Synthesis of monodisperse palladium nanocubes and their catalytic activity for methanol electrooxidation*

Ding Hao(丁 皓), Shi Xue-Zhao(时雪钊), Shen Cheng-Min(申承民),
Hui Chao(惠 超), Xu Zhi-Chuan(徐栉川), Li Chen(李 晨),
Tian Yuan(田 园), Wang Deng-Ke(王登科), and Gao Hong-Jun(高鸿钧)†

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, *China*

(Received 9 November 2009; revised manuscript received 14 May 2010)

The single crystalline palladium nanocubes with an average size of 7 nm were prepared in the presence of poly (vinyl pyrrolidone) (PVP) and KBr using the polyol method. The as-prepared Pd nanocubes were highly uniform in both size and shape. The ordered packing structures including monolayer and multilayer can be fabricated via the rate-controlled evaporation of solution solvent. The electrochemical catalytic activity of these Pd nanocubes towards methanol oxidation was found to be higher than that of spherical Pd nanoparticles of similar size.

Keywords: Pd nanocubes, electrocatalytic activity, methanol oxidation, fuel cell

PACC: 6155F, 8116D, 8630G

1. Introduction

Palladium plays an important role in many fundamental researches and industrial applications due to its unique physical and chemical properties.[1−3] Palladium has been used as a catalyst not only in Suzuki and Heck cross coupling reaction in organic chemistry,[4,5] but also in automobile industry for the reduction of vehicle exhausts.[6] Recent investigation showed that Pd nanoparticles (NPs) are a promising catalyst as a substitute for Pt NPs as anode electrode in polymer electrolyte membrane fuel cell.[7] The catalytic activity of Pd NPs depends strongly on their size and exposed crystalline facets. For example, the Pd (100) deposited onto Au or Pt electrode showed an improved catalytic activity over Pt catalyst for formic acid oxidation.[8] This is probably because the oxidation rate of formic acid on Pd (100) is higher than that on Pt (100).[9] Pd nanowires also exhibited good electrocatalytic activity as well as high stability.[10] To discover the electrocatalytic activity of Pd in fuel cell reactions, various methods have been devoted to the preparation of Pd nanocatalysts, such as oleylamine-mediated synthesis,[11] metal chloride reduction process,[12,13] NH_3-mediated polyol process,[14] loading on carbon nanotubes,[15,16] alcohol reduction process[17−19] and thermal decomposition of palladium complexes.[20] Most recently, it has been found that the catalytic activity of Pt and bimetallic NPs in fuel cell reactions can be improved remarkably by selectively exposing crystalline facets, which can be achieved by shape control in the synthesis.[21,22] Therefore, the study on new strategies for shape control on Pd NPs is quite desirable for the discovery of Pd nanocatalysts. In this paper, we report the synthesis of Pd nanocubes with an average size of 7 nm using a facile polyol reduction process.[18] The as-prepared Pd nanocubes have an fcc crystalline structure. The electrochemical catalytic activity of these Pd nanocubes towards methanol oxidation was found much higher than that of spherical Pd NPs of similar size. It was consistent with the fact found in Pd single crystalline electrode that Pd (100) surface is highly catalytic-active.[9]

2. Experimental

2.1. Materials

Ethylene glycol (EG), poly(vinyl pyrrolidone) (PVP, MW = 58000), and Na_2PdCl_4 were purchased

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60571045 and 50872147) and the National High Technology Research and Development Program of China (Grant No. 2007AA03Z035).

†Corresponding author. E-mail: hjgao@aphy.iphy.ac.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

from acros, cyclohexane and KBr purchased from Beijing Chemicals Lt. All reagents were used as received without further purification.

2.2. Synthesis of palladium nanocubes

The Pd nanocubes were synthesized by a modified polyol method.[18] In a 50-mL flask, 0.0120 g of PVP and 0.200 g of KBr were dissolved in 10-mL EG, and then heated in air under magnetic stirring at 150 °C for 1 h. The palladium precursor was prepared in another vessel by dissolving 0.0371 g of Na_2PdCl_4 in a mixed solution of 1-mL water and 4-mL EG. This solution was injected into the flask using a syringe pump at a rate of 20 mL per hour. The reaction mixture was then heated up to 150 °C in air and kept at this temperature for 1 h. The product is collected by centrifugation and washed with acetone firstly and then with the mixture of ethanol–cyclohexane (volume ratio of 1:5) for five times to remove the excess EG, NaBr and PVP.

