Electrochemistry Communications 37 (2013) 57–60

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

Facet-dependent electrocatalytic activities of Pd nanocrystals toward the electro-oxidation of hydrazine

Ling Zhang [a,b], Wenxin Niu [a,b], Wenyue Gao [a,b], Liming Qi [a,b], Jianming Zhao [a,b], Min Xu [a,b], Guobao Xu [a,*]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, PR China
[b] University of the Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, China

ARTICLE INFO

Article history:
Received 9 September 2013
Received in revised form 3 October 2013
Accepted 3 October 2013
Available online 10 October 2013

Keywords:
Palladium
Electrocatalysis
Hydrazine
Fuel cell
Shape
Facet

ABSTRACT

The different atomic arrangements of noble metal nanocrystals with varying facets will largely affect the catalytic activity. Rhombic dodecahedral, octahedral, cubic Pd single-nanocrystalline crystals are exclusively enclosed by {100}, {111}, and {110} facets, respectively. Herein, the electro-oxidation of hydrazine in basic solutions catalyzed by these Pd single-nanocrystalline crystals was investigated. The onset potentials were about −0.48 V, −0.43 V, −0.38 V, and −0.43 V for {110}-, {111}-, and {100}-faceted Pd nanocrystals and commercial Pd/C catalysts, respectively. {110} facets possess the highest specific activity and mass activity. The specific activity of Pd rhombic dodecahedra was 147% higher than that of commercial Pd/C catalysts. The mass activity of Pd rhombic dodecahedral nanocatalysts at −0.2 V (vs. Ag/AgCl) was 60.3%, 113.6%, and 354% higher than that of Pd octahedra, cubes, and commercial Pd/C catalysts at 600 s, respectively. This study is significant to effectively utilize Pd catalysts in fuel cell, industry productions, and pollutant processes.

1. Introduction

Pd nanocrystals are major catalysts for the organic reactions [1], vehicle exhaust reduction [2], and electrochemical oxidation of the fuel cell molecules [3–6]. Due to the high cost of noble metal nanocrystals, improving the mass and specific activities is particularly important. The catalytic activity of noble metal nanocrystals is highly surface-dependent, which has the close relationship with the external atomic arrangements of noble metal nanocrystals[7]. Most noble metal nanocrystals crystallize into the face-centered cubic (*fcc*) structures with low-index facets including {100}, {111}, and {110} facets [8]. Among them, the external atomic arrangements of *fcc* metal nanocrystals enclosed with {100} and {111} facets are close and the surface atomic coordination number is high. In contrast, there are many stepped atoms which have a low coordination number on the surfaces of {110}-faceted *fcc* metal nanocrystals, and surface atoms arrange loosely. Thus, {110} facet is called high-energy facet [9]. The high-energy facets are thermodynamically unstable and should be synthesized under the careful kinetic and thermodynamic control. Meanwhile, the high-energy facets usually exhibited the prominent surface-enhanced properties [10–15].

Hydrazine is an important anodic material for fuel cell, high-energy propellant for rockets or spacecraft, and compound of interest in biology, chemical and pharmaceutical fields [16–18]. The processing of hydrazine before releasing into the environment becomes critical to human health for the carcinogenic and hepatotoxic effects [19]. Pd nanocrystals with different shapes have been used to catalyze the electrooxidation of glucose, and the electrocatalytic activity is dependent on the nanocrystal facets, spiecies catalyzed and solution enviroments [20,21]. Herein, we choose mono-dispersed Pd cubes, octahedra, and rhombic dodecahedra single-crystalline nanocrystals, which are exclusively enclosed by {100}, {111}, and {110} facets, as the electrocatalyst of hydrazine oxidation, respectively. The specific activity and mass activity of {110}-, {111}-, and {100}-faceted Pd nanocatalysts were higher than those of commercial Pd/C catalysts in the basic solutions to hydrazine electrooxidation, respectively. And rhombic dodecahedral Pd nanocrystals enclosed by {110} facets were most active to catalyze hydrazine, which is possibly due to the high activity of the unsatured-coordinated surface atoms. This study is a significant research involving the surface structure dependent catalytic properties and will be beneficial to the wide applications of noble metal catalysts.

