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Short Communication

Electro-oxidation of formaldehyde and methanol over hollow porous palladium nanoparticles with enhanced catalytic activity

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ABSTRACT

Hollow palladium (Pd) nanoparticles with porous shells are simply synthesized via galvanic replacement reaction. The average particle size of hollow Pd nanoparticles is about 15 nm and the thickness of porous shells is about 3 nm. The electrochemical behaviors of these hollow nanoparticles are characterized by cyclic voltammetry (CV). The hollow porous Pd nanoparticles exhibit considerably higher electrocatalytic activity for electrochemical oxidation of formaldehyde and methanol compared to solid Pd nanoparticles, which are promising electrode nano-catalysts for low temperature fuel cells.

1. Introduction

Electrochemical oxidation of small organic chemicals over nanocatalysts has attracted intensive attention because of its wide applications in energy conversion, chemical synthesis, electrochemical sensors, environment protection, electroless plating, etc. [1–3]. Formaldehyde (HCHO) and methanol (CH_3OH) are single carbon liquid organic compounds at room temperature, which makes them easily stored and highly active. Electrocatalytic oxidation of methanol has been intensively researched for fuel cells. During the oxidation of small organic fuels, formaldehyde is usually produced as an intermediate and it has a very simple molecular structure. Thus formaldehyde is frequently used as a model compound for electrochemical oxidation of small organic chemicals to fully understand the electrochemical process and investigate electrochemical activity of catalysts [4–6]. Formaldehyde is also a widely used reduction reagent for electroless plating of copper via oxidation reaction. Furthermore, formaldehyde is toxic and found in more than 2000 products, there is interesting in electro-oxidation of formaldehyde for its detection and waste treatment [7,8]. Chemical sensor via electrocatalytic oxidation of formaldehyde is simple, low cost, and sensitive and is the present operation used compared with spectral and chromatographic analyses [9,10].

Nano-structured materials of noble metals (Pt, Pd, etc. and their alloys) have high catalytic activity toward electrochemical oxidation of small organic compounds [11,12]. Pt-based materials have been commonly used as the best electrocatalysts for direct methanol fuel cells and formaldehyde electrochemical sensors [13]. Pd colloidal nanoparticles have been widely commercially used as catalysts in the electroless plating industry. However, Pt and Pd are very expensive, especially Pt, which is a main baffle for the commercialization for fuel cells. Pd is considered a substitute for Pt in fuel cells due to its high catalytic activity, relatively lower cost, and reduced generation of a poisonous intermediate during small organic chemical electro-oxidation [14,15]. A variety of nano-structured Pd materials have been fabricated as electrocatalysts [16–21]. Pd hollow nanocubes with the size of 80 nm or 300 nm display high performance for electrochemical detection toward hydrogen peroxide or proton/hydrogen sensing [22]. Pd hollow nanocatalysts with the size of 40–80 nm or 82.0 ± 7.7 nm showed dramatically high catalytic performance for oxygen reduction [23]. Although hollow Pd nano-materials possess these advantages, the large particle size might trigger the hollow nanoparticle agglomeration, resulting in stability decline [27,28]. Besides, it would obviously hinder the catalytic performance owe to the specific surface area is not too high enough to make full use of noble metal Pd with large size, leading to the decrease in catalytic efficiency [21]. Porous structure is another important method to obtain high activity also due to the high exposure of Pd atoms as catalyst [24]. To the best of our knowledge, there are few reports

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about hollow Pd electrocatalysts smaller than 20 nm, especially those with porous shells to expose more Pd atoms for the oxidation of formaldehyde and methanol [4,5].

Herein, we have successfully fabricated about 15 nm of monodispersed hollow Pd nanospheres with porous shells via surface replacement reaction, using Co nanoparticles employed as both sacrificial templates and reducing agents. Hollow porous Pd nanospheres and Pd solid nanoparticles were also investigated respectively for evaluating the electrocatalytic activities toward the oxidation of formaldehyde and methanol.

2. Experimental

2.1. Materials

All chemical reagents were of analytical grade and were used without further purification. Citric acid ($C_6H_8O_7 \cdot H_2O$, 99.5%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99.0%), methanol (CH_3OH, ≥99.5%), and sodium borohydride ($NaBH_4$, ≥97%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Palladium chloride ($PdCl_2$, 99.9%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Potassium hydroxide (KOH, 90%) was purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl, 37%) was purchased from Dongjiang Chemical Reagent Co., Ltd. (Guangdong, China). Formaldehyde (HCHO, 30–40%) was purchased from Overseas Reagent Plastic Co., Ltd. (Guangdong, China). Deionized Milli-Q water was used as the solvent.

