



Rapid Electrochemical Fabrication of Porous Gold Nanoparticles for High-performance Electrocatalysis towards Oxygen Reduction



Liping Wan, Yun Qin, Juan Xiang*

Hunan Provincial Key Laboratory of Efficient and Clean Utilization of Manganese Resources, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history:

Received 18 January 2017

Received in revised form 6 April 2017

Accepted 6 April 2017

Available online 7 April 2017

Keywords:

porous gold nanoparticles

electrocatalysis

oxygen reduction

ABSTRACT

Small-size Au nanoparticles (AuNPs) and nanoporous Au films (npAuFs) are two potential catalysts for electrocatalysis, electrochemical analysis and synthesis. However, the large contact resistance among AuNPs and the poor mass transfer within npAuFs significantly limits their electrocatalysis application. Therefore, how to fabricate available high-active Au catalyst with facile and low-cost method is still a big challenge. In this study, porous gold nanoparticles (pAuNPs) were facilely and rapidly fabricated from gold nanoparticle-loaded electrode through a repeated Au/Hg alloying-dealloying process. In situ electrochemical fabrication ensured good electric contact of pAuNPs on the electrode surface; meanwhile, the pAuNPs were in tenths of nanometer length scales, which ensured rapid mass transport near the liquid/solid interface, facilitating the maximum exploitation of the high binding energy sites within nanoporous structures on electrocatalysis. Testing of the pAuNPs at a proof-of-concept level demonstrated its higher electrocatalytical activity than other two structures towards oxygen reduction in both acidic and alkaline media. The ease of sample preparation in combination with high activity suggested that pAuNPs can potentially cause a wide range of practical applications of Au catalysis.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Noble metals are used widely in a range of electrochemical applications, such as electrocatalysis, electrochemical analysis, and electrochemical synthesis, because of their inertness and catalytic properties. Au is usually regarded as a poor electrocatalyst due to the weak chemisorption properties caused by the filled d-band [1]. To improve the activity of Au, nanoparticles and nanoporous structures have been studied. Among them, Au nanoparticles (AuNPs) are size-dependent catalysts, which may provide excellent electrocatalytic effects in sub-10 nm region [2,3]. However, the contact resistance among AuNPs significantly increases with decreasing particle size, thereby limiting or complicating its electrochemical applications [4]. On the other hand, nanoporous Au film (npAuF), a gold network with nanometer-scale pores, is a good nanomaterial because of its excellent catalytic activity [5,6]. The npAuF catalytic activity is commonly attributed to the high fraction of highly active atomic steps and kinks, which

exponentially increase with the decrease of the ligament sizes of npAuFs [7,8]. Conversely, quasi-spherical AuNPs are enclosed with low-index facets, which results in their poor catalytic performance. However, to date, given the limitation of fabrication approach, the most widely used npAuFs present sub- or micron-sized thickness [9]. Consequently, the mass transport through porous structures is largely hindered when the pore volume is remarkably small [10], which significantly limit the electrocatalysis application of npAuFs.

In the present study, porous gold nanoparticles (pAuNPs) were prepared from AuNPs through a repeated Au/Hg alloying-dealloying process by simple electrochemical cyclic voltammetry (CV) scanning. This fabrication approach is rapid, facile and low-cost. Moreover, the in situ electrochemical fabrication ensured good electric contact of pAuNPs on the electrode surface; meanwhile, the pAuNPs were in tenths of nanometer length scales, which ensured rapid mass transport near the liquid/solid interface, facilitating the maximum exploitation of the high binding energy sites within nanoporous structures on electrocatalysis. In one word, the npAuPs can exploit the maximum advantage and overcome the shortcomings of both AuNPs and npAuFs. Compared with AuNPs and npAuF, pAuNPs demonstrated higher

* Corresponding author.

E-mail address: xiangj@csu.edu.cn (J. Xiang).

electrocatalytic activity towards oxygen reduction in both acidic and alkaline media. The ease of sample preparation in combination with high activity suggested that pAuNPs can potentially cause a wide range of practical applications of Au catalysis.

2. Experimental

2.1. Materials

Chloroauric acid was purchased from Shanghai Fine Chemical Co., Ltd. Sodium Citrate and mercuric nitrate were purchased from Sangon Biotech (Shanghai) Co., Ltd. Other reagents are all of analytical purity. Deionized water (18 M Ω -cm) was treated with a water purification system (Simplicity 185, Millipore Corp., Billerica, MA).

2.2. Instruments

CV, linear sweeping voltammetry (LSV) and electrochemical impedance spectra (EIS) measurements were conducted with a Gamry Reference 600 electrochemical workstation (Gamry Instruments, USA). A platinum wire and an Ag/AgCl were used as the counter and reference electrodes, respectively. RDE measurements of the ORR were carried out using an E5RDE electrochemical workstation (Pine Instruments, USA). The surface area of the working electrode was 0.2 cm².

