



The fabrication of palladium hollow sphere array and application as highly active electrocatalysts for the direct oxidation of ethanol

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ABSTRACT

SiO₂ opals template was prepared on Au substrate with vertical deposition technique from highly monodispersed SiO₂ particles. After that, Pd was electrodeposited on the SiO₂ spheres to fabricate the Pd hollow sphere array after the removal of the SiO₂ template with HF solution. The prepared Pd array had a highly ordered structure with huge surface area and exhibited excellent electrocatalytic activity, stability and anti-poison capability for ethanol electrooxidation in alkaline media, which showed that the Pd hollow sphere array could be used as effective electrocatalysts for direct alcohol fuel cells.

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1. Introduction

Nowadays, direct alcohol fuel cells (DAFCs) have attracted enormous attention as power sources for portable electronic devices and fuel-cell vehicles [1,2]. Compared to gaseous fuels, liquid fuels have higher energy density with lower price, and can be easily handled, stored and transported. Among the various liquid fuels, ethanol is less toxic than methanol and can be produced in large quantities from agricultural products or biomass [3,4].

Researches focused on the electro-oxidation of alcohol have been widely reported on Pt and Pt-based catalysts [5–9]. Compared to Pt, Pd has similar catalytic performance, and what's more, palladium is much cheaper and is 50 times more abundant on earth. Pd has been used to reduce the cell cost and was demonstrated to have good electroactivity in DAFCs [10–15]. Recently, metal nanomaterials with large active surface and well-designed structures have attracted increasing attention. 3D ordered macroporous gold film [16,17], Pt [18], Pt/Ru nanocomposites [19] and PANI [20] were successfully prepared via inverted colloidal crystal template technique and were demonstrated to have wide applications in electrocatalysis, immunoassay [17,20] and DAFCs [18,19]. Sn/Pt nanotube arrays [21] were also synthesized with AAO template and were verified to have enhanced methanol oxidation efficiency compared to directly deposited catalyst. Xu [22] also reported the fabrication of highly ordered Pd nanowire arrays by the AAO template-electrodeposition method with higher electrocatalytic activity than that of commercial PtRu/C electrocatalysts. Therefore, Pd hollow

sphere array with large surface area is expected to have better electrocatalytic property in DAFCs. To our best knowledge, no report has been found on the preparation and application of Pd hollow sphere array in ethanol electrooxidation. Herein, we reported the fabrication of Pd hollow sphere array by sacrificial template method, and the results showed that the Pd hollow sphere array was highly active for ethanol oxidation in alkaline media for DAFCs.

2. Experimental section

2.1. Materials

Palladium chloride (PdCl₂) and tris(hydroxyl-methyl)amino-methane (Tris) were purchased from Chinese Shanghai Regent Company. The monodispersed silica spheres with the diameter of 500 nm were obtained from Alfa Aesar. Polydiallyldimethylammonium chloride (PDDA, 20 wt.% in H₂O) was purchased from Sigma-Aldrich. Other reagents such as anhydrous ethanol, hydrochloric acid, sodium chloride, potassium hydroxide and hydrofluoric acid were of analytical grade and were used as received. All solutions were prepared with Millipore water.

2.2. Preparation of Pd hollow sphere array

The SiO₂ colloidal crystal template was fabricated on Au substrate provided by the 55th Institute of China Electronic Group (Nanjing, China). With vertical deposition, a close-packed silica colloidal crystal layer was formed on the gold substrate [20]. The electrode area was controlled to be 0.3 cm² (0.5 cm × 0.6 cm) by an insulating tape. After that, the electrode was dipped in PDDA solution (0.20% PDDA + 0.02 M Tris + 0.02 M NaCl) for 4 h and then immersed in Pd

