Applied Surface Science 257 (2011) 8028–8032

Contents lists available at ScienceDirect

Applied Surface Science

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

Novel urchin-like Pd nanostructures prepared by a simple replacement reaction and their catalytic properties

Zhipeng Cheng, Jiming Xu*, Hui Zhong, XiaoZhong Chu, Juan Song

Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaiyin Normal University, Huaian 223300, China

ARTICLE INFO

Article history:
Received 16 February 2011
Received in revised form 17 April 2011
Accepted 17 April 2011
Available online 27 April 2011

Keywords:
Pd nanostructure
Urchin-like
Ammonium perchlorate
Catalytic property

ABSTRACT

Novel urchin-like Pd nanostructures were firstly synthesized using a simple replacement reaction between Al and $PdCl_2$ aqueous solution at room temperature without the assistance of any surfactant or ligand. Their phase structure, morphology, specific surface area, and catalytic property were characterized by XRD, TEM, EDS, BET and DSC/TG. The results show numerous one-dimensional Pd nanorods radiate from the center of the aluminum templates to form an urchin-like shape with a diameter of ~0.5–1.0 μm. The as-prepared urchin-like Pd nanostructures can serve as a promising additive to accelerate the thermal decomposition of ammonium perchlorate (AP), a key oxidizer in composite solid propellants.

1. Introduction

As a kind of noble metal, palladium (Pd) has attracted much attention. Over the past few years, Pd nanoparticles with different shapes and sizes have been prepared by various chemical processes [1–5]. Most of the synthetic procedures have depended on organic capping agents, such as surfactants and ligands [6–10]. However, the majority of organic capping agents are toxic and expensive, which would add to the environmental and economic burden. Improvement of these methods and development of low-cost and environmental friendly techniques for Pd materials are great challenges to overcome before their commercial applications.

Pd materials possess a series of unusual properties and exhibit excellent catalytic activity. It has been reported that Pd nanoparticles serve as the vital catalyst in C–C coupling reactions, such as the Heck, Sonogashira, Suzuki, Stille and Ullmann reactions [11]. Moreover, they are widely employed in the field of hydrogen sensing and surface-enhanced Raman spectroscopy (SERS) [2]. For Pd nanoparticles, there is much room for exploring their potential properties in the fields of military and energy fields.

Herein, we firstly present a facile strategy to synthesize novel urchin-like Pd nanostructures via a simple replacement reaction between Al and $PdCl_2$ aqueous solution without the assistance of any surfactant or ligand. The reaction was performed under room temperature and normal pressure. Furthermore, the urchin-like Pd nanostructures showed good catalytic activity for the thermal decomposition of ammonium perchlorate (AP), a key oxidizer in composite solid propellants.

2. Experimental procedure

The aluminum nanoparticles are commercial grade, and were obtained from Beijing Nachen S&T Ltd. Other reagents were of analytical grade purity and were used directly without further purification. In the typical synthetic process, 0.027 g of aluminum nanoparticles was added to a stirred 3×10^{-3} mol L^{-1} $PdCl_2$ solution at room temperature. These aluminum nanoparticles were covered with a stable layer of alumina because of oxidation. Only when the alumina layer was wiped off can the displacement reaction occur. The pH value was adjusted to 2.0 by the addition of 0.5 mol L^{-1} HCl to dissolve the stable layer of alumina. After 1 h of replacement reaction, the residue was separated and washed for several times with distilled water and absolute ethanol, respectively. It was then dried in a vacuum for 5 h at room temperature. For comparison, spherical Pd nanoparticles were prepared according the ref. [12]. More information of the spherical Pd nanoparticles can be seen in Supplementary material, Fig. 1S).

