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Article

Multiple Au cores in CeO₂ hollow spheres for the superior catalytic reduction of *p*-nitrophenol

Kun Zhao ^{a,b,†}, Jian Qi ^{b,c,†}, Shenlong Zhao ^b, Hongjie Tang ^c, Huajie Yin ^b, Lingbo Zong ^a, Lin Chang ^b, Yan Gao ^{b,\$}, Ranbo Yu ^{a,#}, Zhiyong Tang ^{b,*}

^a Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

^b Laboratory for Nanosystem and Hierarchy Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China

^c State Key Laboratory of Multi-Phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

In many catalytic systems the structure of the catalyst plays a crucial role in the reaction especially for catalytic reduction, organic pollutant oxidation and other organic transformations. Herein, we report a template-free approach to the synthesis of multiple Au cores in CeO₂ hollow spheres (MACCHS). This material was fabricated by impregnating CeO₂ hollow spheres with a HAuCl₄ aqueous solution. NaBH₄ was then used to reduce HAuCl₄ to Au nanoparticles to form multiple Au cores in the CeO₂ hollow spheres. We used MACCHS as a catalyst for *p*-nitrophenol reduction and achieved excellent activity. The catalyst showed enhanced stability toward *p*-nitrophenol reduction compared with bare Au nanoparticles and CeO₂ hollow spheres. This simple method to achieve multi-core-in-shell hollow structures will likely have applications in various biological, medical and energy related fields.

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1. Introduction

Catalytic reactions are important processes that are at the heart of various strategies to resolve current energy and environment issues. The construction of new structures for use as novel nanomaterials is critical for important catalytic reactions such as catalytic cracking [1], the water-gas shift reaction [2] and hydrogen generation [3] amongst others. Ceria (CeO₂) is regarded as a suitable material for various catalytic applications because of its strong oxidizing power, low cost, and

long-term stability [4]. CeO₂ is a typical multifunctional rare earth oxide and it has attracted much attention because of its wide range of applications in the chemistry [5], engineering [6], catalysis [7] and fuel cells [8]. For a catalytic system, it is crucial to fabricate novel nanomaterial structures with high activity to act as efficient catalysts. Therefore, the design and synthesis of CeO₂ with various morphologies and nanostructures remains a great challenge. The synthesis of a core-shell or a yolk-shell structure is of great significance because these materials exhibit unique physical and chemical properties [9]. Current meth-

* Corresponding author. Tel/Fax: +86-10-82545580; E-mail: zytang@nanoctr.cn

Corresponding author. Tel/Fax: +86-10-62656765; E-mail: ranboyu@ustb.edu.cn

\$ Corresponding author. Tel/Fax: +86-10-82545603; E-mail: gaoyan@nanoctr.cn

† Kun Zhao and Jian Qi contributed equally to this work.

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ods for the synthesis of metal oxide coated noble metal nanocomposites with well-controlled core-shell structures mostly rely on complicated or environmentally unfriendly processes. They involve either the use of heterogeneous hard/soft templates or etching processes with toxic or corrosive agents such as potassium cyanide and sodium hydroxide [10–15]. To our knowledge most reports about Au/CeO₂ composites describe their behavior during CO oxidation [13,16–21]. Attention has been given to the core-shell structures of metal@CeO₂ such as Pd@CeO₂ and Pt@CeO₂ [22–27]. However, there are some inherent drawbacks including low efficiency, a complicated and tedious process and difficulties in ensuring that the etching reaction occurs exclusively within the shells.

In this study, we report an environmentally friendly, low cost, and template-free synthetic route for the preparation of multiple Au cores in CeO₂ hollow sphere (MACCHS) core-shell structures with multiple gold nanoparticle cores embedded in a porous shell. The unique hollow structure of CeO₂ can efficiently trap Au nanoparticles in the porous shell and the cavities allow the Au nanoparticles to disperse more easily. A facile route in the aqueous phase was used to synthesize hybrid MACCHS materials with a well-controlled multi-cores-in-shell structure by simply adjusting the ratio of the HAuCl₄ solution that was reacted with sodium citrate. Finally, we show for the first time that the incorporation of several Au cores into the shell of the CeO₂ semiconductor, using NaBH₄ as a reductant, enhances the performance of CeO₂ toward the reduction of *p*-nitrophenol to *p*-aminophenol. This represents an important catalytic process in green chemistry. We hope this work will offers useful directions for the scale-up fabrication of other metal oxide coated noble metal materials with tunable core-shell structures. This novel structure may be used as part of an ideal catalytic reaction method because the noble metal nanoparticles do not aggregate and a synergistic effect is exploited because of interactions between the metal nanoparticles.