2.3. Characterizations

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed by using a JEOL 200CX microscope operated at an acceleration voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) of Pd nanocubes was measured on JEOL JEM-2010 electron microscope worked at an acceleration voltage of 200 kV. TEM samples were prepared by placing one drop of the Pd nanocube solution on a carbon-coated copper grid. XRD pattern was recorded using a Rigaku D/MAX 2400 x-ray diffractometer with Cu-Kα radiation source ($\lambda = 1.5405$ Å, 1 Å=0.1 nm). The x-ray photoelectron spectra were obtained with the ESCA LAB5 x-ray photoelectron spectrometer with the monochromatic Mg x-rays.

2.4. Electrochemical measurement

Glassy carbon (GC) electrode with a diameter of 3.0 mm (electrode area ~ 0.07 cm^2) was used as working electrode; 5-mg PVP-capped Pd nanocubes were dissolved in 0.1-mL 0.05% nafion ethanol solution under ultrasonic; 25-μL Pd NPs-nafion solution was dropped onto the surface of glassy carbon (GC) electrode and dried in air for 12 hours. The cyclic voltammogram measurement was carried out at CHI 660D electrochemical work station (Shanghai, China). A standard three-electrode system was used. A platinum wire is used as counter electrode and a saturated calomel electrode (SCE) used as reference electrode. The cyclic voltammogram measurement was performed in 0.5-M NaOH + 1.0-M CH_3OH solution. The electrolyte solution was deaerated by nitrogen for 30 min before measurement. All of the electrochemical reactions were conducted and investigated at room temperature (25±1 °C).

3. Results and discussion

The Pd nanocubes were prepared in the presence of PVP and KBr using polyol method. Figures 1(a) and 1(b) show the typical TEM images of as-prepared Pd nanocubes with an average size of 7.0 nm. The low magnification TEM image (Fig. 1(a)) shows that Pd nanocubes can form monolayer or multilayer ordered structure. The close view of a monolayer of Pd nanocubes (Fig. 1(b)) indicates that the Pd nanocubes are in well-defined shape with a narrow size distribution. The selected area electron diffraction (SAED) image of Pd nanocubes clearly shows the typical *fcc* structure with diffraction rings of {111}, {200}, {220} and {311}, indicating high crystallinity of Pd nanocubes (Fig. 1(c)). The HRTEM image of a single Pd nanocube (Fig. 1(d)) shows lattice fringes with an interfringe distance of approximately 1.9 Å, which is close to the interplane distance of the {200} planes in the *fcc* structured Pd. It demonstrates that the surfaces of *fcc*-structured Pd nanocubes are selectively exposed {100}-surfaces. The HRTEM image also confirms that the nanocubes are of single phase Pd.

The crystal phase of Pd nanocubes was also characterized by x-ray diffraction (XRD). Figure 2 shows the XRD pattern for the 7.0-nm Pd nanocubes. The reflection peaks can be observed at 40.1°, 46.7°, 67.8°, 82.1°, and 86.4°, corresponding to the {111}, {200}, {220}, {311} and {222} planes of Pd, respectively. The reflection peaks are consistent with those of an *fcc* crystalline structure of bulk Pd (JCPDS, Card No.46-1043). An average diameter of 7.6 nm is estimated from the Scherrer formulation, which is consistent with the result of TEM. The intensity ratio of (111) to (200) peak decreases slightly as compared to the standard value calculated from JCPDS data (from 2.38 to 1.97), indicating that the reflection of {100} planes dominates in Pd nanocubes.

