Angewandte
Communications

Nanoparticle Catalysts

DOI: 10.1002/anie.201406490

Palladium Nanoparticles Embedded in the Inner Surfaces of Carbon Nanotubes: Synthesis, Catalytic Activity, and Sinter Resistance**

*Hongyang Liu, Liyun Zhang, Ning Wang, and Dang Sheng Su**

Abstract: *The highly efficient preparation of metal nanoparticles embedded in a carbon nanotube remains a considerable challenge. Herein, we report a simple and template-based procedure for the fabrication of carbon nanotubes with Pd nanoparticles uniformly embedded in the inner carbon surfaces. In addition to the novel structure, the sinter-resistance of the as-prepared Pd/C nanocomposite was much better than that of the traditional carbon-nanotube-supported Pd catalysts. The as-prepared Pd/C nanocomposite has a high recyclability in a liquid-phase Suzuki coupling reaction. This strategy may be extended as a general approach to prepare metal nanoparticles supported on carbon-nanotubes.*

Noble-metal nanoparticles (NPs) have attracted considerable attention owing to their potential applications in catalysis, gas sensors, energy conversion, and fuel cells.[1,2] However, the high surface energy of metal NPs means they easily agglomerate or change shape during catalytic reactions, resulting in a dramatic decrease of their activity and selectivity.[3] To avoid aggregation, considerable efforts have been made in depositing metal NPs on various solid supports, such as silica, zeolites, alumina, metal oxides, carbon, polymers and other composites.[4] Among a wide variety of these supports, carbon-supported metal NPs are of particular interest for their various promising applications.[5] In the family of nanocarbon materials, active carbon (AC) is generally used owing to its high specific surface area and strong resistance to acid. Unfortunately, the high microporosity of AC hampers the diffusion of reactants. And AC has low mechanical strength which decrease its stability and contains impurities which can be detrimental to its activity.[6] Recently, carbon nanotubes (CNTs) have displayed potential application as catalytic supports, by virtue of their large surface areas and absence of microporosity, which can benefit the mass transfer and catalytic activity in liquid-phase reactions.[7] For preparing CNT-supported metal NPs, ion-exchange, electrostatic adsorption, or impregnation of metal ions onto CNT followed by reduction with hydrogen (H_2) are widely used procedures.[8] Although a high dispersion of metal NPs on CNT can be achieved by employing these methods, the metal NPs obtained are usually irregular in size and still have a tendency to be sintered at a moderate temperature to form stable larger clusters because of the relatively weak interaction between supported metal NPs and carbon surfaces.[2] Therefore, methods for the fabrication of CNT-supported metal NPs with uniform particle sizes and high resistance toward sintering at high temperature are still needed.

The use of the inner cavity of the CNT as a nanoreactor is an exciting possibility.[9] Confining metal NPs in the CNT not only can enhance their sinter resistance, but also promote their catalytic performance.[10] Therefore, the synthesis of CNT-confined metal NPs provides a new concept to prepare CNT-supported metal NPs. To date, two main routes are used to introduce NPs into the cavity of CNT: one route is the traditional incipient wetness impregnation method relying on the filling of oxidized CNTs by capillarity with a solution containing a metal salt or preformed NPs.[11] However, the fraction of metal present in the inner cavity of the CNT is only between 15 and 50%;[12] the other approach consists of producing CNT inside anodic aluminum oxide membranes, filling the resulting template with a solution of NPs, and dissolving the alumina membrane.[13]

Herein, we report a simple, efficient and template-based procedure for the fabrication of Pd NPs embedded in the inner cavity of CNT. The Pd NPs obtained are not only uniformly confined into the channel of the CNT, but are also strongly embedded in the inner carbon surface. As illustrated in Scheme 1, the method involves a three-step process. The first step is the generation of ZnO nanowires by traditional chemical-vapor deposition methods (CVD) and the deposition of Pd NPs onto the ZnO surface by the deposit–precipitation process. Then, a carbon layer is uniformly coated onto the surface of ZnO nanowire by a fast coking process with diluted ethylbenzene under high temperature. Finally, the Pd/C nanocomposite with Pd NPs uniformly embedded in the inner surfaces of CNT is obtained, after the removal of ZnO nanowires by HCl at room temperature. In addition to high BET surface areas, the as-prepared Pd/C nanocomposite with porous channels can ensure high permeation and mass-transfer rates for species involved in a catalytic reaction. The Pd/C nanocomposite has a high recyclability in a liquid-phase Suzuki coupling reaction. More