2. Experimental

2.1. Materials

The reagents (CeCl₃·7H₂O, ethanol, H₂O₂ (30 wt%), sodium citrate dihydrate, HAuCl₄·3H₂O, urea and *p*-nitrophenol, analytical reagent) were bought from Beijing Chemical Reagent Factory and used without further purification.

2.2. Synthesis process

The hollow CeO₂ structure was prepared as our previous report [7]. In a typical procedure, 1.08 g urea was dissolved in 171 mL deionized water to form a clear solution. A 72 mL sodium citrate solution (10 mmol/L) was added to this solution and stirred for 10 min. CeCl₃·7H₂O (0.89 g) was then added to the solution, and the resulting mixture was stirred for 15 min. Subsequently, 1.08 mL H₂O₂ (30 wt%) was added to this solution dropwise with vigorous stirring for 30 min. Finally, the mixture was transferred to Teflon-lined stainless steel auto-

claves (200 mL) and heated to 180 °C for 22 h. The resultant solid product was centrifuged, washed three times with distilled water and ethanol and dried at 100 °C for 12 h to give a light yellow powder.

The MACCHS nanomaterials were prepared by the impregnation method. In a typical procedure, 2 mL of HAuCl₄ solution (10 mmol/L) and 2 mL of sodium citrate solution (10 mmol/L) were dissolved in 76 mL deionized water to form a clear solution and it was stirred for 10 min. We then added 0.046 g of the hollow structure CeO₂ to the above-mentioned solution, and the resulting mixture was stirred for 40 min and ultrasonicated for 10 min. The obtained mixture was then centrifuged at 6500 rpm twice to ensure that unreacted HAuCl₄ and sodium citrate were removed completely. Finally, the above-mentioned solid product was added slowly to a 26 mL deionized water and 2 mL sodium citrate solution. This was followed by the addition of 1 mL NaBH₄ solution (10 mmol/L) dropwise with vigorous stirring for 12 h. After centrifugation at 5000 rpm the final purple MACCHS products were dried at 60 °C for 6 h.

2.3. Catalyst characterization

Powder XRD patterns were recorded on a Panalytical X'Pert-pro MPD X-ray powder diffractometer using Cu K_α radiation ($\lambda = 0.154056$ nm). Scanning electron microscopy (SEM) was performed on a Hitachi S-4800. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G² F20 electron microscope operating at 200 kV with a software package for automated electron tomography. The BET (Brunauer–Emmett–Teller) surface area, pore volume and pore size of the catalysts were measured using a Quadrasorb SI-MP instrument. Before each measurement the sample was heated to 300 °C and kept at this temperature for 3 h. XPS spectra were obtained using an ESCALAB 250 Xi XPS system from Thermo Scientific. The analysis chamber was at 1.5×10^{-9} mbar and the X-ray spot was 500 μ m. UV-Vis diffuse reflection absorption spectra (UV-Vis/DRS) of the samples were recorded using a UV-vis spectrometer (Lambda 950, PE, USA) equipped with an integrating sphere accessory in diffuse reflectance mode (R) and BaSO₄ as the reference material.

2.4. Catalytic activity

The catalytic properties of the MACCHS nanomaterials were investigated by the reduction of *p*-nitrophenol to *p*-aminophenol with NaBH₄ solution as the reductant at ambient temperature as a model reaction. First, *p*-nitrophenol (10 mL, 0.034 mmol/L) was added to a NaBH₄ solution (2 mL, 0.1 mol/L) and the mixture was stirred for 10 min. The MACCHS nanomaterial aqueous suspension (10 mL, 1 mg/mL) was then added to the above-mentioned solution, which was stirred until it changed from bright yellow to colorless. The reaction progress was monitored by the UV-Vis absorption spectra of the reaction solutions. To determine the catalytic recycling properties, the catalyst was separated after reaction for 2 min and washed thoroughly with water and ethanol followed by drying at 60 °C for 12 h in a vacuum oven. Finally, the catalyst was redispersed

in a new reaction system for subsequent catalytic experiments under the same reaction conditions.