FE-SEM (Hitachi S-4800) and high-resolution TEM (JEM-2100 F, JEOL Co. Ltd., Japan) was used. High resolution valence band XPS measurements were carried out on an ESCALAB 250 (VG Thermo™) high performance electron spectrometer equipped with a monochromated Al K α X-ray radiation (1484.6 eV). The binding energies were measured with an accuracy of ± 0.1 eV and are given with respect to the Au Fermi edge (E_f) assuming $E_f = 0$ eV. The diameters of AuNPs and pAuNPs were characterized at room temperature in a folded capillary cell with a Zetasizer Nano ZS instrument (Malvern Instruments, Southborough, UK). At least four replications were performed for each sample.

2.3. Synthesis of AuNPs

AuNPs were synthesized by using a seed-mediated growth method using AuNPs in diameters of 12 ± 2 nm as the primary seeds [11]. The obtained AuNPs colloidal suspension was centrifuged at 9000 rpm for 10 min at 4 °C. The precipitated AuNPs were re-dispersed in PBS to achieve a concentration of ~ 0.3 mg/mL and stored at 4 °C for later use. The average diameter of obtained AuNPs was ~ 90 nm according to the Dynamic Light Scattering results as well as TEM images.

2.4. Fabrication of pAuNPs

AuNP-loaded glass carbon electrode (AuNP/GC) was prepared by dropping 10 μ L of AuNPs solution onto a glass carbon (GC) electrode surface and dried at room temperature. Then, the AuNP/GC was treated by potential scanning between -0.25 and 1.25 V for 200 cycles (500 mV s⁻¹) in 0.5 M H₂SO₄ solution to clean the surface. Following it, continuous CV scan was conducted in 0.65 mM Hg(NO₃)₂ (in 0.1 M HNO₃) solution to fabricate pAuNPs via alloying and dealloying mercury onto the AuNPs. Later, the pAuNP/GC electrode was in 0.1 M HNO₃ solution for complete removal of residual Hg by CV scan between 0.4 and 1.0 V at a scan rate of 100 mV s⁻¹.

2.5. Preparation of npAuF

All processes for the fabrication of npAuF were carried out in the ZnCl₂/DMSO electrolyte in air [12]. The electrolyte was prepared by dissolving a hydrous ZnCl₂ in DMSO at room temperature with the concentration of ZnCl₂ set at 1.5 M. The organic electrolyte was not deaerated and dewatered in the whole fabrication process. Electrochemical alloying-dealloying on gold electrode was realized by CV in a potential range of 1.4 V to -0.4 V in a three electrode cell, which consisted of a Pt plate as the counter electrode and Zn plate as the reference electrode, respectively. All of the three electrodes were placed in the same cell without a salt-bridge connection. After electrochemical treatment, the gold electrode was taken out and cleaned quickly by DMSO, ethanol, and deionized water in sequence. The npAuF's surface roughness was evaluation as follows. The npAuF was predipped in Ar-saturated 1.0 M H₂SO₄ for 1 h. Then CV was performed within 0.4 – 1.35 V at a scan rate of 100 mV s⁻¹. After integrating the charges corresponding to the reduction of Au oxide (Q_o), the npAuF's surface roughness was calculated with the ratio of Q_o to 400 μ C cm⁻².

3. Results and Discussion

3.1. Fabrication and characterization of pAuNPs

The scheme of the electrochemical fabrication processes for pAuNPs from AuNPs is shown in Fig. 1. AuNP-loaded glass carbon (GC) electrode (AuNP/GC) was prepared by dropping AuNP (100 nm) solution onto a GC electrode surface and subsequent drying at room temperature. Continuous CV scan was conducted in a Hg(NO₃)₂ solution to fabricate pAuNPs through alloying and dealloying mercury onto the AuNPs. Fig. 2A displayed the typical CV responses with the appearance of two pairs of redox current peaks during the fabrication of pAuNPs. The peak pair C₁/A₁

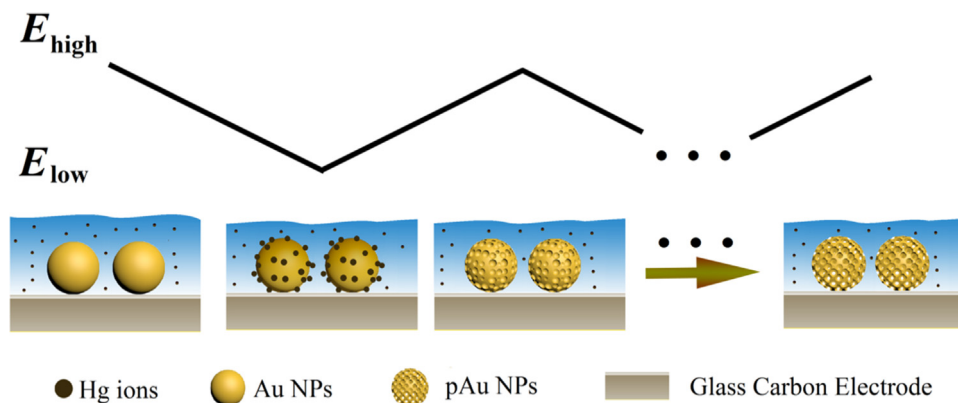


Fig. 1. Scheme of the electrochemical fabrication processes for pAuNPs from AuNPs.

Download English Version:

<https://daneshyari.com/en/article/4767183>

Download Persian Version:

<https://daneshyari.com/article/4767183>

[Daneshyari.com](https://daneshyari.com)