The as-prepared product was characterized by powder X-ray diffraction (XRD) patterns, using a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation (k = 1.5418 Å, D/max 18 kV). X-ray photoelectron spectroscopy (XPS) pattern was recorded on a Escalab MkII X-ray photoelectron spectrometer using Mg Kα X-ray as the excitation source. Transmission electron microscopy (TEM) was performed on a Philips Tecnai 12 transmission electron micro-

* Corresponding author. Tel.: +86 0517 83525085; fax: +86 0517 83525085.
E-mail address: xujm68@126.com (J. Xu).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.04.085

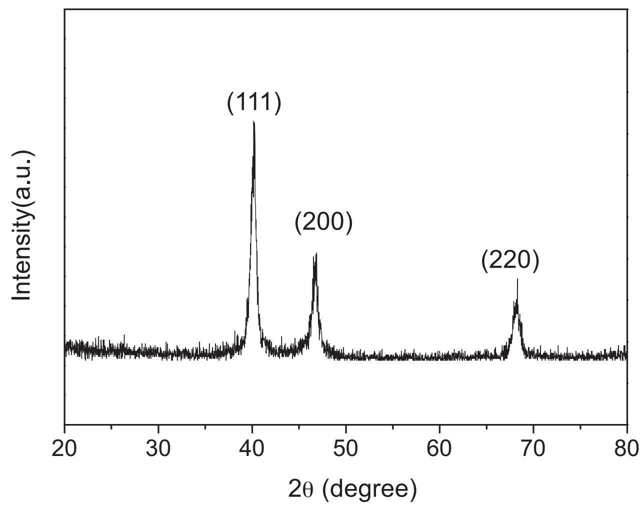

Fig. 1. XRD patterns of the urchin-like Pd nanostructures.

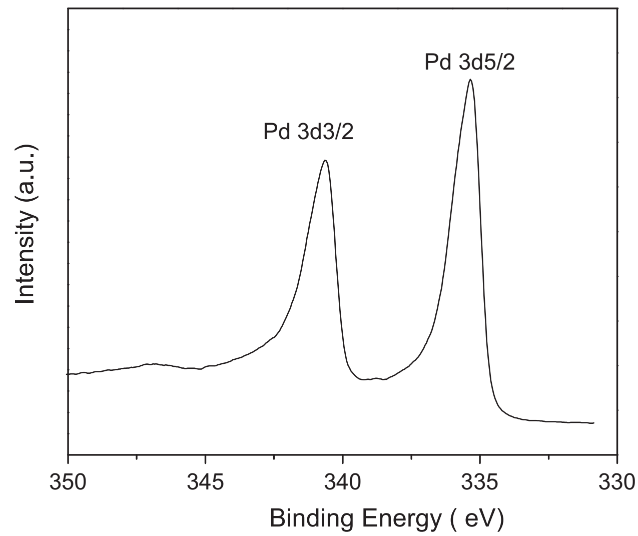

Fig. 2. XPS spectrum of the Pd 3d region.

scope. The specific surface area was obtained from Bechman Coulter SA 3100 plus instrument using N_2 absorption at −196 °C. Philips DX-4 energy dispersive spectroscopy (EDS) was used to determine the elemental compositions at the selected area. The catalytic roles of Pd nanostructure in the thermal decomposition of AP were studied by thermogravimetric analysis (TG) and differential scanning calorimeter (DSC) in N_2 atmosphere over the temperature range of 100–500 °C. The heating rate was fixed at 20 °C min^{-1}. AP and Pd nanostructure were mixed at a mass ratio of 98:2 to prepare the target samples for thermal decomposition analyses. A total sample mass of 20 mg was used.

3. Results and discussion

Fig. 1 shows powder X-ray diffraction (XRD) pattern of the resulting product. All diffraction peaks at 40.1°, 46.6°, and 68.1° can be assigned to the (1 1 1), (2 0 0), and (2 2 0) planes of the fcc geometry of crystalline Pd (JCPDS PDF card no. 46-1043). A significant broadening of diffraction lines can indicate very small crystallites. The crystallite size was 12.2 nm from the width at half height of diffraction line 111, as estimated from the Debye–Scherrer formula.