3. Results and discussion

3.1. Material synthesis and structure characterization

Scheme 1 shows a typical two-step procedure for the synthesis of the catalysts. In the first step, the synthesis of hollow CeO_2 involves the hydrothermal treatment of the solution containing the mixed sodium citrate, urea, H_2O_2 and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. When the solution was heated to 180°C the urea hydrolyzes and reacted with Ce^{3+} and H_2O_2 to form $\text{Ce}(\text{OH})_4$ ($2\text{Ce}^{3+} + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O} = 2\text{Ce}(\text{OH})_4 + 6\text{H}^+$). $\text{Ce}(\text{OH})_4$ then transforms into CeO_2 hollow CeO_2 spheres. In the second step, the synthesized hollow CeO_2 with adsorbed AuCl_4^- ions were separated from the solution by centrifugation and washed twice with pure water to remove the incompletely absorbed AuCl_4^- ions. The AuCl_4^- ions in the CeO_2 hollow spheres then mixed with the sodium citrate solution. The NaBH_4 solution was then added leading to the formation of the MACCHS. The final products were purified by centrifugation and washing with pure water. The desired multi-core Au nanoparticles in hollow CeO_2 were thus obtained.

The crystal structure of the MACCHS was further investigated by XRD. As shown in Fig. 1, two series of peaks are present and these are attributed to face-centered-cubic Au and fluorite CeO_2 , respectively. The characteristic 2θ peaks at ca. 28.60° , 33.09° , 47.56° , 56.39° , 59.14° , 69.53° , 76.78° , 79.14° and 88.75° correspond to the (111), (200), (220), (311), (222), (400), (331), (420) and (422) crystal facets of the CeO_2 fluorite structure. The two weak peaks belong to the (111) and (220) lattice planes of Au nanoparticles.

The morphology and structure (Fig. 2) of the CeO_2 hollow spheres were investigated by different characterization techniques including SEM, TEM, high resolution TEM (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). We found that the products were roughly spherical with a size distribution of about 500–600 nm in diameter (Fig. 2(a)). Each sphere was characteristic of the hollow structure (Fig. 2(b)). Elemental mapping by HAADF-STEM revealed that Ce and O were homogeneously dis-

Fig. 1. XRD patterns of the MACCHS (1) and the CeO_2 hollow sphere (2).

Fig. 2. (a) SEM image of the CeO_2 hollow spheres; (b) TEM image of the CeO_2 hollow spheres. (c) HRTEM image of the CeO_2 hollow spheres (Inset is a selected area electron diffraction (SAED) image indicating the polycrystalline nature of the CeO_2 hollow spheres.); (d) HAADF-STEM mapping image of the CeO_2 hollow spheres and the corresponding line-scan profiles.

Scheme 1. Schematic of the MACCHS preparation procedure.

tributed within the hollow spheres (Fig. 2(d)) while the edge of the structure was enriched with Ce and O. This is consistent with STEM-EDS line scans (Fig. 2(d)). The selected area electron diffraction (SAED) image demonstrates the polycrystalline nature of the hollow CeO_2 and the HRTEM image further indicates that each nanoparticle in the shell is highly crystalline with interplanar spacings of 0.31 and 0.19 nm corresponding to the (111) and (220) planes of CeO_2 , respectively (Fig. 2(c)).

As shown in Fig. 3, the products are similar to the former CeO_2 hollow spheres (Fig. 3(a)), and each sphere is characteristic of a single-shelled hollow structure with a multicore-shell nanostructure morphology (Fig. 3(b)). Elemental mapping by HAADF-STEM revealed that Ce and O distributed within the single-shelled hollow sphere while the edge of all shells were enriched in Ce and O. Interestingly, the Au in the cores (diameter of the Au cores is about 34.58 nm) as well as in a few smaller nanoparticles were distributed in the shell of the CeO_2 hollow spheres, which is also consistent with the STEM-EDS line scans (Fig. 3(d)). The SAED image shows the polycrystalline nature of the hollow CeO_2 and the HRTEM image further indicates that the unique structure is a nanocomposite of Au and CeO_2 (Fig. 3(c)). Elemental mapping by HAADF-STEM also reveals that Ce and O are homogeneously distributed within the MACCHS.

3.2. Chemical composition

A detailed X-ray photoelectron (XPS) analysis of the surface element composition of the MACCHS shows clearly that the shell is composed of Au, Ce and O. As shown in Fig. 4, there are strong Ce 3d peaks and noble metal Au peaks in the XPS spectra of the MACCHS nanomaterials. The XPS spectrum of the Au 4f of

Fig. 4 XPS profiles of the MACCHS. (a) Au 4f core level; (b) Ce 3d core level.

the MACCHS has two peaks indicative of metallic Au at binding energy of 83.7 and 87.3 eV for the Au 4f_{7/2} and Au 4f_{5/2} levels. This implies the complete in situ reduction of Au³⁺ ions by NaBH₄. Regarding the typical signals of the Ce 3d XPS spectrum, the peaks located around 881.6 and 899.9 eV can be attributed to Ce 3d_{5/2} and Ce 3d_{3/2}, respectively. The four additional peaks in the spectrum come from satellite peaks of Ce 3d. The TEM, energy dispersive X-ray spectroscopy (EDS) and XPS results confirm the formation of a multi-cores-in-shell hollow structure for our as-synthesized MACCHS nanomaterials by a simple and green route in the aqueous phase.

