating in independent nucleation events. Then, when the reaction temperature is increased, L-arginine is able to provide enough OH[−] ions to induce the hydrolysis of Ce³⁺ to form CeO₂ nanocrystals, and the as-formed CeO₂ nanocrystals assemble tightly with the loss of the L-arginine molecules. The final result is a densely coated and well-crystallized CeO₂ sheath with only minimal amounts of residual L-arginine molecules adsorbed on the surface of CeO₂ NPs.

We designed a series of control experiments to gain deeper insight into the generality of this L-arginine-assisted method. As shown in Figure 3 A–F, 10 nm and 18 nm Pd cubes were also successfully encapsulated by a CeO₂ shell. From Figure 3 C,F, it is clear that in the core position, the Pd cubes have sharp corners. According to a previous report,^[24] Br[−] ions could adsorb strongly onto the (100) surface of the Pd cube during synthesis. To study the influence of the adsorption, we used only polyvinylpyrrolidone-protected irregular Pd NPs without Br[−] capping cubes as seeds in the seeded growth process. As shown in Figure 3 G–I, changing of the capping agent does not impede the formation of core-shell nanostructures. Uniform Pd NP@CeO₂ samples were also obtained. Furthermore, other kinds of Pd NPs could be embedded into CeO₂ nanospheres by this synthetic strategy. Thus, one-dimensional Pd nanowire@CeO₂ (Figure 3 J–N), 9 nm Pd cuboctahedron@CeO₂ (see Figure S7), and 6 nm Pd octahedron@CeO₂ (see Figure S8) core-shell nanostructures were successfully synthesized. Finally, the thickness of the CeO₂ shell could also be controlled well by directly changing the feeding amount of Ce (see Figure S9 for details).

Before catalytic testing, the as-obtained Pd@CeO₂ samples with different Pd core sizes were loaded on commercial γ -Al₂O₃ supports to further increase the catalytic performance of the Pd@CeO₂ nanospheres. The Pd@CeO₂ samples were loaded onto needlelike γ -Al₂O₃ uniformly, and they maintained the original monodispersity (see Figure S10A for TEM images). No scattered or agglomerated NPs were found. The anti-sintering characteristics of the as-obtained 6 nm Pd@CeO₂/Al₂O₃ were first examined by calcination at 600 °C for 5 h in air. By comparing TEM images, it was found that there were no changes in size, shape, or the hybrid

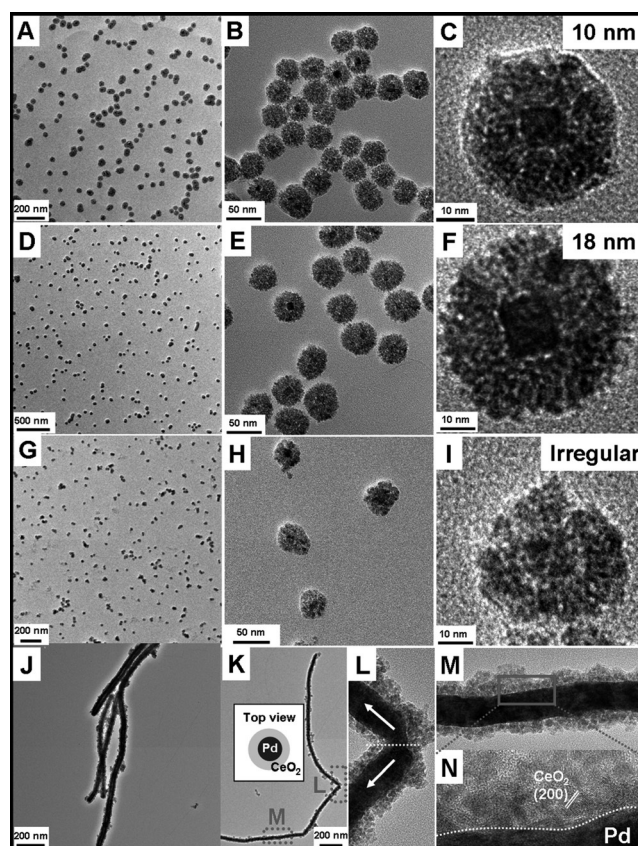


Figure 3. TEM images of A–C) 10 nm Pd cube@CeO₂, D–F) 18 nm Pd cube@CeO₂, G–I) irregular Pd@CeO₂, and J–N) Pd nanowires@CeO₂. Scale bars: A) 200, B) 50, C) 10, D) 500, E) 50, F) 10, G) 200, H) 50, I) 10, J) 200, K) 200 nm.

nanostructure (Figure S10B). Moreover, no agglomeration occurred. The excellent anti-sintering ability of Pd@CeO₂ could be attributed to strong protection by the CeO₂ sheath, as well as the support effect of commercial Al₂O₃.