2.2. Preparation of hollow porous Pd nanoparticles

Hollow porous Pd nanoparticles were fabricated by modifying the protocol previously reported by Liang et al. and through replacement reaction using Co nanoparticles as sacrificial templates [14]. Briefly, a 10 mM of H_2PdCl_4 aqueous solution was firstly prepared by completely dissolving 88.6 mg of $PdCl_2$ in 50 mL of 20 mM HCl under ultrasonic treatment for 30 min. In addition, 100 mL of mixed aqueous solution that contains $CoCl_2$ (0.5 mM) and citric acid (1 mM) was heated to 95 °C under the flow of high purity N_2 gas. Afterward, 10 mL of 0.1 M $NaBH_4$ aqueous solution was added to the mixed solution all at once under vigorous stirring. The color of the solution changed into brown with the production of H_2, immediately. After 5 min, 5 mL of 10 mM H_2PdCl_4 aqueous solution was rapidly injected into the resulting solution with vigorous stirring and maintained the heating to 95 °C for 30 min. Finally, the obtained solution was centrifuged and the particles were washed with deionized water and then dried at 50 °C for 12 h in air.

2.3. Preparation of solid Pd nanoparticles

100 mL of mixed solution containing H_2PdCl_4 (0.5 mM) and citric acid (1 mM) was stirred vigorously for 5 min at 95 °C. Additionally, 10 mL of 0.1 M $NaBH_4$ aqueous solution was immediately added to the mixture under vigorous stirring. The obtained solution was centrifuged and the particles were washed with deionized water and then dried at 50 °C for 12 h at air.

2.4. Characterization

The morphology and structure of hollow porous Pd nanoparticles were characterized by field emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 450) and high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 FEI), respectively. The X-ray diffraction (XRD, Rigaku D/Max 2500, Japan) with Cu-Kα radiation was taken to measure the crystallographic structure of the products.

2.5. Electrochemical measurements

The electrochemical measurements were carried out on electrochemical workstation (Zennium Zahner, Germany). A conventional three-electrode cell system was conducted at room temperature. The drop-casting films of hollow porous Pd nanoparticles on a glassy carbon electrode (GCE, diameter: 5 mm, area: 0.196 cm^2) were used as the working electrode. The saturated calomel electrode and the platinum-plate electrode served as the reference electrode and the counter electrode, respectively. Prior to CV measurements, the GCE was polished with 50 nm of α-Al_2O_3 powder to a mirror finish, and then 20 μL of hollow Pd nanoparticle solution was deposited on the GCE to obtain the working electrode with a metal loading of 20.4 $\mu g\ cm^{-2}$. After the solution drying, 10 μL of 0.1 wt.% Nafion solution was dropped on the surface of the above catalyst modified CGE and dried at 60 °C before electrochemical experiments. The electrochemical catalytic activity of the hollow porous Pd nanoparticle catalyst was carried out by CV and the electrochemical surface area (ECSA) was calculated by integrating the hydrogen adsorption charge on the CV at room temperature in 0.5 M of H_2SO_4 solution. Formaldehyde and methanol oxidation tests were carried out in a solution containing 1.0 M KOH + 1.0 M HCHO and a solution containing 1.0 M KOH + 1.0 M CH_3OH with a scan rate of 50 $mV\ s^{-1}$, respectively. For comparison, solid Pd nanoparticles were also carried out by using the above electrochemical measurement under the same conditions.

3. Results and discussion

The formation procedure of porous hollow Pd nanoparticles can be illustrated in Fig. 1. Co nanoparticles were firstly synthesized as sacrificial templates and reducing regents. Afterward, the hollow porous Pd nanoparticles were fabricated by the $PdCl_4^{2-}$ reduction using the Co nanoparticles in aqueous solution as shown in Eq. (1):

$$PdCl_4{}^{2-} + Co \rightarrow Pd + Co^{2+} + 4Cl^-. \quad (1)$$

$PdCl_4^{2-}$ can be reduced to Pd by Co since the Co^{2+}/Co (−2.8 V vs. SHE) redox pair value is much lower than the $PdCl^{2-}/Pd$ (0.59 V vs. SHE) redox pair value [25]. Avoiding oxidation of Co nanoparticles in the presence of atmospheric oxygen, the high purity N_2 gas was introduced into the reaction solution during the whole process. The nanostructures of porous hollow Pd spheres largely depended on the reduction reaction of $PdCl^{2-}$ with the Co sacrificial templates and its properties.

The morphology and structure of the Pd nanoparticles were confirmed by TEM and SEM measurements as shown in Fig. 2. Typical TEM images of Pd nanoparticles clearly exhibited that the as-prepared hollow Pd spherical particles were monodispersed uniform nanoparticles with bright centers and dark edges (Fig. 2a and b), indicating the successful formation of hollow structured Pd spherical nanoparticles. The average particle size of Pd hollow spherical nanoparticles was around 15 nm. The surface of Pd hollow shells seemed rough, and the thickness was approximately 3 nm. The SEM image (Fig. 2e) also indicated that the as-prepared nanoparticles possessed a rough surface structure, showing that these nanoparticles were spherical rather than ring-like. The solid Pd nanoparticles were also prepared with the same size as that of Pd hollow nanoparticles to evaluate the electrocatalytic performances comparatively. The structure and morphology of solid Pd nanoparticles were observed with TEM images (Fig. 2c, d). The average size of the solid Pd nanoparticles was about 15 nm. The solid Pd nanoparticles were also observed by high-resolution TEM (Fig. 2d). The color and brightness of the centers of solid Pd nanoparticles were obviously the same as those of the edges, and the surface of nanoparticle was smooth. The observation results of the solid Pd nanoparticles were significantly different from the hollow Pd nanoparticles.