



Full Length Article

Highly active and durable methanol electro-oxidation catalyzed by small palladium nanoparticles inside sulfur-doped carbon microsphere



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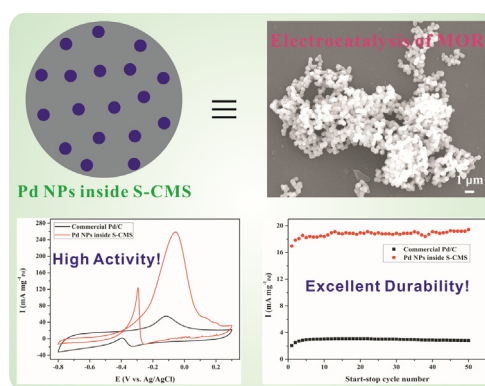
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HIGHLIGHTS

- Small Pd NPs inside S-doped CMS was synthesized.
- r-GSH was used as the reductant and capping agent as well as the C and S sources.
- The synthesized catalyst demonstrates high electro-catalytic activity toward MOR.
- The synthesized catalyst shows excellent stability of electro-catalytic activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 August 2016

Received in revised form 29 October 2016

Accepted 1 November 2016

Available online 14 November 2016

Keywords:

Small palladium nanoparticle

Doped carbon microsphere

MOR

Electro-catalytic activity

Operation durability

ABSTRACT

In this work, small palladium nanoparticles (Pd NPs) inside sulfur-doped carbon microsphere (S-CMS) were synthesized to achieve both high electro-catalytic activity and long durability for methanol oxidation reaction (MOR) in direct methanol fuel cells (DMFCs). The highly dispersed Pd NPs encapsulated in S-CMS with an architectural feature like the plum pudding model were obtained via a facile one-pot hydrothermal synthesis employing reduced glutathione (r-GSH) as both reducing and capping agents, followed by a simple carbonization procedure. The synthesized Pd NPs inside S-CMS was found to provide larger effective surface for MOR compared to commercial Pd/C. Mass activity 5.9 times higher than that of Pd/C was acquired, originating from the small size of Pd NPs and their interactions with the heteroatom-modified CMS coating. Due to the decreased agglomeration and dissolution, the proposed encapsulated Pd NPs also kept more stable during continuous start-stop operation, suggesting its great potential as an effective anode material to be used in DMFCs.

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1. Introduction

The appealing characteristics of direct methanol fuel cells (DMFCs), such as high energy density, low operating temperature, and environmentally benign quality have attracted significant attention from both academic and industrial communities in

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recent years [1–9]. Among the various reactions in DMFCs, methanol oxidation reaction (MOR) in anode has been widely recognized as a key step affecting the overall energy density and efficiency, for which catalysts with high activity, good poisoning resistance, and low cost are required. Pd-related catalysts have been proved to be very promising to promote MOR because it has been found that Pd-based structures can catalyze MOR in alkaline media with high activity [10–12]. In addition, Pd-related catalysts are more available and less expensive than the commonly used Pt-related catalysts [13–17]. Therefore, increased efforts have been devoted recently to fabricate Pd-based electro-catalysts to release their maximum power for MOR [10–17].

Conventionally, noble metal catalysts are loaded onto the low-cost carbon black to provide large surface area and good electrical conductivity [18]. However, the absence of interactions (incorporation of proton affinity, adjustment of electronic density, etc.) with active metal catalysts compromises the potential of pristine carbon black as a perfect support [19,20]. Moreover, recent studies have confirmed that the structure of carbon black is easily corroded and collapsed upon a relatively high potential or during a long-term operation [21–24]. The corrosion of support can result in the poisoning of metal catalysts, and the structure collapse will induce the aggregation/coalescence of metal catalyst particles, both leading to a sharp degradation of electro-catalytic activity [25–28].

To overcome the inherent drawbacks of carbon black, various support methods, such as novel carbon structures, carbides, nitrides, and metal oxides, have been proposed for loading noble metals [9,10,20,29–33]. Among those proposed improvements, encapsulating metal catalyst particles with a support layer has been widely viewed as an effective approach to improve the durability of electro-catalysts [34–39]. On one hand, the support coating out of noble metals can inhibit the accumulation of CO and other carbonaceous species formed on the catalyst surface [40]. On the other hand, encapsulation of metal catalyst particles within a stable matrix effectively restricts the leaching of highly oxidized metal ions into solution phase [41]. Furthermore, introducing a segregation layer to coat noble metal particles can significantly reduce the aggregation and coalescence of particles. In this scenario, recently we have successfully encapsulated Pt particles into carbon microsphere by using a hydrothermal-carbonization protocol, and found that the encapsulated Pt keeps very stable and active for glucose electro-catalysis even in the presence of Cl^- [39]. Thus, it can also be anticipated that encapsulated Pd particles possess superior catalytic features as encapsulated Pt particles. However, to the best of our knowledge, no report has appeared so far to encapsulate Pd particles. Moreover, as there exist some differences between Pt and Pd particles, the methodology realized for Pt cannot be directly applied to Pd and some improvements are desired.