The catalytic reaction CO + NO → CO₂ + N₂ has received increased attention because of its dual effect of reducing NO and oxidizing CO at the same time.^[25] It is one of the first model reactions investigated in the field of three-way catalysts and dates back many decades.^[26] However, the catalytic reduction of NO by CO is more challenging than the traditional model reaction of CO oxidation and requires a catalyst with higher activity, stability, and selectivity. Catalytic activity was evaluated by the use of a fixed-bed reactor coupled with mass spectrometry. Figure 4 shows the rate data for NO reduction over six kinds of Pd–CeO₂ hybrid samples, which had previously been loaded on commercial Al₂O₃: 6 nm Pd cube@CeO₂, 10 nm Pd cube@CeO₂, 18 nm Pd cube@CeO₂, 9 nm Pd cuboctahedron@CeO₂, 6 nm Pd octahedron@CeO₂, and 6 nm Pd–CeO₂ (simply loaded form). Rapid and almost linear evolution is observed between ln(rate) and 1/T, thus indicating that the catalytic reaction is a typical first-order reaction. The kinetic data in Figure 4 can be divided into three different regions.

In region I, the reaction rate decreases with increasing size of the Pd core (see Figure S11 for the corresponding light-off

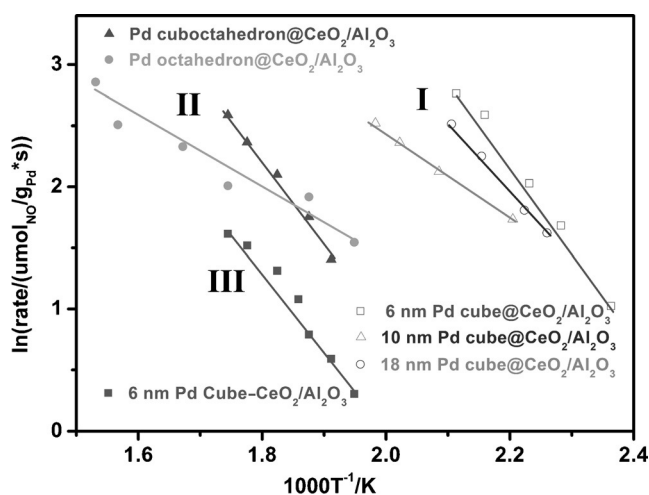


Figure 4. Kinetic data. Arrhenius-type plots for NO reduction by CO over 6 nm Pd cube@CeO₂/Al₂O₃, 10 nm Pd cube@CeO₂/Al₂O₃, 18 nm Pd cube@CeO₂/Al₂O₃, 9 nm Pd cuboctahedron@CeO₂/Al₂O₃, 6 nm Pd octahedron@CeO₂/Al₂O₃, and simply loaded 6 nm Pd cube-CeO₂/Al₂O₃. The rates of the catalysts are calculated on the basis of the total mass of the Pd metal. The Pd content in these nanocatalysts was determined by ICP analysis (see Table S1).

curves). It is typical size-dependent catalytic performance that the smaller a Pd core is, the greater is its catalytic activity. To intuitively display the size effect, metal dispersion data was obtained by CO pulse experiments at room temperature. The values found were 5.59, 4.93, and 3.40% for the 6, 10, and 18 nm Pd cube@CeO₂/Al₂O₃ sample, respectively. Thus, according to the metal dispersion data, the rates of these three kinds of nanocatalysts with different Pd core sizes were calculated to be 206×10^{-6} , 183×10^{-6} , and 164×10^{-6} mol (g_{Pd, active sites})⁻¹, respectively, at a reaction temperature of 192°C.

In region II, the different catalytic performance could mainly be attributed to a shape effect. It is well-known that a Pd cube and a Pd octahedron are enclosed by six (100) and eight (111) faces, respectively. This catalytic result firmly confirmed that Pd (100) faces have much higher catalytic ability than Pd (111) faces. Since a Pd cuboctahedron has six (111) and six (100) faces, this kind of core-shell nanocatalyst exhibited medium catalytic performance. However, such size and shape effects are much weaker than the structure effect. As shown in region III, the simply loaded 6 nm Pd cube-CeO₂/Al₂O₃ catalyst showed the poorest catalytic performance.