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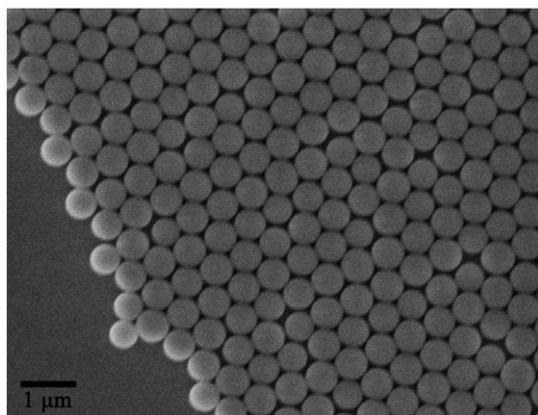


Fig. 1. Typical SEM image of the SiO₂ colloidal crystal template prepared by vertical deposition.

solution (0.05 g L⁻¹ PdCl₂ + 0.1 M HCl) for 10 min. Subsequently, electrodeposition was carried out potentiostatically at 0.2 V (vs. SCE) until the charge reached 0.05 C. The Pd film electrode for comparison was prepared under similar condition except using a common Au substrate. All the electrochemical experiments were performed on a CHI660C electrochemical workstation (Shanghai CH Instruments Co.) using a traditional three-electrode system. A platinum sheet (1.0 cm × 1.0 cm) and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The electrolyte solution was deaerated with N₂ and N₂ was flowed over the solution during the reaction. Finally, the Pd hollow sphere array modified electrode was fabricated by dissolving the SiO₂ template in aqueous HF (5%) for 3 min.

2.3. Characterization

The morphology of the Pd hollow sphere array modified electrode was characterized by field-emission scanning electron microscopy

(FESEM, HITACHI S4800). The EDX measurement was performed by using the FESEM's accessory (S4800 TYPE II). The Pd hollow sphere array modified electrode served as the working electrode with Pd loading of 0.09 mg cm⁻². CVs were performed in 1.0 M KOH and 1.0 M KOH + 1.0 M C₂H₅OH solutions at room temperature at a scan rate of 100 mV s⁻¹ in the potential range from -0.8 V to 0.2 V (vs. SCE). Chronoamperometric experiments were carried out at -0.3 V (vs. SCE) in 1.0 M KOH solution containing 1.0 M C₂H₅OH at room temperature for 3600 s.

3. Results and discussion

Monodispersed SiO₂ spheres were first assembled on gold substrate to form a highly ordered colloidal crystal template by vertical deposition. Fig. 1 is the SEM image of the SiO₂ colloidal crystal template that exhibits a (111) close-packed arrangement of SiO₂ spheres and hexagonal array structure. The thickness of the inverse opals was controlled to be one layer.

Electrodeposition has been proved to be an efficient method for the growth of uniform and continuous metallic arrays [22–25], which presents some advantages such as easily controllable reaction condition including the applied potential, the deposition time, the charge and the thickness. What's more, this method is fast, simple, and energy efficient. Since the surface of SiO₂ sphere is negatively charged, which is similar to [PdCl₄]²⁻ in aqueous solution, it is difficult for Pd to be electrodeposited into the interstitial spaces of the SiO₂ template directly. Hence, it is necessary for SiO₂ spheres to be functionalized with positively charged PDDA for 4 h before electrodeposition. In the assembly, [PdCl₄]²⁻ could be adsorbed around SiO₂ spheres by electrostatic adsorption and be further reduced to Pd which formed a shell outside the SiO₂ template. Finally, Pd hollow sphere array was fabricated after the removal of the templates with HF solution.

Fig. 2 shows the typical SEM images of the prepared Pd spheres. Fig. 2a is the arrangement of highly ordered Pd spheres before the dissolution of template, which indicates that Pd is well deposited around hexagonal array structures. In Fig. 2b, a core-shell structure can be