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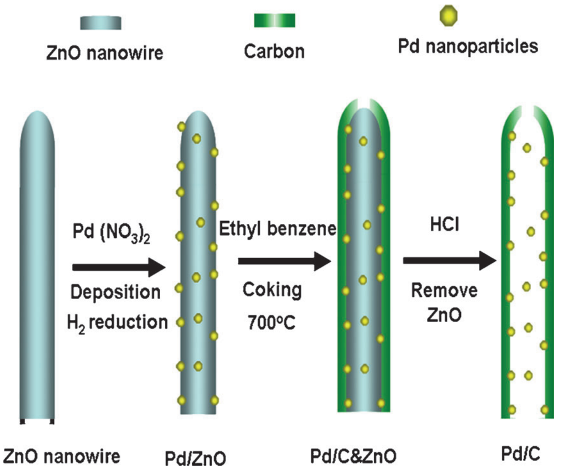
[*] Prof. Dr. H. Y. Liu, Dr. L. Y. Zhang, Prof. Dr. D. S. Su
Shenyang National Laboratory for Materials Science
Institute of Metal Research, Chinese Academy of Sciences
72 Wenhua Road, Shenyang 110016 (China)
E-mail: dssu@imr.ac.cn
dangsheng@fhi-berlin.mpg.de

Prof. Dr. N. Wang
Department of Physics, Hong Kong University of Science and Technology, Hong Kong (P.R. China)

[**] This work is financially supported by National Natural Science Foundation of China (No. 21203214, 21133010, 21261160487, 51221264), the National Basic Research Program (973 Program, No. 2011CBA00504), the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDA09030103, and the Sinopec China No. 21203214.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406490.



Scheme 1. The three-step for fabrication of Pd/C nanocomposites with Pd NPs embedded in the inner surface of carbon nanotube. 1) deposition of Pd NPs onto ZnO nanowire; 2) coating of carbon layers; 3) removal of ZnO nanowire with diluted HCl.

importantly, as a result of the novel structure, the sinter-resistance of the as-prepared Pd/C nanocomposite is much better than that of commercial CNT-supported Pd catalysts.

Figure 1 A,B show representative SEM and TEM images of the ZnO nanowires prepared by the traditional CVD method. The collected ZnO nanowires are fairly uniform in shape and size. The average length and width of the ZnO nanowires is 2–10 μm and 50–200 nm, respectively. The Pd NPs supported on the ZnO nanowires were easily and uniformly deposited by the deposit–precipitation process (Figure 1 C,D; more TEM images were shown in Figure S1 of the Supporting Information). The average size of Pd NPs is 2–4 nm. The weight loading of Pd NPs is 1.9 %, which is confirmed by the inductively coupled plasma (ICP) analysis.

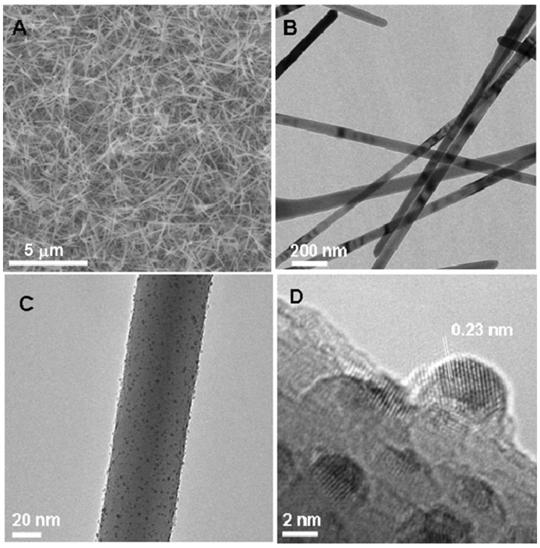


Figure 1. A) SEM and B) TEM images of a ZnO nanowire. C,D) TEM images of the Pd/ZnO template.

The X-ray diffraction (XRD) pattern of Pd/ZnO (Figure S2) also indicates that highly dispersed Pd NPs supported on the ZnO nanowire are obtained, confirming the TEM observations.

The ZnO nanowires decorated with Pd NPs were then employed as a substrate for the in situ growth of the carbon layer by a fast coking reaction of ethylbenzene at the temperature of 700 °C just for 2 min. A carbon layer is uniformly coated on the surface of Pd/ZnO nanowire (Figure 2 A,B) and no gap between the carbon layer and ZnO nanowire is observed (Figure 2 C). The average thickness of the carbon layer is 3–5 nm. Note that the Pd NPs on the ZnO surface are also embedded by the carbon layer (Figure 2 D). In addition, we can find that the 1D morphology and the structure of the ZnO nanowire are perfectly retained after being coated by the carbon layer. The average size of the Pd NPs in the Pd/ZnO/C nanocomposite is changed to 3–5 nm, which is a bit bigger than that of initial Pd/ZnO template (2–4 nm), resulting from the slight aggregation of smaller Pd NPs during the coking process.