To find an explanation for this structure effect, we undertook CO temperature-programmed desorption (CO-TPD) and quantitative H₂ temperature-programmed reduction (H₂-TPR) analysis. For the as-obtained 6 nm Pd cube@CeO₂ sample, a strong peak was observed at 233.7°C (see Figure S12), which is the expected temperature for CO desorption from Pd.^[27] In contrast, for the simply loaded 6 nm Pd-CeO₂/Al₂O₃ hybrid nanomaterial, the intensity of the desorption peak was much weaker. This result demonstrates that the core-shell materials have higher CO-desorption capabilities. Generally, for Pd catalysts, CO species adsorb strongly on the Pd surface in the low-temperature region, and the reaction rate is controlled by the desorption of

CO.^[28] The faster the CO gas desorbs, the higher catalytic activity it has. The result of CO-TPD analysis suggests that the higher catalytic activity of the Pd@CeO₂ core-shell materials most likely results from their higher CO-desorption capability as compared to that of the simply loaded material. In the H₂-TPR profiles of the core-shell NPs (see Figure S13), a sharp peak corresponding to the reduction of PdO species on the CeO₂ surface appeared at 41.5°C, and a negative peak corresponding to the decomposition of palladium hydride appeared at about 80.6°C, whereas the simply loaded Pd-CeO₂ sample exhibited a similar H₂-consumption peak at about 52.7°C. Another broad positive peak was also observed at about 94.1°C. These different peak positions indicate variation in the distribution of PdO with support composition.^[29] According to previous reports,^[30,31] it is suggested that the H₂-TPR peak of the Pd-CeO₂/Al₂O₃ sample at 52.7°C could be attributed to the reduction of PdO species on Ce-Al-O surfaces. H₂ consumption for these peaks was calculated by using CuO as a standard. A consumption of 0.25 mmol g⁻¹ was measured for the core-shell sample (see Table S2), which is clearly lower than the 0.42 mmol g⁻¹ expected theoretically for PdO production (Pd content: 4.5 wt% in Pd@CeO₂/Al₂O₃), thus indicating that the Pd exists partially in the form of Pd metal. On the other hand, the simply loaded sample shows a higher consumption of 0.72 mmol g⁻¹ than the 0.45 mmol g⁻¹ expected for theoretical PdO production (Pd content: 4.8 wt% in Pd@CeO₂/Al₂O₃), possibly as a result of the concurrent reduction of surface Ce⁴⁺. This result confirmed that the formation of the Pd@CeO₂ core-shell nanostructure can increase the stability of Pd metal and the reducibility of PdO species. Thus, the core-shell materials exhibit remarkably enhanced catalytic performance relative to that of the simply loaded materials.

A nowadays widely accepted possible mechanism of such catalytic reactions involves Ce³⁺ in an important role: NO can reoxidize Ce³⁺ to Ce⁴⁺, and CO can subsequently reduce Ce⁴⁺ to Ce³⁺.^[32,33] In an XPS spectrum of the 6 nm Pd cube@CeO₂/Al₂O₃ sample after the catalytic reaction, an Ce³⁺ signal was also clearly observed (see Figure S14), thus indicating that Ce³⁺ participates in the catalytic reaction. Previous studies have shown that N₂O is the main by-product. Thus, we collected the gas mixture during catalysis at different temperatures and analyzed the N₂O content by high-performance liquid chromatography after precolumn derivatization. For the 6 nm Pd cube@CeO₂ sample, the N₂O content was 5, 30, and 75 ppm at 100, 150, and 200°C, respectively (see Table S3). The simply loaded Pd-CeO₂/Al₂O₃ material showed much poorer selectivity, thus indicating the importance of embedding the highly active Pd NPs in CeO₂ nanostructures not only for catalytic activity but also for selectivity.

In summary, high-quality Pd@CeO₂ core-shell nanospheres with tunable core size, shape, shell thickness, and hybrid nanostructure have been successfully fabricated in water by a low-cost and straightforward biomolecule-assisted method. Without the addition of any expensive and toxic specific ligands (especially thiols and halide ions), L-arginine plays the key role as a linker between CeO₂ and Pd. Moreover, L-arginine could also function as an adhesive to

make CeO₂ assemble to form the original sheath. The densely coated and well-crystallized CeO₂ sheath was formed by increasing the reaction temperature. Because of effective protection by the CeO₂ shell and the support effect of γ -Al₂O₃, the obtained Pd catalyst exhibited excellent high-temperature stability. In a model reaction of catalytic CO oxidation by NO, as-obtained 6 nm Pd cube@CeO₂/Al₂O₃ exhibited the best catalytic activity among the various kinds of Pd@CeO₂ core-shell nanostructures. The effects of the size and shape of the Pd core and the effects of the hybrid nanostructure on catalytic performance were studied in depth. We believe that our interesting findings can direct the design of novel functional core-shell nanocatalysts with high efficiency. Furthermore, such “biomolecule-assisted” strategies in the synthesis of inorganic NPs are expected to be of great significance in nanosynthesis for real-world applications.