In this study, advancements were made based on our previous proposed strategy to synthesize encapsulated Pd particles as a highly active and stable catalyst. Sulfur-doped carbon microspheres (S-CMS) were added as coating layers to small palladium nanoparticles (Pd NPs) to facilitate the electro-catalysis of methanol in alkaline media. The preparation procedure is described in detail and the catalytic performance of the encapsulated Pd particles for MOR is illustrated.

2. Experimental

2.1. Chemicals

In this study, four chemicals, i.e., K_2PdCl_4 , reduced glutathione (r-GSH), NaOH and methanol were prepared for the following processes. K_2PdCl_4 purchased from Shanghai Aladdin Reagent Co. was

employed as the supplier of Pd. r-GSH and NaOH were purchased from Sigma-Aldrich and Sinopharm Chemical Reagent Co., respectively. Ultrapure water produced by a laboratory water purification system was used through the overall experiment. Unless mentioned, all chemicals were of analytical grade and utilized without further purification.

2.2. Synthesis of small Pd NPs inside S-CMS

K_2PdCl_4 was initially dissolved into 50 mM stock solution, while 0.307 g r-GSH was first dissolved with 18 mL ultrapure water. Then, 2 mL of 50 mM K_2PdCl_4 stock solution was added into the r-GSH solution under a vigorous stir for 5 min. Afterwards, the mixture was transferred into a 50 mL Teflon-lined stainless solvothermal reactor with PTFE inner for reaction of 4 h under 180 °C. After the reaction, the products were cooled to room temperature and washed with adequate ultrapure water. The washed products were collected by centrifugation at 8000 rpm for 5 min. Finally, the collected materials were treated with a calcination procedure at 600 °C of 4 h in N_2 atmosphere for further characterization and evaluation.

As illustrated in Fig. 1, the catalyst was prepared via a simple one-pot hydrothermal synthesis using r-GSH as both reducing and capping agents simultaneously, followed by a routine carbonization process. Benign r-GSH with a highly reactive thiol group is not only capable of reducing metal salts, but also able to coordinate with formed noble metals like Pd efficiently through sulfydryl. Thus, using r-GSH allows the reduction of metal ions in a kinetically controlled manner [7,42]. As well, r-GSH can serve as a green carbon source with abundant heteroatoms to tune the electrochemical properties of carbon-based supports. To this end, the synthesized small Pd NPs inside S-CMS with an architectural feature like the plum pudding model, not only exhibit highly stable electro-catalytic performance for MOR as desired, but also provide a dramatic mass activity significantly higher than that of commercial Pd/C.

2.3. Characterization

X-ray diffraction (XRD) was carried out on an XRD-6100Lab diffractometer (Shimadzu, Japan) to study the crystal phase. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB 250Xi spectrometer (Thermo Fisher, USA) to probe the surface component. Scanning electron microscopy (SEM) operated on a JEOL JSM-6010PLUS/LA microscope was used to observe the surface morphology of materials. Transmission electron microscopy (TEM) images of samples were obtained using a JEOL JSM-2100 microscope. Elemental mapping patterns of the synthesized catalyst were obtained with an XM-2 energy disperse spectrometer (EDAX, USA). Inductively coupled plasma optical emission spectroscopy (ICP-OES) performed on an IRIS-1000 instrument (Thermo Elemental, USA) was used to determine the exact mass of Pd in catalysts.

2.4. Electrochemical measurements

All electro-chemical measurements were carried out on a CHI760E electro-chemical workstation (Shanghai Chenhua Instrument Co.) with a three-electrode system consisting of a catalyst-modified screen-printed working electrode (the detailed fabrication of screen-printed electrodes (SPE) had been described in the previous work [43]), a Pt wire counter electrode, and a Ag/AgCl reference electrode. Unless stated, all potentials reported here were referred to the Ag/AgCl electrode at room temperature. The working electrode was prepared by immobilizing catalysts onto the SPE surface via Nafion as a binder. The detailed procedure of electro-

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