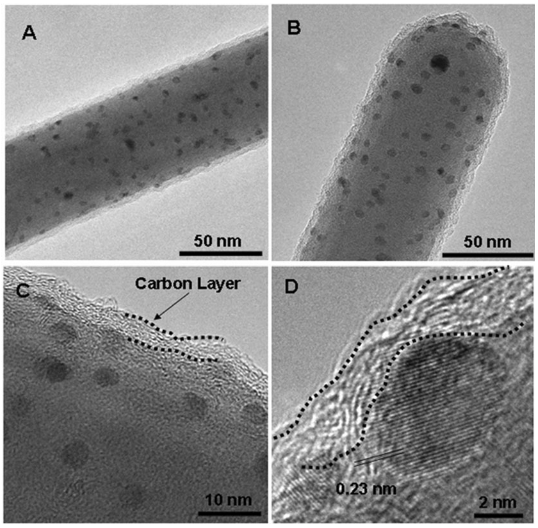


Figure 2. A,B) TEM images of Pd/ZnO template coated with a carbon layer. C,D) High-magnification TEM images.

Figure 3 shows TEM images of the final obtained Pd/C nanocomposite after removing the ZnO nanowires by diluted HCl (1 mol L^{-1}) at room temperature. All the products have tubular structures (Figure 3 A,B). In particular, these tubular structures almost replicate the original morphologies of the 1D ZnO nanowires. The CNTs resulting from the ZnO template have inner diameters of 50–200 nm, agreeing well with the diameter of the initial ZnO templates, and their walls are quite smooth and about 3–5 nm thick. All the Pd NPs are uniformly embedded in the inner surface of the CNT and no Pd NPs are observed on the outer surface. (More TEM images were shown in Figure S3.) The loading of Pd NPs in the as-prepared Pd/C nanocomposite is about 1.83 %, as determined by the ICP analysis, which reveals that most of the Pd NPs are retained and they are located on the inner surface

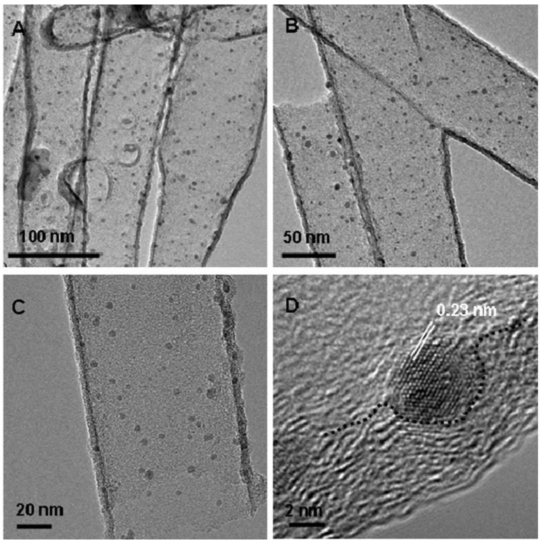


Figure 3. A,B) TEM images of the as-prepared Pd/C nanocomposite with Pd NPs uniformly embedded in the inner carbon surface. C,D) High-magnification TEM images.

of the carbon nanotube (compared with that of the initial Pd weight loading (1.95%) in Pd/ZnO substrate). In the HRTEM image (Figure 3D), the interplanar distance of the nanoparticle is 0.23 nm, in agreement with the lattice spacing of the (111) plane of Pd. More importantly, the Pd NPs are partly embedded in the inner surface of the CNT, which may reduce the active area of Pd nanoparticles, but some Pd atoms is still exposed (Figure 3D). This novel structure of the as-prepared Pd/C nanocomposite may distinctly enhance the interaction between the Pd NPs and the inner surface of CNT. All the TEM results indicate that we have developed an efficient method to prepare a novel Pd/C nanocomposite with Pd NPs uniformly embedded in the inner surface of the CNT.

