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Methodology for the preparation of composite material with hollow structure with excellent catalytic activity for pollution gas oxidation

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2020-04-01

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First Place

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Reflective Essay

I am developing a new methodology for the preparation of composite material with a hierarchical porous structure, high surface area, and strong synergistic effect to produce reliably high activity and recycle stability for Carbon monoxide (CO) oxidation. CO oxidation is not only a model reaction commonly used in catalytic research but also a reaction process of great practical significance. Catalytic oxidation of CO is the most direct, simple, cheap, and effective way to eliminate CO, so it is widely used in real life. For example, the application of gas purification in gas masks, tobacco harm reduction, automobile exhaust purification, and the elimination of CO pollution in a closed system (submarine, aircraft, spacecraft, etc.) has attracted more and more attention in recent years. Our goal is to synthesize the most effective catalyst for the treatment of carbon monoxide. Increase the active contact area with reactants as much as possible in enough space and accommodate the most active part in the smallest unit volume. Porous supported nanomaterials are broadly concerned because of their superb structural properties such as high specific surface area, low density, enough porosity, and good thermal stability. Therefore, the porous structure has excellent performance, especially in the field of catalysis, which has unique structural characteristics. Our group has studied the porous materials such as manganese dioxide, cerium dioxide, silica, alumina, etc. by modifying them, we can make them better combined with the active point and obtain suitable catalytic materials. I am still collecting further data and trying to test the activity and stability under extreme conditions, such as high temperature and high pressure.

As an undergraduate researcher, I also need a lot of relevant knowledge to maintain my research. In addition to collecting data from experiments, I need a lot of experience related to my research field to enrich myself. I found many useful documents from the research database of the UCSB library, where I searched the published articles, which included the details related to each experiment, such as the conditions of hydrothermal synthesis, the physical properties, the micro atomic and molecular scale in-situ detection of crucial reaction intermediates, and the research of the effects of size, geometry, and electronic structure, metal oxidation valence on the reaction activity and mechanism. In UCSB Library, I have learned various characterization methods to explore the reaction mechanism of CO catalytic oxidation, understand the essence and critical issues of CO catalytic oxidation in different environmental atmosphere, to achieve the purpose of guiding catalyst design.

Thanks to the library resources of UCSB Library, I can get as much information as possible to support my documentary study and help me find new preparation methods and future research directions. I gradually learned the process of discovering knowledge through understand the data summarized by other researchers. I realized that in the whole research process, the library is so important to us in providing useful previous research publications to let us continue our predecessors' thinking and explore new knowledge. With Article Indexes & Research, I found many practical research tools on databases, such as Reaxys and SciFinder, which helped me to brainstorm, especially gave me new ideas on the direction of material synthesis and gave me suggestions on the future projects. Combined with the knowledge of experiments, reading of literature, and understanding of reference publications from library resources, I have made use of various preparation methods from previous works, including the traditional impregnation, co-precipitation, ion exchange, etc. I compare the feasibility of each option under comprehensive conditions to see which is more suitable for the materials we study.

UCSB Library providing so much information that I can learn how to write papers through online library resources. In addition, I was fortunate to participate in CHEM 184 about literature research provided by the library last winter. Under the guidance of Mr. Huber, I experienced the resource convenience brought by the library more deeply. Mr. Huber introduced us to the organization of information in chemical science, including data collection and various literature indexes provided by the library, as well as different types of primary literature and other resources useful to material researchers. I appreciate learning a lot to support my future research career. For me, research is a process to help me digest the inherent knowledge and explore new fields, while the library is an important tool for my research. With the help of library resources, I can explore more efficiently, the materials I study will effectively reduce pollution in the future and make our community better.

Methodology for the preparation of composite material with hollow structure with excellent catalytic activity for pollution gas oxidation