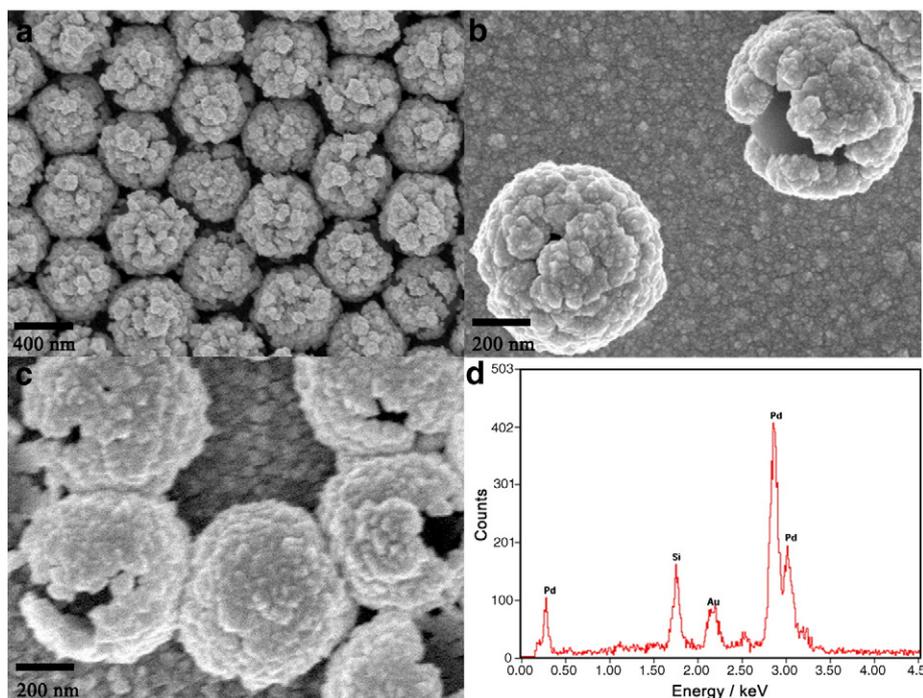


Fig. 2. (a)(b) SEM and high-magnification images of Pd hollow sphere array before the removal of the SiO₂ template, (c) SEM image of several Pd spheres after the removal of the SiO₂ template, (d) EDX of the sample in c.

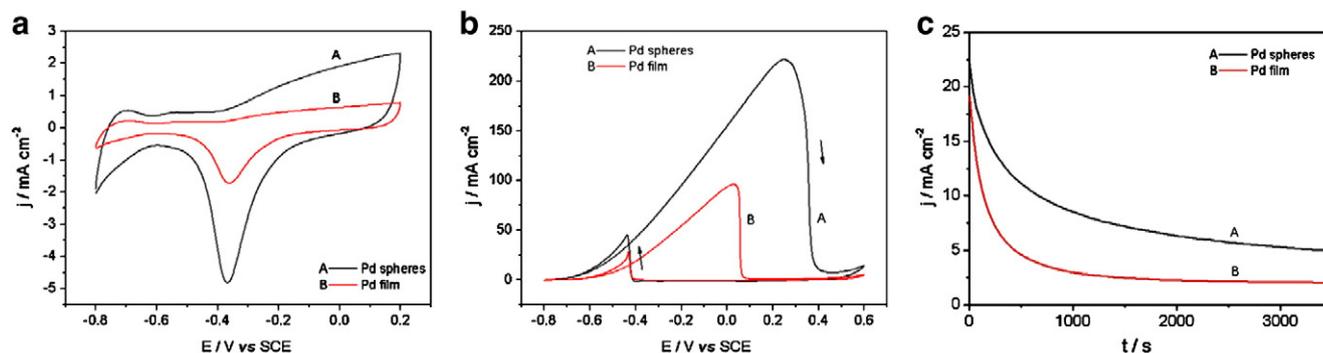


Fig. 3. CVs in 1.0 M KOH solution without ethanol (a), containing 1.0 M ethanol (b) and the chronoamperometric curves for ethanol electrooxidation at -0.3 V (vs. SCE) (c) (Pd hollow sphere array modified electrode (curve A) and Pd film electrode (curve B)).

clearly observed from a single sphere in which the SiO_2 core is partially wrapped by a Pd layer with a thickness of about 70–80 nm. After the SiO_2 template is dissolved by HF solution, most area of the substrate looks the same as that in Fig. 2a, however, from the “broken” Pd spheres in Fig. 2c, it can be seen that SiO_2 template has been removed completely from the substrate. EDX spectroscopy was further used to determinate the elements composition of the sample. The result shows that only Pd exists in the prepared sample except Si and Au of the substrate, which is consistent with the SEM results.