Because the embedding of Pd NPs into the inner surface of the CNT can physically separate the particles and kinetically locks their motion, we can expect suppression of their sintering induced by thermal treatment at elevated temperatures. Thus, the as-prepared Pd/C samples were subjected to thermal treatments in He at 500 °C for 4 h. For comparison, commercial CNT-supported Pd NPs (Pd/CNT) with 2.1% weight loading was also prepared by the same deposition–precipitation process and were subjected to the similar heat treatment. TEM images of the as-prepared embedded Pd/C nanocomposite and Pd/CNT catalyst before and after the high-temperature treatment are displayed in Figure 4. The corresponding size distribution histograms are presented in Figure S4. Note that the average size of the Pd NPs in the as-prepared Pd/C nanocomposite is generally maintained after the high-temperature treatment (Figure 4A,B). However, as to the CNT-supported Pd catalyst, after high-temperature treatment, the average size of the Pd NPs dramatically increases from 2–4 nm to 5–10 nm (Figure 4C–F). The XRD results in Figure S5 also provide the further evidence that the sinter-resistance of the Pd NPs in the Pd/C nanocomposite is much better than that of the CNT-supported Pd catalyst, in agreement with the TEM observations.

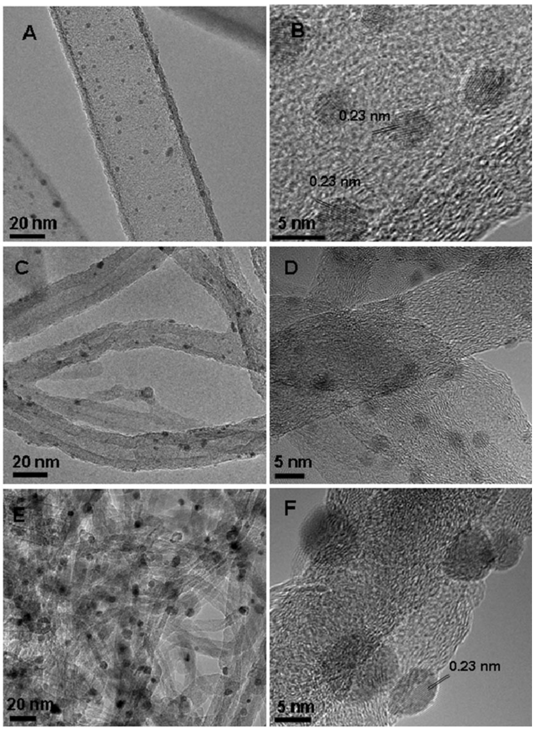


Figure 4. A,B) TEM images of the as-prepared Pd/C nanocomposite after treating in He for 4 h at 500 °C. C,D) TEM images of the fresh Pd/CNT catalyst. E,F) TEM images of the Pd/CNT catalyst after treating in He for 4 h at 500 °C.

The as-prepared Pd/C nanocomposite was further characterized by Raman measurements. Two major Raman bands are located at 1363 and 1605 $\mathrm{cm^{-1}}$ (Figure S6A). The band at 1363 $\mathrm{cm^{-1}}$ corresponds to the D peak arising from the breathing motion of sp^2 rings, and the band at 1605 $\mathrm{cm^{-1}}$ is in good agreement with the G band. The measured intensity I_D/I_G ratio is about 3.35, indicating the amorphous phase makes a significant contribution to the carbon layer. The Pd/C nanocomposite exhibit a type IV hysteresis (Figure S6B), which reveals mesoporous characteristics and leads to a BET specific surface area of 123 $\mathrm{m^2\,g^{-1}}$. Moreover, a broad peak around 50–80 nm can be observed in the pore size distribution (the inset in Figure S6B), which indicates that the as-prepared Pd/C nanocomposite has abundant porous channels ensuring high permeation and mass-transfer rates for species involved in a catalytic reaction.

The Suzuki cross-coupling reaction of iodobenzene and phenylboronic acid was used to evaluate the catalytic performance of the as-prepared Pd/C nanocomposite. The reaction was carried out by using ethanol and water as the solvent, and K_2CO_3 as the base. Figure 5A shows the catalytic performance of as-prepared Pd/C nanocomposite with time at 85 °C. A 78.7% conversion of iodobenzene was obtained after just 5 min reaction. The catalytic performance gives further evidence that the Pd NPs are not completely embedded in the carbon support, there are still exposed active Pd atoms catalyzing the Suzuki coupling reaction. To investigate the stability of as-prepared Pd/C nanocomposite, a series of recycling experiments for the Suzuki coupling of iodobenzene