Fig. 2 shows the XPS spectrum of the Pd 3d region. The peaks at binding energies of 335.65 and 340.93 eV can be ascribed to Pd 3d5/2 and 3d3/2, respectively, which are in accordance with that reported for metallic Pd in the literature [13].

Fig. 3 shows the TEM images of the aluminum template and the Pd nanostructures. Fig. 3a demonstrates that the aluminum template has a spherical morphology with sizes ranging from 30 to 200 nm. The template can serve as a good reducing agent to fabricate Pd nanostructures because aluminum can easily reduce palladium ion into palladium nanocrystals which are consumed completely in the acidic solution. More information about the aluminum template can be seen in Supplementary material, Figs. 2S and 3S. Fig. 3b–d shows the morphology of the Pd nanostructures at different magnifications. Fig. 3b clearly indicates that Pd, which has a dominantly novel urchin-like morphology, has been successfully prepared by the simple replacement reaction. The Pd nanostructures are composed of numerous nanorods radiating from the center of the nanostructure and forming an urchin-like shape with a diameter of ∼0.5–1.0 μm (see Fig. 3c). The higher-magnification TEM image is shown in Fig. 3d, from which the average diameter and the length of the nanorods can be identified as ∼50 and 400 nm, respectively. Further, consistent with the XRD analysis, the nanorods are seen to have rough surfaces composed of crystallites smaller than 15 nm as indicated by the arrows.

Fig. 4 shows the TEM and EDS images of the intermediate product of the reaction when the aluminum nanoparticles reacted with $PdCl_2$ for 20 min. It is found that the aluminum nanoparticles not only act as reducing agents for Pd ion but also provide the template for Pd nanorod deposition. The Pd nanorods coat the surface of the aluminum template to form a core–shell structure.

The key idea of our method for the synthesis of the Pd nanostructures is to exploit the replacement reaction between Al nanoparticles and $PdCl_2$. As the standard reduction potential of the Pd^{2+}/Pd redox pair (0.951 V vs. the standard hydrogen electrode [SHE]) is much higher than that of the Al^{3+}/Al redox pair (−1.662 V vs. SHE), the redox reaction in achieving the Pd nanostructures can be expressed as follows:

$$3Pd^{2+} + 2Al \rightarrow 2Al^{3+} + 3Pd \quad (1)$$

Al nanoparticles are gradually oxidized to aluminum ions when the solution of Al nanoparticles is added to the $PdCl_2$ acidic solution. The mixing solution turns from gray to black stage by stage, which suggests the oxidation of the Al nanoparticles and the formation of Pd nanostructures.

Based on the above analyses, the formation process of the urchin-like Pd nanostructures can be explained. As this replacement reaction occurs, the Pd atoms nucleate and grow into very small nanocrystals, which is indicated by the above XRD analysis and TEM image (Fig. 3d). Subsequently, the growth of the Pd nanocrystals is initiated preferentially by thermodynamic or kinetic factors [14], leading to the formation of one-dimensional Pd nanorods that radiate from the center of the aluminum template (see Fig. 4). When this template is completely consumed, the pure urchin-like Pd nanostructure composed of numerous nanorods can be obtained. The formation process of urchin-like Pd nanostructures was given in Scheme 1.

The BET surface area of the urchin-like Pd nanostructure is 73.23 m^2 g^{-1}, which is larger than the reported specific surface area (64 m^2 g^{-1}) of hollow Pd spheres with a smaller average diameter (300 nm) [15]. Obviously, the remarkable increase in specific surface area of the Pd nanostructure can be attributed to the surface area of the numerous 1D nanorods. The large BET surface area will be favorable for its catalytic effect.

Fig. 5 shows the TG and DSC curves of pure AP and AP in presence of urchin-like Pd nanostructures. For the pure AP, two mass losses were observed, as indicated by two peaks at 324 and 437 °C in the first derivative curve of raw TG data. Therefore, the ther-