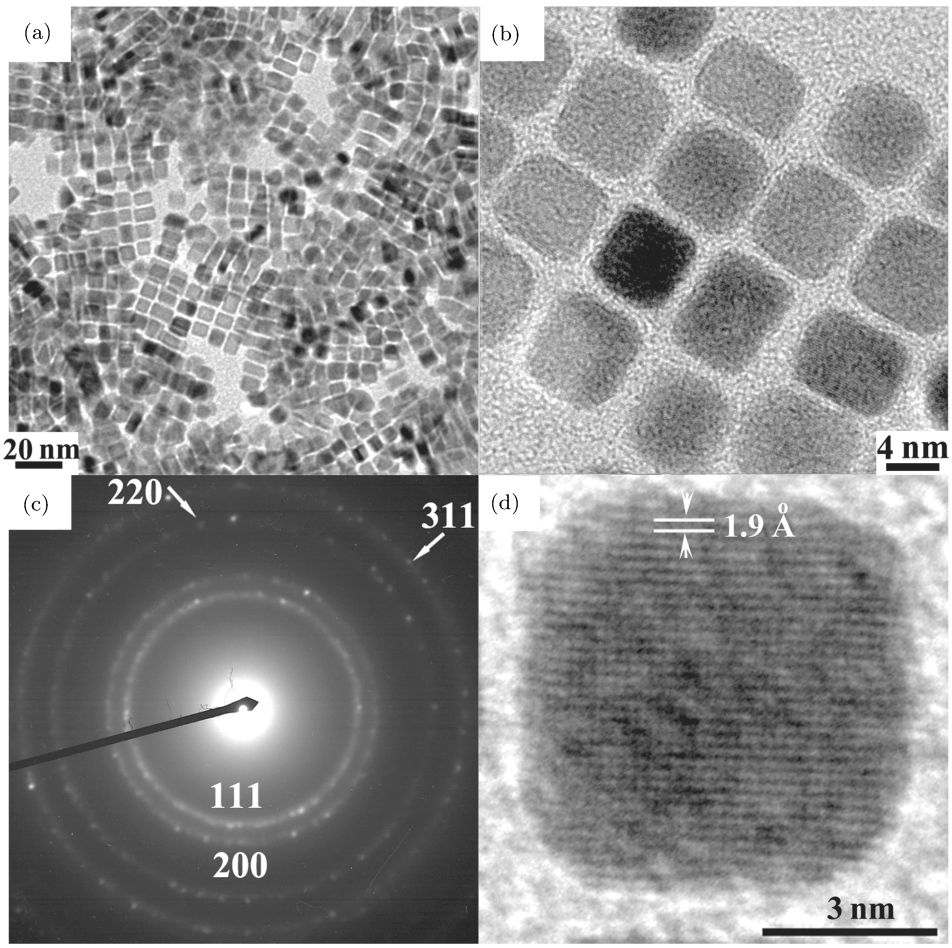


Fig. 1. TEM images of Pd nanocubes with an average size of 7 nm. (a) Low magnification image of nanocubes; (b) high magnification image of a monolayer of Pd nanocubes; (c) SAED pattern of Pd nanocubes; and (d) HRTEM image of Pd nanocubes.

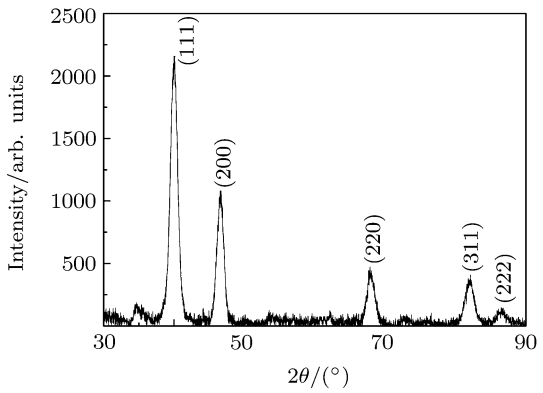


Fig. 2. XRD pattern of the ∼ 7 nm Pd nanocubes. All reflection peaks match well with the standard ones of Pd (JCPDF 46-1043).

KBr plays a critical role in the formation of nanocubes because the Br^- ions from KBr act as an etchant to affect the growth of Pd nanocubes. Introduction of the bromide results in chemisorption on the surface of Pd seeds and alters the order of surface free energies. In reaction process, the addition of Pd atoms from solution deposited on to the Pd nanocrystal surface can be etched by Br^- ions, which leads to the anisotropic growth of Pd nanostructures and promotes the formation of {100} facets.[18] The existence of specific anions has been proven to be an effective etchant for the control synthesis of metal nanostructures.[23−25] We found that only irregular polyhedral particles can be obtained with PVP alone. On the other hand, we can only obtain aggregate Pd nanoparticles when using KBr and no PVP. Br element can be observed from XPS spectra when the as-prepared Pd nanocube samples are washed using a mixed solution of ethanol–cyclohexane for 8 times, indicating that Br has adsorbed on the surface of Pd nanocube by chemisorption.

