Catalysis Today 260 (2016) 55–59

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Facile synthesis of Pd nanoparticles encapsulated into hollow carbon nanospheres with robust catalytic performance

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ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form 8 April 2015
Accepted 8 April 2015
Available online 5 May 2015

Keywords:
Carbon
Hollow structure
Pd
Template
Catalysis

ABSTRACT

Pd nanoparticles (NPs) encapsulated into hollow carbon spheres (Pd@HCS) have been prepared by a feasible template method. The present method is facile, efficient and suitable for large-scale production. The as-prepared Pd NPs are not only uniformly confined into the hollow carbon spheres, but also partly embedded in the inner surface of the carbon shell, which could effectively prevent Pd NPs from aggregation or leaching during the reaction. The obtained Pd@HCS nanocomposite exhibits robust catalytic performance in the reduction of 4-nitrophenol to 4-aminophenol, comparing with that of commercial carbon nanotube supported Pd NPs.

1. Introduction

Metal nanoparticles (NPs) have drawn wide attentions in catalysis due to their unique physical and chemical properties [1]. However, the metal NPs such as Pt, Pd, Au etc. are energetically unstable owing to their high surface-to-volume ratios, leading to aggregating or sintering to minimize their surface chemical potentials [2]. Considerable efforts have been made to overcome this issue by employing isolated nanoreactors to confine the metal NPs [3–8]. Recently, metal NPs encapsulated into hollow carbon spheres (HCSs) have become the research hotspot in chemistry [9–15]. Such a novel hollow structure not only functions as a barrier to prevent encapsulated metal NPs from aggregation or leaching, but also the chemical and thermal stability of the carbon shell are beneficial for catalytic applications. The Pt, Au, Pd and PtCo bimetallic NPs embedded into HCSs have been reported and show excellent performance in catalytic reactions [16–22].

Several methods have been developed for the synthesis of metal NPs encapsulated into HCSs, such as soft template, ship-in-a-bottle, galvanic replacement and so on [23–27]. Although these achievements have been made, most of them still suffer from low efficiency, resulting in a low yield of the final product. In addition, the sizes of metal NPs in the HCSs are usually larger than 10 nm, which greatly attenuates their catalytic activity and limits their further applications [28].

Herein, we report a facile method for large-scale synthesizing Pd NPs confined into HCSs (Pd@HCS). The synthetic procedure of the Pd@HCS nanocomposite is illustrated in Fig. 1. First, the Pd NPs supported on commercially available ZnO NPs are prepared by the deposit-precipitation method. Then, a carbon layer is uniformly coated onto the surface of ZnO NPs by a fast coking process with diluted ethylbenzene at 700 °C. Finally, the ZnO NPs are quickly removed by diluted HCl solution and the Pd@HCS nanocomposite is obtained. The as-prepared Pd NPs are not only uniformly encapsulated into the HCSs, but also partly embedded in the inner surface of the carbon shell, which can effectively prevent the aggregation and leaching of Pd NPs, enhancing their stability and performance in catalytic reaction. The as-prepared Pd@HCS nanocomposite displays a robust catalytic performance in the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), comparing with that of the commercial carbon nanotube (CNT) supported Pd catalysts.

2. Experimental

Synthesis of Pd@HCS nanocomposite: Pd nanoparticles (NPs) supported on the ZnO NPs are obtained by the deposit-precipitation method. The ZnO NPs (10 g) are dipped into an aqueous solution containing $Pd(NO_3)_2$ as precursor salts. The pH value of the aqueous solution is maintained between 8 and 9 by adding NaOH. Then,

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http://dx.doi.org/10.1016/j.cattod.2015.04.003
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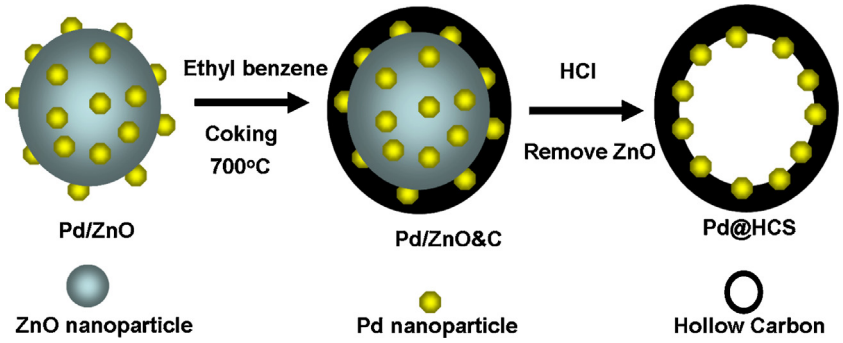

Fig. 1. Schematic illustration of the preparation of Pd@HCS nanocomposite.