As shown in Fig. 5(a), the EDS analysis confirms that the MACCHS nanomaterial consists of Ce, O and Au that originate from CeO_2 and Au, respectively. More importantly, the Au nanoparticles were successfully coated by a CeO_2 cavity structure and the Au content is about 0.6 wt%. Interestingly, the MACCHS has a stronger absorption of visible light compared with hollow CeO_2 , as shown in Fig. 5(b). This comes from the plasmonic effect of the Au nanoparticles. A clear adsorption peak is present from 500 to 600 nm [28]. This raises the potential for MACCHS to be used for photocatalytic reactions such as photocatalytic phenol oxidation [29,30].

Fig. 3. (a) TEM image of the MACCHS (inset is a statistical diagram of the Au cores); (b) HAADF-STEM mapping image of the MACCHS; (c) SAED image indicating the polycrystalline nature of the CeO_2 hollow spheres with Au; (d) Line-scan profiles for the MACCHS.

Fig. 5. (a) EDS analysis for the MACCHS (the inset is a table showing the ratio of elements in the MACCHS); (b) UV-Vis diffuse reflectance spectra of the MACCHS (1) and the CeO_2 hollow spheres (2).

Table 1

BET surface area, average pore diameter, and total pore volume of the CeO₂ hollow spheres and the MACCHS.

Catalyst	BET surface area (m ² /g)	Average pore diameter (nm)	Total pore volume (cm ³ /g)
CeO ₂ hollow sphere	60.1	2.1, 4.9	0.097
MACCHS	53.1	1.9, 4.3	0.087

N₂ adsorption-desorption results, i.e., the specific surface area, pore volumes and pore diameters are shown in Table 1. By comparison with the hollow structured CeO₂ catalyst, a small amount of post-added Au (e.g., 0.6 wt% Au) does result in changes. On the other hand, the pore size distributions move toward smaller pores for the MACCHS. This observation suggests that a certain amount of Au-species were located in the larger pores of the hollow structured CeO₂ catalyst, which decreased the size of the pores. The holes on the surface of the hollow MACCHS were large enough for *p*-nitrophenol diffusion and the Au nanoparticles were not completely coated by CeO₂. Therefore, the reactant may easily come into contact with the Au nanoparticles. The large specific surface area of the MACCHS is an advantage for the catalytic reduction of *p*-nitrophenol.

3.3. Catalytic activity evaluation

To determine the advantages of the novel nanostructure MACCHS catalyst, we investigated the reduction of *p*-nitrophenol to *p*-aminophenol by NaBH₄ at room temperature as a model reaction [31,32]. The reduction of aromatic nitro compounds to amines is an important process in synthetic organic chemistry and in the industrial production of many industrially important chemicals. The reduction process was monitored by UV-Vis absorption spectroscopy (Fig. 6). A yellow solution was obtained after mixing the *p*-nitrophenol solution with NaBH₄ solution. This was characterized by the 400 nm *p*-nitrophenol absorption peak. When the MACCHS catalyst was added, the absorption peak at 400 nm quickly disappeared while a median absorption peak appeared at 300 nm. This is evidence for the reduction of *p*-nitrophenol to *p*-aminophenol. This change is shown by the UV-Vis spectra in Fig. 6. The reaction occurred rapidly completing within 2 min. The Au nano-

Fig. 6. UV-Vis spectra for the reduction of *p*-nitrophenol by NaBH₄ in the presence of the MACCHS catalyst (Au: 0.6 wt%) at room temperature. (1) 0 min; (2) 2 min.

Fig. 7. Catalytic activity of the MACCHS (1), bare Au nanoparticles (2) and hollow CeO₂ spheres (3) during the reduction of *p*-nitrophenol using NaBH₄ in 5 cycles, respectively.

particles that are trapped in the CeO₂ hollow spheres play a critical role in the *p*-nitrophenol reduction reaction. UV-Vis spectra of the reaction solutions showed that the use of a small amount of the MACCHS nanomaterial as a catalyst resulted in the reaction being complete within 2 min. The solution color changed from bright yellow to colorless.