2. Experimental

2.1. Reagents

$PdCl_2$ and hydrazine hydrate (85%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cetyltrimethylammonium bromide (CTAB) was obtained from Acros Organics (USA). L-Ascorbic acid and HCl were obtained from Beijing Chemical Reagent Company. Commercial Pd/C (wt. 10%) catalysts are purchased from Beijing Yili Fine Chemicals Co. Ltd. All the chemicals were of analytical grade and used without further purification. Doubly distilled water was used throughout the experiments. A 10 mM H_2PdCl_4 solution was prepared

* Corresponding author. Tel./fax: +86 431 85262747.
E-mail address: guobaoxu@ciac.ac.cn (G. Xu).

1388-2481/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elecom.2013.10.006

by dissolving 0.1773 g $PdCl_2$ in 10 mL of 0.2 M HCl solution and further diluting to 100 mL with doubly distilled water.

2.2. Instruments

Scanning electron microscopy (SEM) images were taken using an FEI XL30 ESEM FEG scanning electron microscope operated at 25 kV. Electrochemical measurements were carried out in a conventional three-electrode cell at the room temperature with a 800b electrochemical working station (Chenhua Inc. Xi'an). The working electrodes were Pd nanocrystal modified glassy carbon electrode and bulk Pd electrode, respectively. And the auxiliary electrode and the reference electrode were a thin platinum grid and an Ag/AgCl electrode (saturated KCl), respectively.

2.3. Synthesis of Pd nanocubes, octahedra, rhombic dodecahedra

Pd nanocubes, octahedra, and rhombic dodecahedra were obtained with the seed-mediated method as previously reported [22,23]. First, 22 nm cubic Pd seeds were synthesized. Briefly, 500 μL aliquot of 10 mM H_2PdCl_4 solution was added to 9420 μL of 12.5 mM CTAB aqueous solution heated at 95 °C under stirring. After 5 min, 80 μL of freshly prepared 100 mM ascorbic acid aqueous solution was added, and the reaction was allowed to proceed for 20 min. Second, Pd nanocubes, octahedra, and rhombic dodecahedra were synthesized by the overgrowth of the smaller Pd seeds at given temperatures and concentrations of KI. 100 μL aliquot of 10 mM H_2PdCl_4, 100 μL aliquot of 22 nm Pd cubes, and 40 μL aliquot ascorbic acid solutions were added into 4 mL of 100 mM CTAB solution, sequentially. Octahedral and rhombic dodecahedral Pd nanocrystals were produce in the presence of 5 μM KI at 40 and 80 °C, respectively. Cubic Pd nanocrystals were synthesized at 60 °C without KI. The reactions proceeded for 15, 2, and 1 h at 40, 60, and 80 °C, respectively. Finally, the products were washed for four times with water by centrifugations and dispersed in water, using as the catalyst to the hydrazine electro-oxidation.

2.4. Catalysis of Pd nanocrystals to the electro-oxidation of hydrazine

Glassy carbon electrodes and bulk Pd electrode were polished with 1 and 0.3 μm aluminium slurry colloid on the cloth, successfully, and then ultrasonicated with water to clean the surface. After the electrode surfaces were dry, 8 μL of 0.2 $mg \cdot mL^{-1}$ Pd catalyst solutions was dropped on the electrodes and dried at the room temperature. The Pd catalyst modified glassy carbon electrodes were used to catalyze hydrazine electro-oxidation in 0.1 M NaOH solutions.

3. Results and discussion

3.1. Characterization of Pd nanocubes, octahedra, and rhombic dodecahedra

Fig. 1 shows the SEM images of cubic, octahedral, and RD Pd nanocrystals. The sizes of the nanocrystals were about 70 nm. Pd nanocubes, octahedra, and RD are typical shapes which are enclosed with {100}, {111}, and {110} low-index facets, respectively. The models of the nanocrystals are shown in the corner of their SEM images. As shown in Fig. 1A, a cube is composed of six equivalent cubic faces, twelve edges, and eight vertices, respectively. Fig. 1B shows the SEM image of Pd octahedra and the model. The octahedron is enclosed by eight equivalent triangular faces, and has twelve edges and six vertices, respectively. Rhombic dodecahedral Pd nanocrystals and the model are shown in Fig. 1C. Rhombic dodecahedron is composed of twelve equivalent rhombus faces, twenty edges, and sixteen vertices, respectively.