In order to understand the composition of synthesized Pd nanocubes, XPS was used to investigate the interaction between PVP molecules and the Pd atoms during the formation of PVP-capped Pd nanocubes. Figure 3 shows the XPS spectra of the PVP-capped

Pd nanocubes. The XPS full-spectrum indicates only palladium, oxygen, and carbon, indicating that PVP molecules have capped the surface of Pd NPs. In Fig. 3(b), the XPS spectrum of the Pd shows double peaks with the binding energies at 335.9 eV and 341.2 eV, corresponding to $Pd_{3d5/2}$ and $Pd_{3d3/2}$, respectively. Compared to the standard spectra of metal Pd^0, the binding energies of Pd nanocubes increase slightly (from 335.1 eV to 335.9 eV and from 340.4 eV to 341.2 eV). The binding energy of O_{1s} in PVP-capped Pd NPs has also shifted to higher values, i.e. from 531.2 eV to 532.8 eV. These results confirm that the PVP can be adsorbed on the surface of Pd particles by the bonding between Pd and O.

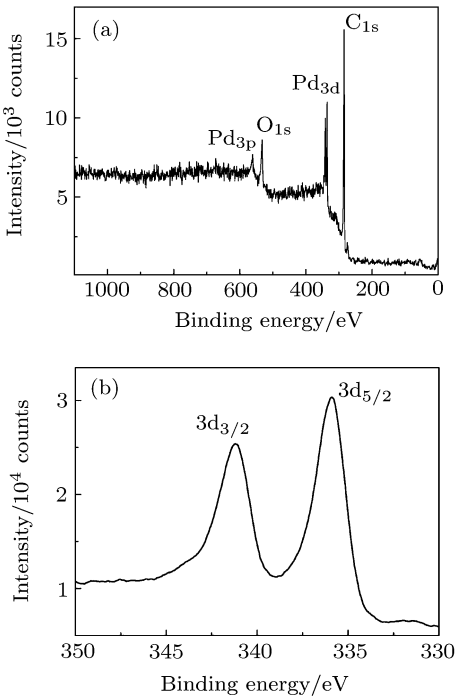


Fig. 3. XPS spectra of Pd nanocubes: (a) XPS full-spectrum of Pd nanocubes and, (b) Pd spectrum.

The electrochemical catalysis properties of Pd nanocubes towards direction methanol oxidation are investigated: 5-mg PVP-capped Pd nanocubes are dissolved in 0.1-mL 0.05% nafion ethanol solution under ultrasonic; and 25-μL NPs-nafion solution is dropped onto the surface of glassy carbon electrode (S = 0.07 cm^2) and dried in air for 12 hours. For comparison, an equal amount of 8-nm PVP-capped Pd spherical nanoparticles is also measured under the same electrochemical conditions. Cyclic voltammograms of these NPs in 0.5 M NaOH +1.0 M methanol solution are shown in Fig. 4. The electrode potentials are depicted versus saturated calomel electrode (SCE). From Fig. 4, it can be seen clearly that the current density of Pd nanocubes is evidently higher than that of Pd spherical nanoparticles. The current densities of methanol oxidation of Pd nanocubes and Pd nanospheres are 0.67 and 0.13 mA/cm^2, respectively. The evaluation of catalytic activity of NPs is the onset potential for methanol oxidation. The experimental results clearly show that the onset potential for methanol oxidation of Pd nanocubes shift toward low potential region, to −540 mV with respect to SCE, which is 24 mV more negative than that of 8 nm Pd nanospheres. These results indicate that Pd nanocubes offer a high electrocatalytic activity towards methanol oxidation. The reason is that the cubic-shaped Pd NCs are abundant in {100} facets, which are highly catalytic-active.[9]

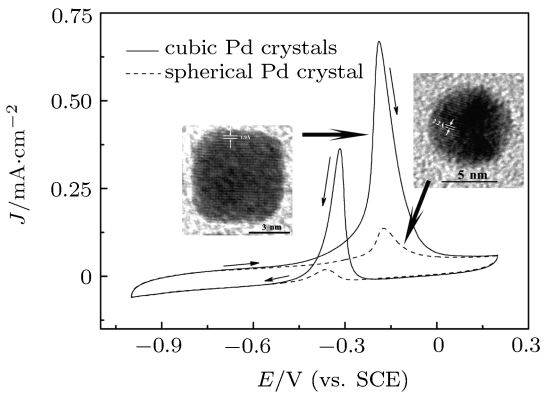


Fig. 4. Cyclic voltammograms of methanol oxidation on Pd nanocubes (solid curve) and spherical Pd NPs (dashed curve) in 0.5 M NaOH +1.0 M methanol solution (scan rate: 20 mV/s). The electrode potentials are versus saturated calomel electrode (SCE).