As shown in Fig. 7, the MACCHS exhibited high activity and good recyclability. The conversion decreased slightly after 5 successive cycles. For comparison, when bare Au nanoparticles were used as the catalyst the catalytic activity decreased rapidly. This behavior indicates severe aggregation. These results indicate that a CeO₂ core-shell support is required to stabilize the Au nanoparticles by preventing their aggregation and leaching. This produces an excellent catalyst with high activity and good recyclability [33,34]. The prepared CeO₂ core-shell support may be considered to be a reasonable MACCHS for the encapsulation of small Au nanoparticles. Fine tuning the synergistic interactions between the Au nanoparticles and the CeO₂ support is important in achieving high activity. The results indicate that the MACCHS structure is an ideal candidate for nanoreactor.

3.4. Catalytic reaction process

Scheme 2 shows a proposed mechanism for the reduction of

Scheme 2. Schematic showing the MACCHS catalytic reduction of *p*-nitrophenol to *p*-aminophenol in a NaBH₄ solution.

p-nitrophenol to *p*-aminophenol with NaBH₄ solution catalyzed by MACCHS. “Three-dimensional” intimate contact between the multiple Au cores and the CeO₂ shell maximizes the metal-support interaction, which facilitates interfacial charge transfer. A uniform structural composition wherein several Au cores are encapsulated by a CeO₂ shell provides a homogeneous environment for the reduction reaction. All these features along with our preliminary promising results indicate significant potential for the scale-up synthesis of metal core@semiconductor oxide shell nanocomposites. In heterogeneous catalysis, further investigations for its applications are thus warranted.

4. Conclusions

A simple and facile template-free approach was developed to prepare a MACCHS catalyst using a combination of hydrothermal and impregnation treatments. The reduction of *p*-nitrophenol to *p*-aminophenol using a NaBH₄ solution as a model reaction showed that the MACCHS nanomaterials can effectively promote catalytic reduction reactions and retain their excellent stability. These materials may find a wide range of potential application such as in CO oxidation, gas sensing, removal of pollutants in waste water, and even in biological and medical fields. Our synthesized hollow core-shell materials with a multi-core-in-shell structure are a powerful platform for nanoreactors and we believe that this synthetic strategy can be extended to the production of new composite materials with enhanced properties for advanced applications.

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Graphical Abstract

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Multiple Au cores in CeO₂ hollow spheres for the superior catalytic reduction of *p*-nitrophenol

Kun Zhao, Jian Qi, Shenlong Zhao, Hongjie Tang, Huajie Yin, Lingbo Zong, Lin Chang, Yan Gao*, Ranbo Yu*, Zhiyong Tang*
University of Science and Technology Beijing;
National Center for Nanoscience and Technology;
Institute of Process Engineering, Chinese Academy of Sciences

A novel catalyst with multiple Au cores in CeO₂ hollow spheres was synthesized using an impregnation method, and it exhibited high activity and stability during the catalytic reduction of *p*-nitrophenol to *p*-aminophenol.

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多金核二氧化铈空心球用于硝基苯酚催化加氢

赵 昆^{a,b,†}, 齐 健^{b,c,†}, 赵慎龙^b, 唐红杰^c, 尹华杰^b, 宗玲博^a, 常 琳^b,
高 燕^{b,§}, 于然波^{a,#}, 唐智勇^{b,*}

^a北京科技大学冶金与生态工程学院冶金物理化学系, 北京100083

^b国家纳米科学中心纳米系统与多级次制造重点实验室, 北京100190

^c中国科学院过程工程研究所多相复杂系统国家重点实验室, 北京100190

摘要: 催化剂的微观结构在催化还原反应、有机物氧化反应及有机物转化反应中起着关键作用. 本文利用无模板方法合成了多金核中空二氧化铈微球催化剂. 将制备好的二氧化铈中空微球浸渍到一定浓度的氯金酸溶液中, 然后多次洗涤除去表面吸附的氯金酸离子, 最后通过硼氢化钠还原制成中空氧化铈微球包覆的多金核的核壳结构催化剂. 将该核壳结构材料用于硝基苯酚加氢反应与金纳米粒子及氧化铈微球相比, 多金核中空二氧化铈核壳结构表现出优越的活性和稳定性. 通过这种浸渍洗涤再还原的简单方法合成的多金核二氧化铈催化剂有望应用于生物医药和能源环境等领域.

关键词: 多金核; 二氧化铈空心球; 硝基苯酚; 催化还原

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*通讯联系人. 电话/传真: (010)82545580; 电子信箱: zytang@nanoctr.cn

#通讯联系人. 电话/传真: (010)62656765; 电子信箱: ranboyu@ustb.edu.cn

§通讯联系人. 电话/传真: (010)82545603; 电子信箱: gaoyan@nanoctr.cn

†赵昆与齐健为共同第一作者.

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