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- [1] L. Zhang, J. Zhu, S. Guo, T. Li, J. Li, E. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 2403.
- [2] J. Wu, L. Tan, K. Hwang, H. Xing, P. Wu, W. Li, Y. Lu, *J. Am. Chem. Soc.* **2014**, *136*, 15195.
- [3] E. Auyeung, W. Morris, J. Mondloch, J. Hupp, O. Farha, C. Mirkin, *J. Am. Chem. Soc.* **2015**, *137*, 1658.
- [4] L. M. Demers, M. Östblom, H. Zhang, N. H. Jang, B. Liedberg, C. A. Mirkin, *J. Am. Chem. Soc.* **2002**, *124*, 11248.
- [5] A. P. Alivisatos, K. P. Johnsson, X. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez, P. G. Schultz, *Nature* **1996**, *382*, 609–611.
- [6] X. Wang, D. Liu, S. Song, H. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 15864.
- [7] X. Wang, D. Liu, J. Li, J. Zhen, F. Wang, H. Zhang, *Chem. Sci.* **2015**, *6*, 2877.
- [8] S. Song, X. Wang, H. Zhang, *NPG Asia Mater.* **2015**, *7*, e179.
- [9] X. Wang, D. Liu, J. Li, J. Zhen, H. Zhang, *NPG Asia Mater.* **2015**, *7*, e158.
- [10] X. Wang, X. Li, D. Liu, S. Song, H. Zhang, *Chem. Commun.* **2012**, *48*, 2885.
- [11] C. Sun, H. Li, L. Chen, *Energy Environ. Sci.* **2012**, *5*, 8475.
- [12] J. Kašpar, P. Fornasiero, M. Graziani, *Catal. Today* **1999**, *2*, 285.
- [13] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* **2003**, *301*, 935.
- [14] J. Qi, J. Chen, G. D. Li, S. X. Li, Y. Gao, Z. Y. Tang, *Energy Environ. Sci.* **2012**, *5*, 8937.
- [15] K. Yoon, Y. Yang, P. Lu, H. Peng, K. Masias, P. Fanson, C. Campbell, Y. Xia, *Angew. Chem. Int. Ed.* **2012**, *51*, 9543–9546; *Angew. Chem.* **2012**, *124*, 9681–9684.
- [16] T. Kayama, K. Yamazaki, H. Shinjoh, *J. Am. Chem. Soc.* **2010**, *132*, 13154.
- [17] S. Zhang, C. Chen, M. Cargnello, P. Fornasiero, R. Gorte, G. Graham, X. Pan, *Nat. Commun.* **2015**, *6*, 7778.
- [18] M. Pagliaro, P. Fornasiero, *ChemCatChem* **2015**, *7*, 1979.
- [19] M. Cargnello, J. Jaén, J. Garrido, K. Bakhmutsky, T. Montini, J. Gámez, R. Gorte, P. Fornasiero, *Science* **2012**, *337*, 713.
- [20] N. Wieder, M. Cargnello, K. Bakhmutsky, T. Montini, P. Fornasiero, R. Gorte, *J. Phys. Chem. C* **2011**, *115*, 915.
- [21] L. Adjianto, A. Sampath, A. Yu, M. Cargnello, P. Fornasiero, R. Gorte, J. Vohs, *ACS Catal.* **2013**, *3*, 1801.
- [22] L. Adjianto, D. Bennett, C. Chen, A. Yu, M. Cargnello, P. Fornasiero, R. Gorte, J. Vohs, *Nano Lett.* **2013**, *13*, 2252.
- [23] C. Chen, X. Fang, B. Wu, L. Huang, N. Zheng, *ChemCatChem* **2012**, *4*, 1.
- [24] M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu, Y. Xia, *Nano Res.* **2011**, *4*, 83.
- [25] S. Roy, M. Hegde, *Catal. Commun.* **2008**, *9*, 811.
- [26] J. Kašpar, C. Leitenburg, P. Fornasiero, A. Trovarelli, M. Graziani, *J. Catal.* **1994**, *146*, 136.
- [27] X. C. Guo, J. T. Yates, *J. Chem. Phys.* **1989**, *90*, 6761.
- [28] H.-J. Freund, G. Meijer, M. Scheffler, R. Schlögl, M. Wolf, *Angew. Chem. Int. Ed.* **2011**, *50*, 10064–10094; *Angew. Chem.* **2011**, *123*, 10242–10275.
- [29] B. Yue, R. Zhou, Y. Wang, X. Zheng, *Appl. Catal. A* **2005**, *295*, 31.
- [30] M. Luo, X. Zheng, *Appl. Catal. A* **1999**, *189*, 15.
- [31] M. Luo, Z. Hou, X. Yuan, X. Zheng, *Catal. Lett.* **1998**, *50*, 205.
- [32] G. Ranga Rao, P. Fornasiero, R. Di Monte, J. Kašpar, G. Vlaic, G. Balducci, S. Meriani, G. Gubitosa, A. Cremona, M. Graziani, *J. Catal.* **1996**, *162*, 1.
- [33] P. Fornasiero, G. Ranga Rao, J. Kašpar, F. L'Erario, M. Graziani, *J. Catal.* **1998**, *175*, 269.

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