2020/4/2

Presented by Dylan Bian

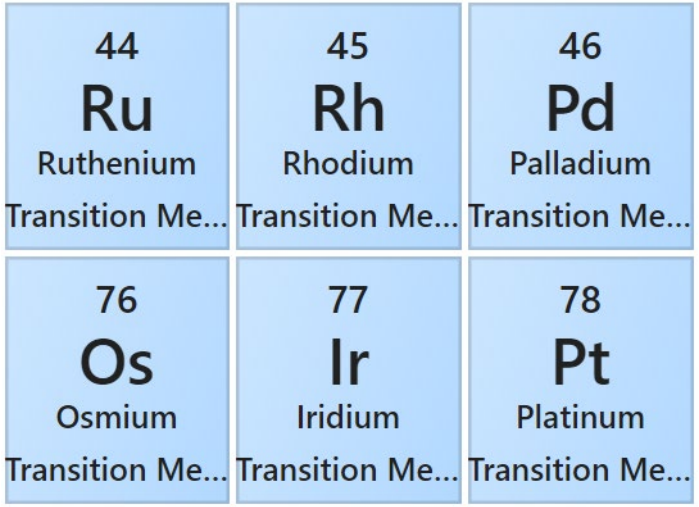
Chemistry Major

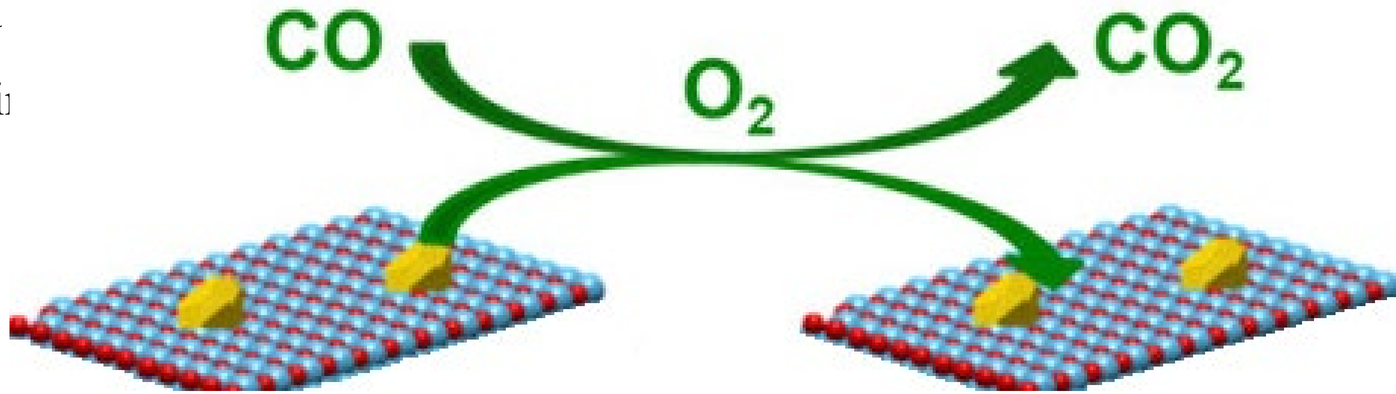
College of Creative Studies

Introduction

There is a growing demand for new heterogeneous catalysts for cost-effective catalysis. CO oxidation among the porous catalytical material has received intensive study in heterogeneous catalysis. Supported noble metal catalysts have a wide range of application prospects in heterogeneous catalysis, but poor thermodynamic stability greatly hinders their practical application.

Noble-metal particles are the most widely studied and applied catalysts in recent decades due to their excellent activity and selectivity for many catalytic reactions.



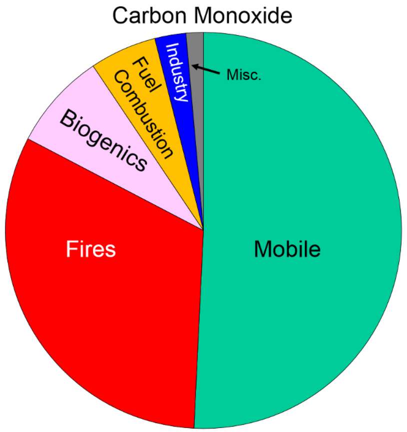


Introduction

"Carbon monoxide is a colorless odorless poisonous gas formed when carbon in fuels is not burned completely. It is a byproduct of motor vehicle exhaust, which contributes more than two-thirds of all CO emissions nationwide. In cities, automobile exhaust can cause as much as 95 percent of all CO emissions."

“Carbon monoxide enters the bloodstream and reduces oxygen delivery to the body‘s organs and tissues. The health threat from CO is most serious for those who suffer from cardiovascular disease. Healthy individuals are also affected, but only at higher levels of exposure. Exposure to elevated CO levels is associated with visual impairment, reduced work capacity, reduced manual dexterity, poor learning ability, and difficulty in performing complex tasks.”

It should be noticed that High concentrations, e.g., from a car running in an unvented garage or from poorly vented kerosene heaters, can be fatal.



PART 01 Theoretical Basis

01

Ultrafine active precious metal particles are in a thermodynamically unstable state. To decrease the surface energy, the aggregation and growth of metal particles usually occur in a high-temperature environment or under light irradiation conditions during the catalytic and relevant processes; this results in the passivation and deactivation of the catalysts. Furthermore, the leaching of noble-metal particles was found to be the main reason for the decrease in the catalytic activity of these particles in reactions.

02

Noble metal nanoparticles have a high specific surface area and surface energy and are in a state of thermodynamic instability. High instability would lead the metal particles reduce the surface energy of catalysts, in the process of catalysis, especially under high temperature or light conditions, they are accessible to large aggregate particles, which leads to passivation and deactivation of the catalyst. It is a reasonable solution to separate precious metal particles in a small cavity because it can effectively prevent the migration and deactivation of particles. Besides, this separation method can also reduce the leaching of active components in catalyst particles during the chemical process, which is another crucial aspect of designing new nanocatalysts.

Nobel-metal based catalysts

Noble-metal particles are the most widely studied and applied catalysts in recent decades due to their excellent activity and selectivity for many catalytic reactions.