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 is obtained by reducing in hydrogen at 200 °C for 2 h. The Pd weight loading is confirmed by the ICP analysis. The Pd/ZnO@C sample is prepared by a fast coking process on 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 NPs confined into the HCSs are collected. The Pd NPs supported on commercial carbon nanotube (Pd/CNT) as the controlled catalyst is synthesized by the same deposit-precipitation method.

Catalytic study and characterization: 4-nitrophenol (3 mL, 1×10^{-4} mol) is mixed with freshly prepared aqueous solution of $NaBH_4$ (0.1 mL, 3×10^{-1} mol). The Pd@HCS and Pd/CNT catalysts (3 mg) are then added with constant magnetic stirring. UV/vis absorption spectra are recorded to monitor the change in the reaction mixture. Transmission electron microscopy (TEM) is performed by a Tecnai G2 F20 electron microscope operated at 200 kV. The specific surface area is measured by the BET method using nitrogen adsorption-desorption isotherms on a Micrometrics ASAP system. X-ray diffraction (XRD) is conducted on a Philips diffractometer using Cu *K*a radiation. Raman spectroscopy is performed on a Lab Ram HR 800 using a 633 nm laser. The elemental analysis is

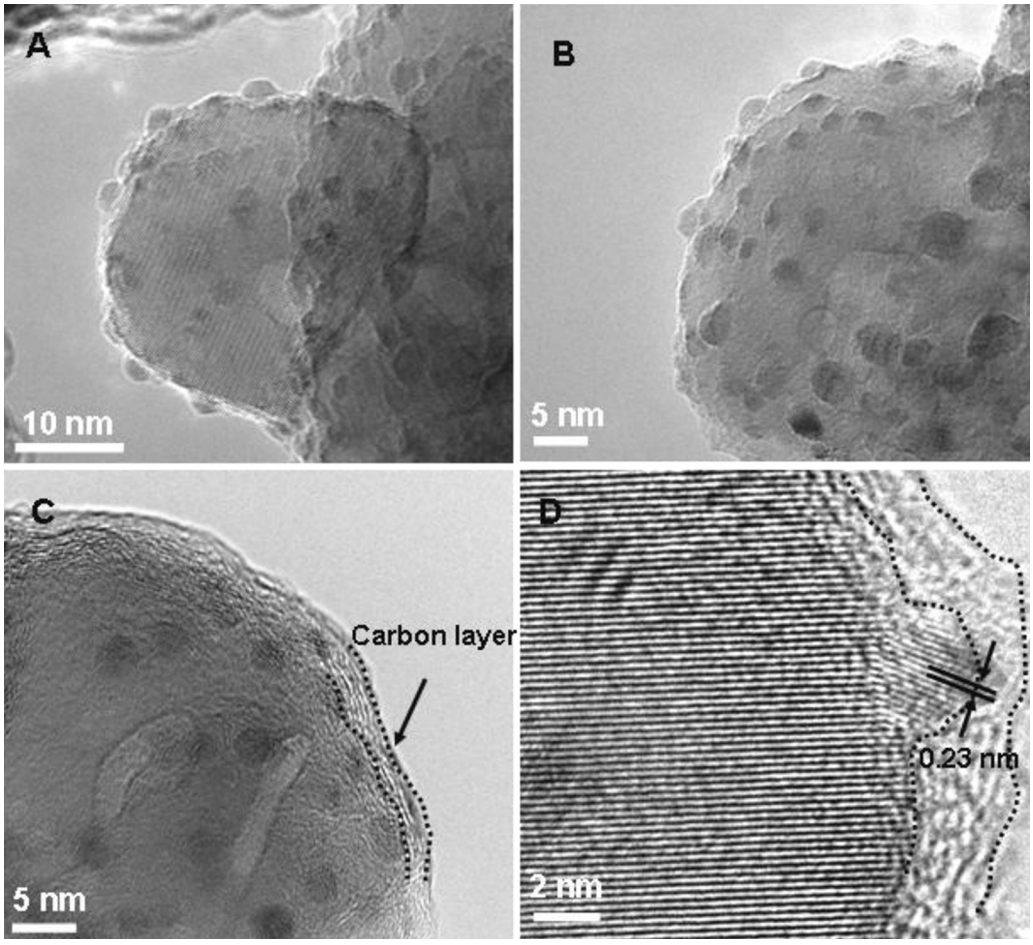

Fig. 2. (A and B) TEM images of Pd/ZnO template. (C) TEM images of the Pd/ZnO template coated with a carbon layer. (D) High-magnification TEM images of Pd/ZnO@C.