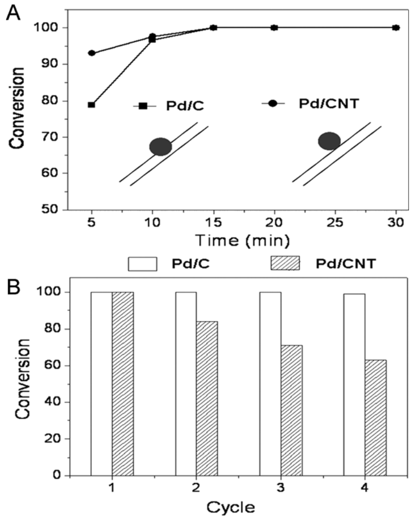


Figure 5. A) Conversion of iodobenzene in the Suzuki coupling reaction for the as-prepared Pd/C nanocomposite and Pd/CNT catalyst. B) Conversion on recycling of the Pd/C nanocomposite and Pd/CNT. Reaction condition: 85 °C, iodobenzene (4 mmol), phenylboronic acid (4.8 mmol), K_2CO_3 (8 mmol), C_2H_5OH (25 mL), H_2O (15 mL), catalyst (15 mg). Inset in (A): Diagram of the location of Pd NPs on the different carbon supports.

and phenylboronic acid were conducted. As shown in Figure 5B, the catalytic activity over the Pd/C nanocomposite hardly decreases even after 4 runs. However, for the commercial CNT-supported Pd catalyst (Pd/CNT), only a 63% conversion is obtained after 4 runs. Apparently, the excellent reusability of the as-prepared Pd/C nanocomposite results from the strong interaction between the Pd NPs and the inner surface of carbon nanotube as presented in the inset of Figure 5A.

In summary, we have developed an efficient and facile method for synthesizing Pd/C nanocomposite with Pd NPs uniformly embedded in the inner surface of the carbon nanotube. The as-prepared Pd/C nanocomposite is catalytically active and recyclable in the Suzuki coupling reaction. The novel structure of as-prepared Pd/C nanocomposite dramatically enhances the sinter-resistance of the Pd NPs on the carbon surface, compared with that of the traditional CNT-supported Pd catalyst. This highly efficient process may be applicable to prepare various metal NPs confined within carbon nanotubes.

Experimental Section

The ZnO nanowires were synthesized by a modified physical vapor deposition process under atmospheric pressure.[14] The source materials (a mixture of 0.5 g of ZnO powder and 0.5 g of active carbon) were loaded into a ceramic boat that was positioned in the middle of a quartz tube. A quartz glass was used as the substrate to collect samples, which was placed downstream from the source material in the temperature zone of 700 °C. Prior to heating, the quartz tube was purged with Ar gas (30 mL min^{-1}) for 30 min. Then, it was heated to 1000 °C under a mixture of Ar (50 mL min^{-1}) and O_2 (10 mL min^{-1}) for 1 h. The surface of the substrate appeared white after the reaction, indicating the deposition of ZnO nanowires. Pd nanoparticles (NPs) supported on the ZnO nanowire were obtained by the deposition–precipitation method. The as-prepared ZnO nanowire was dipped into an aqueous solution containing $Pd(NO_3)_2$ as precursor salts. The pH value of the aqueous solution was maintained, by adding NaOH, between 8 and 9. Then, the mixture was stirred at the temperature of 70 °C for 2 h, collected by filtration, washed, and dried at room temperature under vacuum overnight. Finally, the Pd/ZnO template was obtained by reducing under hydrogen at a temperature of 200 °C for 2 h. The Pd weight loading was confirmed by the ICP analysis. The Pd/C/ZnO sample was prepared by fast coking the Pd/ZnO template under a mixed gas flow of ethylene (2% ethylbenzene, He balance, 100 mL min^{-1}) for just 2 min at 700 °C. After washing in 1% HCl aqueous solution for 2 h, the Pd/C nanocomposite with Pd NPs embedded in the inner surfaces of carbon nanotube was collected.

The commercial carbon nanotube supported Pd NPs (Pd/CNT) as the controlled catalyst was synthesized by the same deposition–precipitation method. The Suzuki cross-coupling reaction was conducted in a flask in the presence of iodobenzene (4 mmol), phenylboronic acid (4.8 mmol), K_2CO_3 (8 mmol), water (15 mL), ethanol (25 mL), and catalyst (15 mg) at 85 °C under reflux. The reaction was monitored by gas chromatography (Agilent 7890A) with FID and TCD. Transmission electron microscopy (TEM) was performed by a Tecna G2 F20 S-TWIN electron microscope operated at 200 kV. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms on a Micrometrics ASAP 3020 system. X-ray diffraction (XRD) was conducted on a Philips diffractometer using Cu Kα radiation. Raman spectroscopy was performed on a LabRam HR 800 using a 633 nm laser. The elemental analysis was performed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, IRIS Intrepid).

Received: June 23, 2014

Keywords: carbon nanotubes · heterogeneous catalysis · nanoparticles · palladium · sinter resistance

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