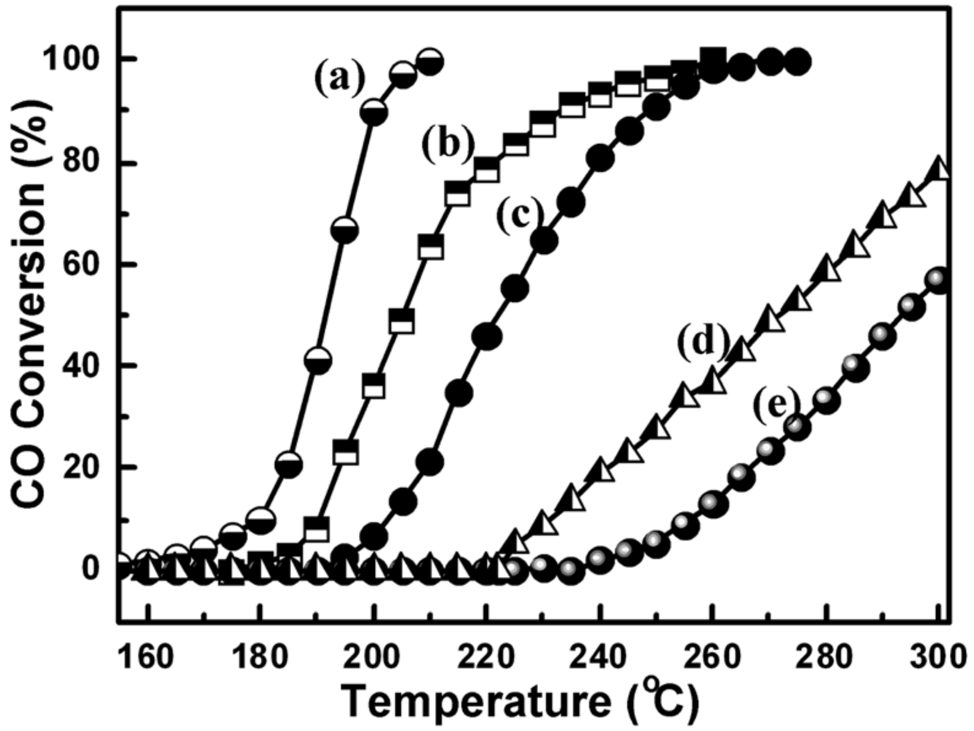


Figure 2 Catalytic activity of Au@CeO2 NP-CeO2 NT(a).
J. Mater. Chem. A, 2013,1, 288-294.

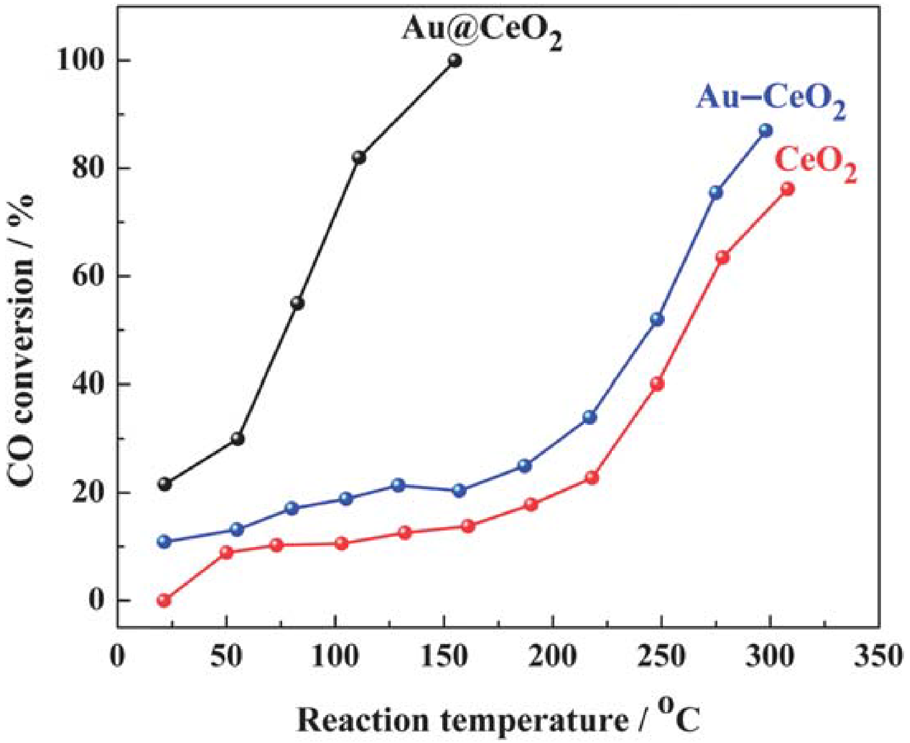
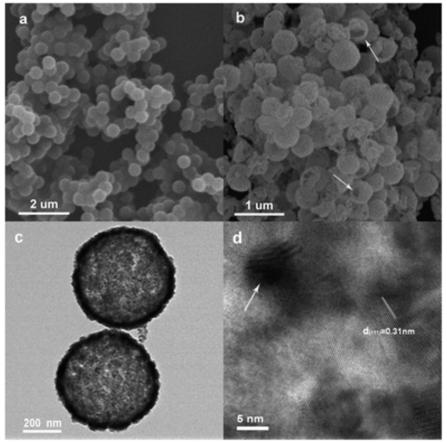


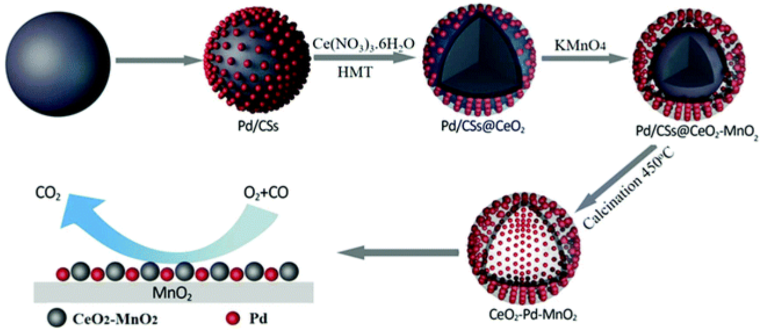
Figure 1 Catalytic activity of Au@CeO2, Au-CeO2, and pure CeO2
Energy Environ. Sci., 2012, 5, 8937-8941