4. Conclusions

In summary, we have successfully synthesized palladium nanocubes with an average size of 7 nm using a polyol method in the presence of PVP and KBr. TEM and XRD analyses indicate that Pd nanocubes are *fcc* structured. The ordered packing structure in monolayers and multilayers are observed on a carbon-coated TEM grid. PVP molecules act as a surfactant during the formation of Pd nanocubes. The electrochemical catalytic study shows that Pd nanocubes toward methanol oxidation exhibit an improved catalytic activity over that of spherical Pd NPs of a similar size.

References

[1] Narayanan R and El-Sayed M A 2005 *Langmuir* **21** 2027

[2] Shen C M, Su Y K, Yang H T, Yang T Z and Gao H J 2003 *Chem. Phys. Lett.* **373** 39

[3] Xiao C W, Ding H, Shen C M, Yang T Z, Hui C and Gao H J 2009 *J. Phys. Chem.* C **113** 13466

[4] Burda C, Chen X B, Narayanan R and El-Sayed M A 2005 *Chem. Rev.* **105** 1025

[5] Kim S W, Kim M, Lee W Y and Hyeon T 2002 *J. Am. Chem. Soc.* **124** 7642

[6] Nishihata Y, Mizuki J, Kao T, Tanaka H, Enishi M, Imura M, Kamoto T and Hamada N 2002 *Nature* **418** 164

[7] Wang B 2005 *Journal of Power Sources* **152** 1

[8] Baldauf M and Kolb D M 1996 *J. Phys. Chem.* **100** 11375

[9] Hoshi N, Kida K, Nakamura M, Nakada M and Osada K 2006 *J. Phys. Chem.* B **110** 12480

[10] Ksar F, Surendran G, Ramos L, Keita B, Nadjo L, Prouzet E, Beaunier P, Hagège A, Audonnet F and Remita H 2009 *Chem. Mater.* **21** 1612

[11] Mazumder V and Sun S 2009 *J. Am. Chem. Soc.* **131** 4588

[12] Larsen R, Ha S, Zakzeski J and Masel R I 2006 *Journal of Power Sources* **157** 78

[13] Xu C W, Cheng L Q, Shen P K and Liu Y L 2007 *Electrochem. Commun.* **9** 997

[14] Li H Q, Sun G Q, Jiang Q, Zhu M Y, Sun S G and Xin Q 2007 *Journal of Power Sources* **172** 641

[15] Sun Z P, Zhang X G, Liu R L, Liang Y Y and Li H L 2008 *Journal of Power Sources* **185** 801

[16] Zhu Y, Kang Y Y, Zou Z Q, Zhou Q, Zheng J W, Xia B J and Yang H 2008 *Electrochem. Commun.* **10** 802

[17] Wang R F, Liao S J and Ji S 2008 *Journal of Power Sources* **180** 205

[18] Xiong Y J, Cai H G, Wiley J B, Wang J G, Kim M J and Xia Y N 2007 *J. Am. Chem. Soc.* **129** 3665

[19] Xiong Y, Chen J, Wiley B, Xia Y, Yin Y and Li Z Y 2005 *Nano Lett.* **5** 1237

[20] Kim S W, Park J, Jang Y, Chung Y, Hwang S, Hyeon T and Kim Y W 2003 *Nano Lett.* **3** 1289

[21] Wang C, Daimon H, Onodera T, Koda T and Sun S 2008 *Angew. Chem. Int. Ed.* **47** 3588

[22] Xu D, Liu Z P, Yang H Z, Liu Q S, Zhang J, Fang J Y, Zou S Z and Sun K 2009 *Angew. Chem. Int. Ed.* **48** 4217

[23] Xiong Y J, Wiley B, Chen J Y, Li Z Y, Yin Y D and Xia Y N 2005 *Angew. Chem. Int. Ed.* **44** 7913

[24] Filankembo A, Giorgio S, Lisiecki I and Pileni M P 2003 *J. Phys. Chem.* B **107** 7492

[25] Wiley B J, Xiong Y J, Li Z Y, Yin Y D and Xia Y N A 2006 *Nano Lett.* **6** 765