The internal atomic arrangements of Pd nanocubes, octahedra, and rhombic dodecahedra are continuous, so they are single-crystalline. And the internal atoms of Pd nanocrystals adopt the same arrangements (*abcabc*…) due to the intrinsic *fcc* structures. However, the surface

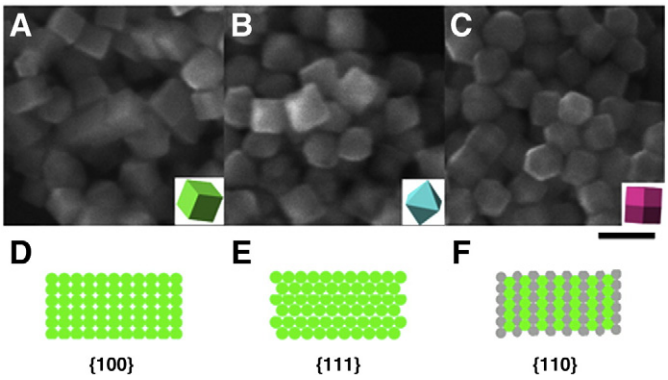

Fig. 1. (A–C) SEM images of Pd nanocubes (A), octahedra (B), and rhombic dodecahedra (C) and corresponding models. Scale bar, 100 nm. (D–F) Surface atomic arrangement models of {100} (D), (111) (E), and {110} (F) facets in the top view.

atomic arrangements of Pd nanocrystals can be different, which lead to the formations of different facets. Fig. 1D–E shows the surface atomic arrangements models of {100}, {111}, and {110} facets. For {110} facets, the atomic arrangements on the top layer are loose, and the atomic coordination number is 7 (saturated coordination number of *fcc* metals is 9). The atoms on the {111} surfaces are the closest, and the coordination number is 9. The coordination number of {100} surface atoms is 8.

3.2. Calculation of electrochemical active surface area (EASA)

The EASA of Pd catalysts was calculated from the reduction peak area of surface $Pd(OH)_2$. Fig. 2A shows the cyclic voltammograms of glassy corbon electrodes modified with four different types of Pd catalysts in 0.1 M NaOH solution. The characteristic reduction peaks standard the reduction of $Pd(OH)_2$ on the Pd surface, reflecting the number of active Pd sites. And the EASA value is calculated from the following equation,

$$\mathrm{EASA} = Q/mC \tag{1}$$

where Q is the Coulombic amount of the reduction peak area of $Pd(OH)_2$, C is the reduction charge of Pd(OH) monolayer on the Pd surface ($420\ \mu C \cdot cm^{-2}$) and m is the mass of Pd on the glassy carbon electrode (1.60 μg). The calculated EASA of Pd nanocrystals with different shapes is shown in Table 1.

3.3. Electrocatalysis of hydrazine oxidation

The mass activity of metal nanocrystals is a good parameter to value the effectiveness of catalyst utilization. And the specific activity indicates the intrinsic catalytic activity of the metal nanocrystals. The mass activity and specific activity are obtained with the following equations,

$$\mathrm{Mass\ activity} = \mathrm{i/m} \tag{2}$$

$$\mathrm{Specific\ activity} = \mathrm{Mass\ activity/EASA} \tag{3}$$

where i is the current of hydrazine electro-oxidation.

Fig. 2B shows the mass activity to catalyze hydrazine electro-oxidation of all Pd catalysts in 0.1 M NaOH solutions obtained with cyclic voltammetry techniques. In the positive scan direction, the onset and peak potentials of hydrazine electro-oxidation were different with the facets, as shown in Table 1. The onset potential was in the order, rhombic dodecahedral (−0.48 V) < octahedral (−0.27 V) < cube (−0.21 V) ≈ commercial Pd/C (−0.21 V), indicating that hydrazine molecules are most easily oxidized on {110} surfaces of Pd nanocrystals. The peak currents were about 246, 234, 183, 120 $A \cdot g^{-1}$ for rombic dodecahedral, octahedral, cubic Pd nanocatalysts and commercial Pd/C catalysts, respectively. It is showed that the efficiency of rhombic dodecahedral