What we mainly learn from the previous work

Lu's group have reported the fabrication of hollow Pd–CeO2 nano-composite spheres (NCSs) by a facile hard-template method in an aqueous phase, followed by the elimination of the polymer templates by simple calcination. In these hollow Pd–CeO2 NCSs, the aggregation of Pd nanoparticles can be efficiently avoided by the protection of the CeO2 crystal. The high dispersity of Pd species can be well maintained even after calcination at 700 °C. The synthesized hollow Pd–CeO2 NCSs exhibit high catalytic activity for the selective reduction of aromatic nitro compounds under ambient conditions and CO oxidation.



Wang's group reported an assembly method of sandwich manganese dioxide palladium cerium dioxide hollow spheres using carbon spheres as sacrificial templates. This kind of palladium loaded hollow ball has high stability and CO oxidation activity. Its unique sandwich structure effectively prevents the aggregation of Pd nanoparticles in the process of high temperature calcination and catalysis. This can be attributed to the sandwich structure and the strong synergistic effect between palladium and porous MnO2-CeO2 shell. This unique structure design provides a new way for the synthesis of noble metal-based catalysts with excellent activity and stability



PART 02 Main Content

Ce

Mn

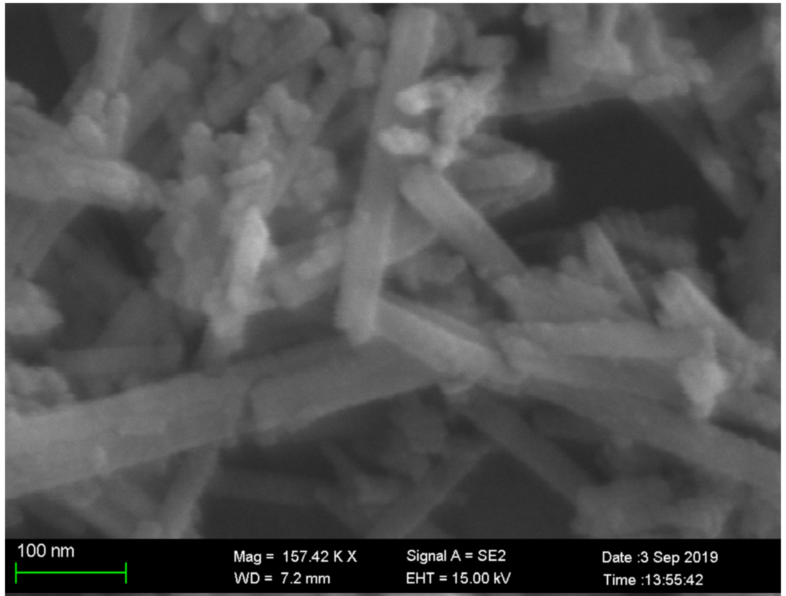
Al

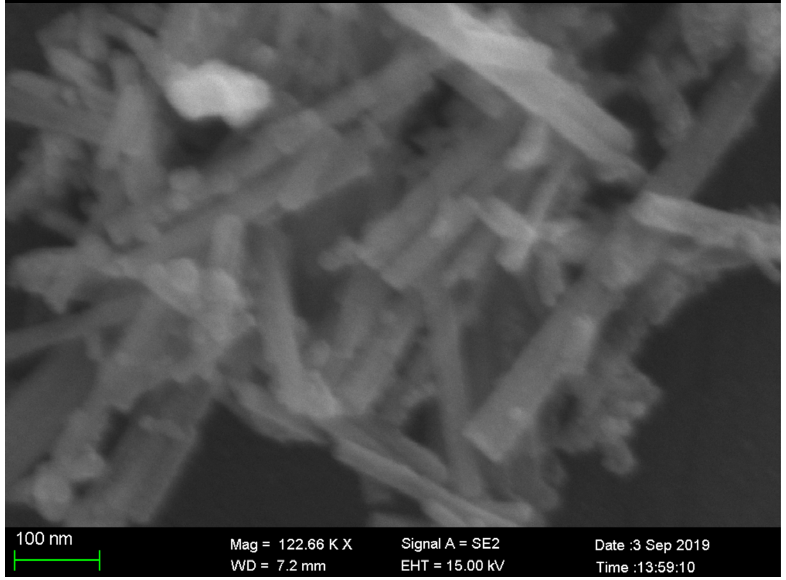
CeO_2 nanorods

MnO_2@Pd@MnO_2 hollow spheres

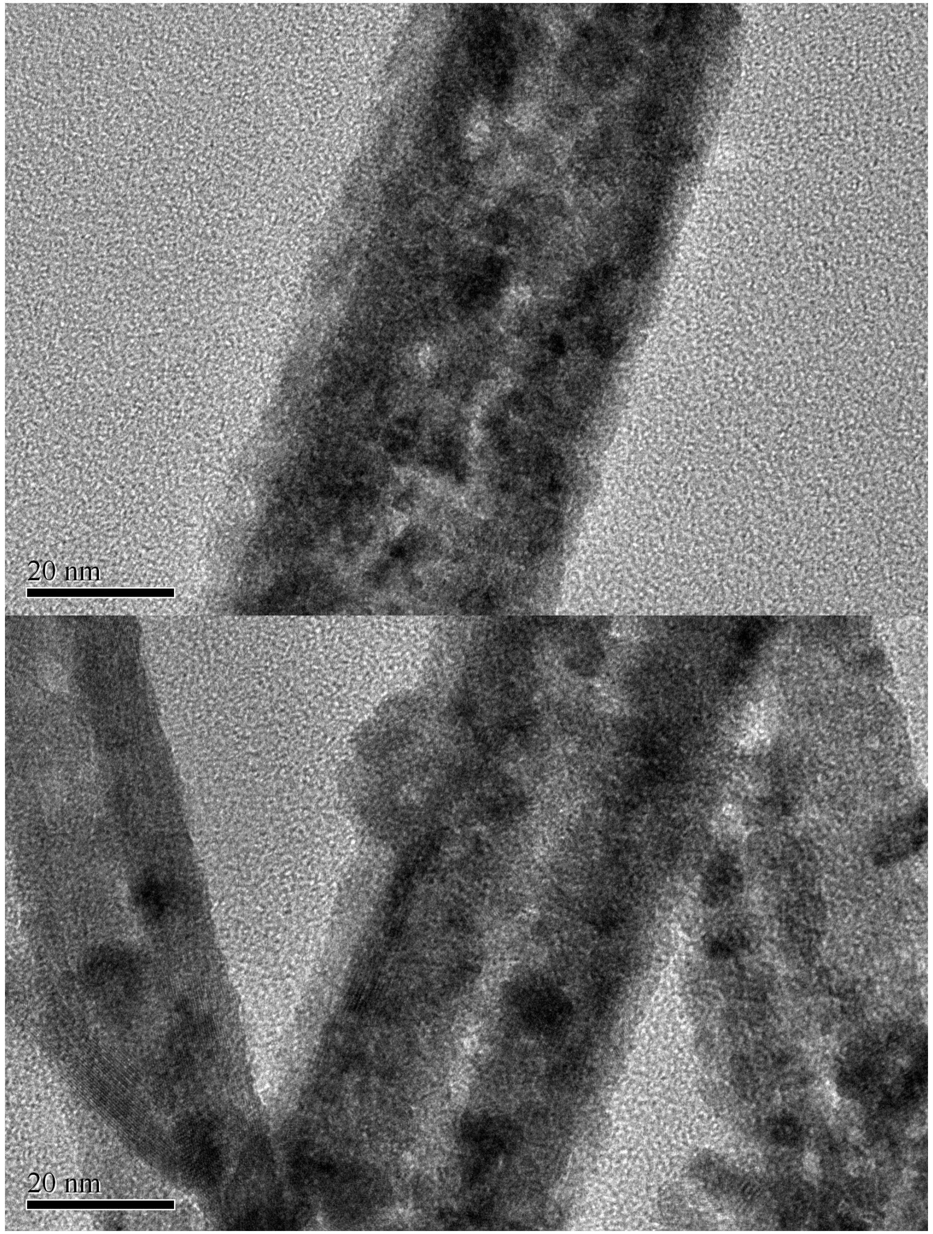
Aluminate porous ceramics

It was found that solvents, surfactants and organic solvents had significant effects on the formation and growth of nano ceria. A very effective hydrothermal method without surfactant and organic template can be used to synthesize CeO2 nanowires. By controlling the composition and conditions of synthesis, the length width ratio of nanorods can be precisely controlled in a wide range. In the theory of molecular motion, the Stokes Einstein relation tells us that the diffusion coefficient (d) of non solvent solute is inversely proportional to the viscosity (η) of solution.