The catalytic properties of the Pd hollow sphere array modified electrode and Pd film electrode for the direct oxidation of ethanol were compared by using CVs. Fig. 3a shows the CVs of Pd hollow sphere array modified electrode (curve A), and Pd film electrode (curve B) in 1.0 M KOH solution without ethanol. The anodic peaks between -0.75 and -0.60 V (vs. SCE) originate from the desorption of atomic hydrogen on the Pd electrocatalysts. The electrochemically active specific surface area of the Pd modified electrode can be evaluated through the hydrogen desorption region of CVs measured in 1.0 M KOH solution in the absence of ethanol [26]. The area of hydrogen desorption on the CV curves represents the charge passed for the hydrogen desorption, Q_{H} , which is proportional to the electrochemically active area of the Pd-modified electrode [22,27]. The Q_{H} values of the Pd hollow sphere array modified electrode and Pd film electrode are calculated to be 0.37 and 0.15 mC cm^{-2} , respectively. The higher Q_{H} value could be attributed to huge surface area of the hollow Pd spheres. Fig. 3b shows the CV curves of ethanol oxidation on the Pd-modified electrode in a 1.0 M KOH solution containing 1.0 M ethanol. The onset potential for the ethanol oxidation on the Pd sphere array modified electrode is -0.547 V, which is 43 mV more negative than -0.504 V observed on the Pd film electrode, indicating enhancement in the kinetics of the ethanol oxidation reaction [22]. Ethanol oxidation is characterized by well-separated anodic peaks in the forward and reverse scans. The magnitude of the anodic peak current in the forward scan is directly proportional to the amount of ethanol oxidized on the Pd-modified electrodes. The peak current density is 222 and 97 mA cm^{-2} for the Pd sphere array modified electrode and Pd film electrode, respectively, indicating that the catalytic activity of Pd hollow sphere array is much higher than that of Pd film. At the same time, two well-defined current peaks in the CVs can be observed in Fig. 3b. The peak current of forward scan is related to the oxidation of freshly chemisorbed species issued from alcohol adsorption, and the peak of reverse scan represents the removal of carbonaceous species not completely oxidized in the forward scan. Hence, the ratio of the forward anodic peak current density (I_f) to the reverse anodic peak current density (I_b) quantifies the catalyst tolerance to carbonaceous species accumulation, and a high ratio of I_f/I_b indicates efficient oxidation of alcohol during the forward anodic scan, with little accumulation of carbonaceous residues [15]. In our experiment, the I_f/I_b value of Pd hollow sphere array modified electrode is close to 5, much higher than that of Pd film electrode, indicating that the Pd hollow sphere array could make the electrooxidation of the ethanol

more efficient and decrease the probability of catalyst's poisoning, which confirmed that the Pd sphere array modified electrode had excellent anti-poison capability.

Chronoamperometric tests were performed to investigate the long-term performance of the Pd hollow sphere array modified electrode at a fixed potential of -0.30 V in a 1.0 M KOH solution containing 1.0 M ethanol. As is shown in Fig. 3c, a slower current decay could be observed on Pd sphere array modified electrode than that on Pd film electrode, and the current density was still considerably higher than that on Pd film electrode even if the oxidation reaction reached the steady state. All these results confirmed that the Pd hollow sphere array had better steady state electrolysis activity than Pd film for the oxidation of ethanol in an alkaline media.

4. Conclusions

In conclusion, novel Pd hollow sphere array has been successfully fabricated on Au substrate with vertical deposition followed by electrodeposition method. The prepared Pd hollow sphere array has huge electrochemically active surface area and possesses excellent electrocatalytic activity and stability for ethanol electrooxidation in alkaline media. The higher I_f/I_b value indicates that the Pd hollow sphere array has excellent anti-poison capability. All these results indicate that the Pd hollow sphere array is a promising high performance electrocatalyst for Pt-free DAFCS.

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