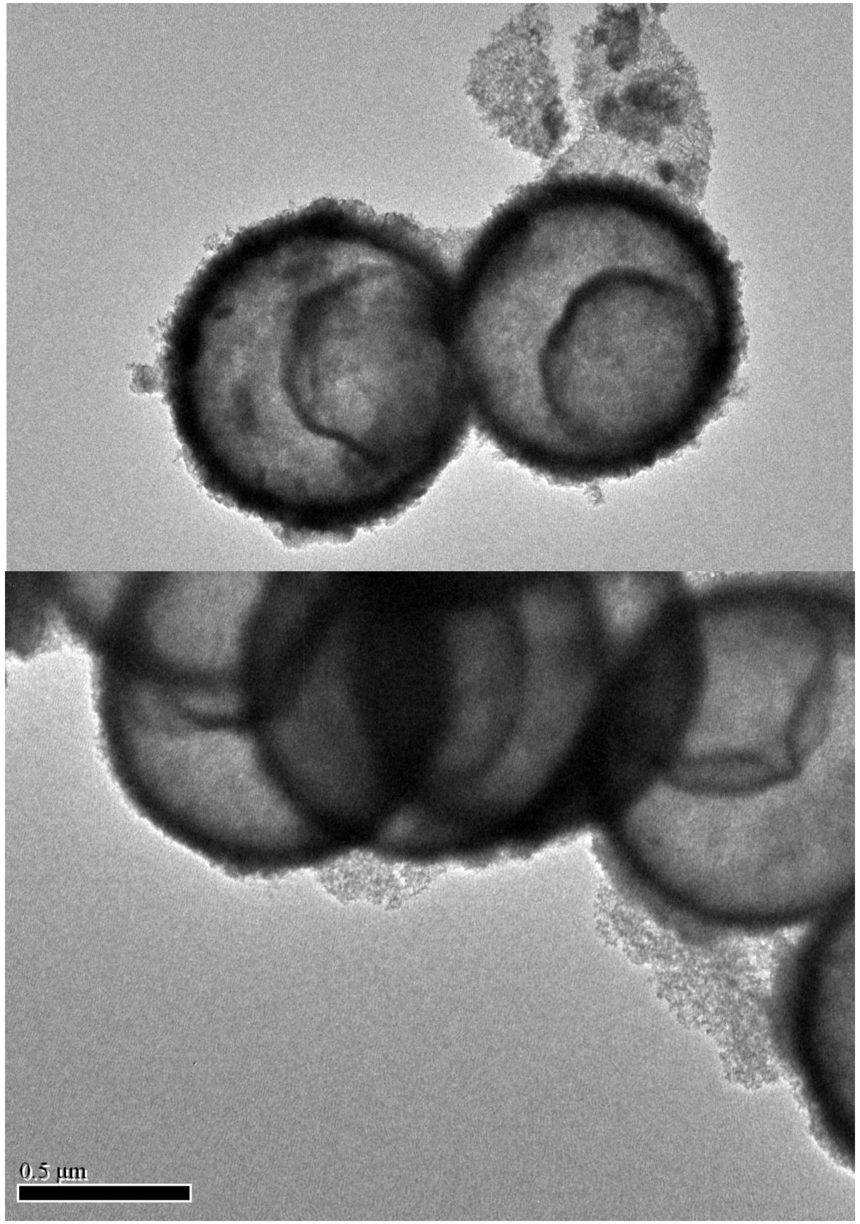




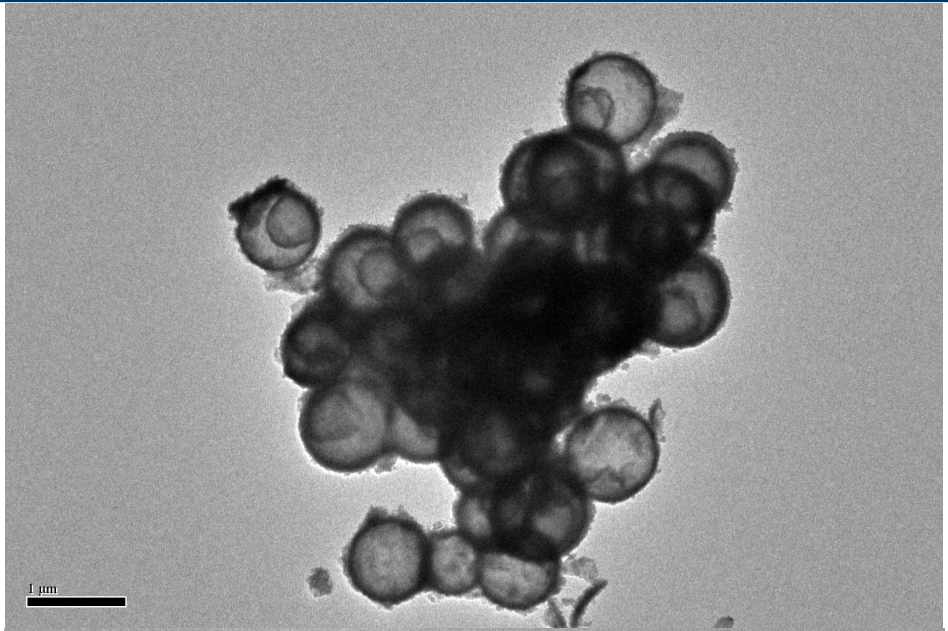
As we increase the viscosity of the solution and slow down the mass transfer rate, it is beneficial to the anisotropic growth of one-dimensional CeO2 nanostructures. We control the length of nanorods to be about 500nm and the range is 0.1 to 3.5 μ m under the condition of many times of debugging and synthesizing. The diameter ranges from 35 to 50 nm. The electron microscope images of CeO2 nanorods show that our products are composed of nanocrystals with good crystallinity. A high dispersion nanorod sample and its large surface area provide excellent conditions for loading precious metals.

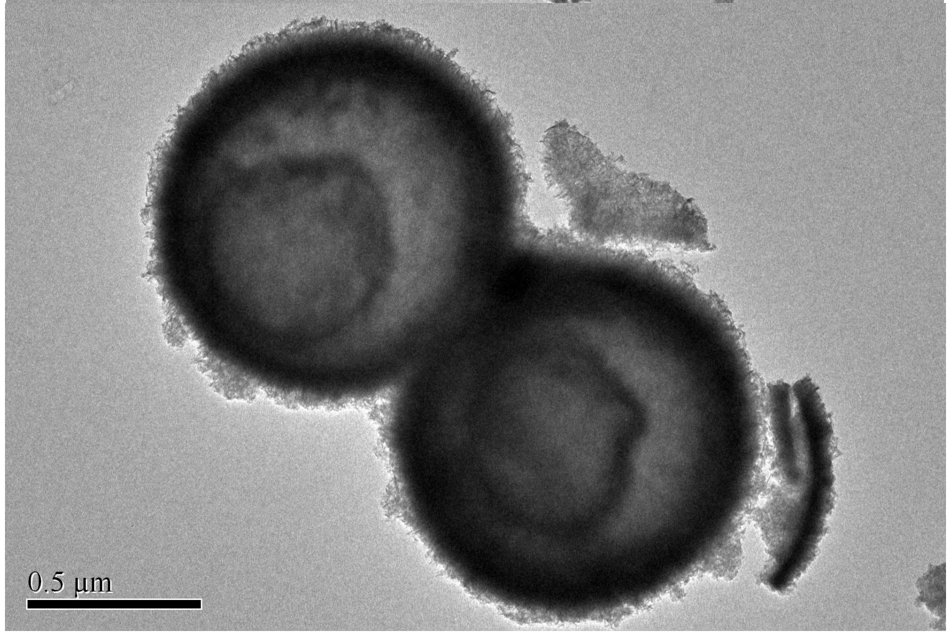


In order to make full use of palladium, we need a strong and effective support to load platinum on the support to improve the dispersion of metal and enhance the catalytic activity of the catalyst. In addition, we are committed to the synthesis of non-toxic, pollution-free green catalyst support, and the relatively fragile shell on the stability of a major challenge. Therefore, it is an ideal choice to embed precious metal particles in the layered porous oxide shell of hollow spheres. we found the hollow structure of sandwich MnO_2@Pd@MnO_2 by template method, in which metal-nanoparticles are embedded in the porous MnO_2 shell.

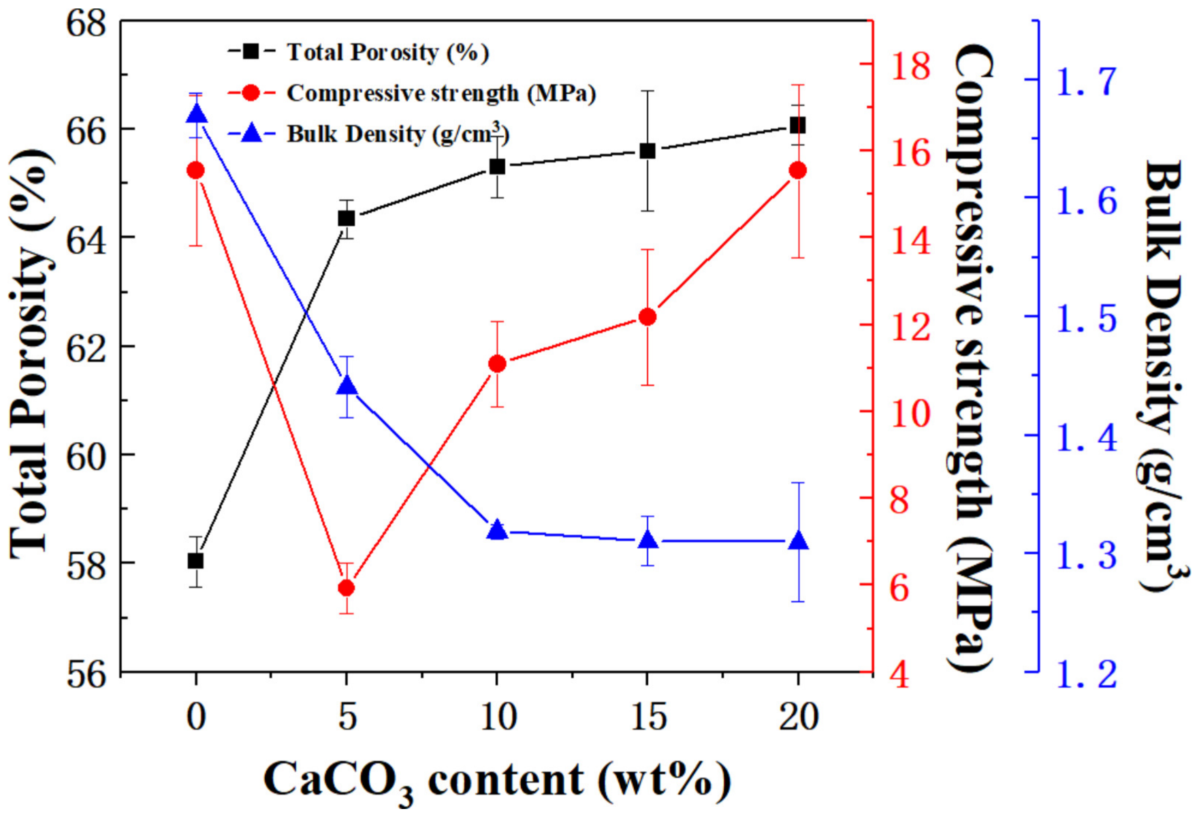


Compared with the conventional supported catalyst, sandwich structure design can significantly improve the thermal stability of the catalyst without considerably reducing its catalytic activity. The catalytic activity of sandwich shape MnO2@Pd@MnO2 hollow spheres has not decreased obviously after five cycles with 16 hours at a constant temperature and high temperature. The complete conversion of carbon monoxide at 105 ℃ shows that the supported catalyst has strong catalytic activity for CO oxidation. This method provides a new way to prepare a catalyst with high activity and excellent thermal stability.



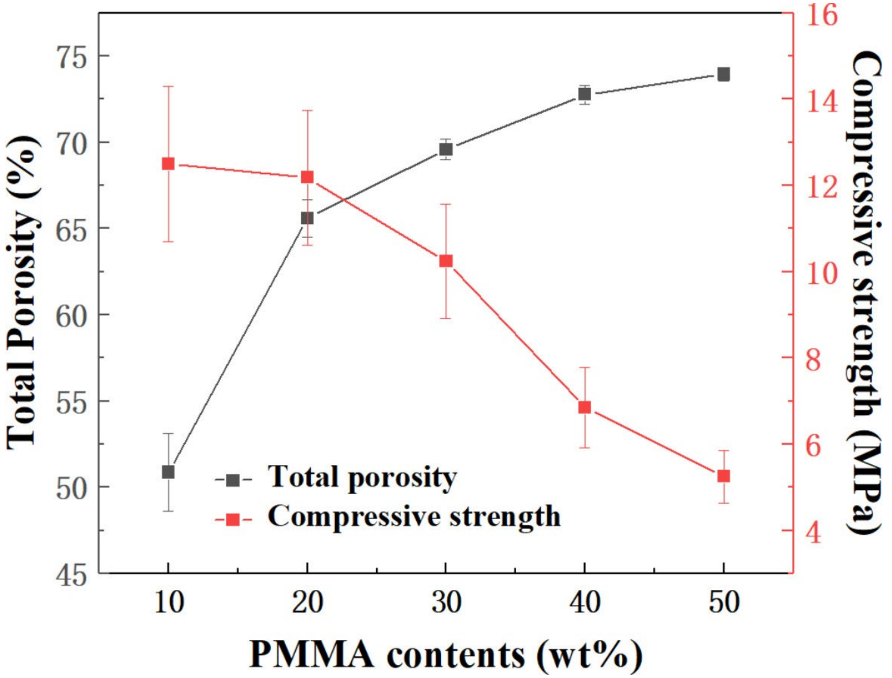


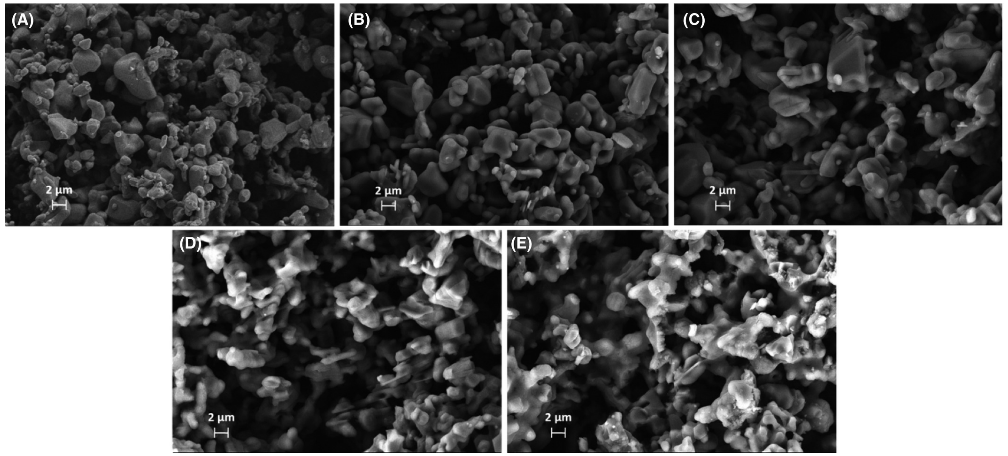
Al2O3 and CaCO3 were used as raw materials, PMMA microspheres were used as pore-forming agent, by adjusting the amount of calcium carbonate and polymethyl methacrylate microspheres, porous calcium aluminate ceramics with controllable shrinkage were prepared. At the same time, we studied the effect of CaCO3 and PMMA on the phase composition, porosity, shrinkage, and strength of porous calcium aluminate ceramics. As we increase the calcium carbonate from 0 to 20%, the sintering shrinkage and total shrinkage of our porous materials are gradually reduced, the porosity is increased from 58% to 66%, and the compressive strength is increased from 5.9 MPa to 15.5 MPa.



Journal of the American Ceramic Society, First published: 19 February 2020, DOI: (10.1111/jace.17075)

The results show that the addition of calcium carbonate can improve the porosity and strength of the sample at the same time. With the increase of PMMA content, the shrinkage of porous calcium aluminate ceramics first decreased and then increased. By adjusting the amount of calcium carbonate, the shrinkage, pore size, porosity, and strength of porous calcium aluminate ceramics can be effectively controlled. This is of great significance for the preparation of porous ceramic materials with low shrinkage or zero shrinkage, high porosity, high strength, and low processing cost. The advantages of high compressive strength and a large Porosity can help us to carry out precious metal loading catalysis in the future.





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PART 03

Future Directions

We think that a qualified catalyst can not only bear high temperature, but also have appropriate structural strength, and the density and thermal expansion coefficient are small. The most important thing is to have good compatibility with the carrier and reduce the application cost as much as possible. In the past two years, we have tested the preparation of various porous materials, and tested the loading capacity of some of them for precious metals and the catalytic efficiency for waste. Among them, the three representative materials I mentioned show excellent physical properties in our experiments, also provide us with guiding ideas in the future research on the methodology of porous material synthesis. In the coming year, we will supplement more data and look forward to publishing our results.


Carbon
8.28
Dylan Bian
Jun - Sept 2019
9.3
CeO2
CeO2
SiO2
Pd MnO2
Pt/SiO2
1.8
ml
1.0
0.5
0.03g/0.04g Pd/C
Pd MnO2

THANKS

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Citation Format: ACS(American Chemical Society)

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