



Effects of heat treatment temperature and atmosphere on electrocatalytic properties of platinum nanocrystals



Xiuxiu Jiang, Tongfei Shen, Haibo Li, Lei Wang, Qiaoli Yue, Jifeng Liu *

Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Department of Chemistry, Liaocheng University, Liaocheng 252059, Shandong, China

ARTICLE INFO

Article history:

Received 21 March 2014
Received in revised form 18 June 2014
Accepted 20 June 2014
Available online 15 July 2014

Keywords:

Platinum nanocrystals
Heat treatment
Atmosphere
Oxygen reduction reaction
Durability

ABSTRACT

Platinum nanocrystals (Pt NCs) have excellent catalytic activity toward oxygen reduction reaction (ORR). The morphology (*e.g.* size, facet, shape) of Pt NCs will change upon heating and the effect of this change in morphology on ORR activities of Pt NCs is unclear. In this work, the effects of heat treatment temperature and atmosphere on ORR activities of catalysts Pt NCs supported on carbon nanotubes were studied. Pt NCs were synthesized *via* a homogeneous aqueous chemical reduction method and then were dispersed and adsorbed onto carbon nanotubes support. It was found that after heat treatment at 300 °C, the Pt NCs have larger active surface areas, higher activity and longer durability toward ORR. And when the heat treatment was conducted in atmosphere of 20% H_2 –80%Ar (by volume), the catalysts had higher ORR activity than that heated in pure Ar gas. This work demonstrated that Pt NCs after heat treatment in a suitable atmosphere will cause a fine tuning of the surface atomic configuration, which determine the activity and long-term durability of Pt NCs catalysts.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The oxygen reduction reaction (ORR) plays an important role in controlling the performance of fuel cells, which directly convert chemical energy into electricity by electrochemical reactions [1,2]. The present technical bottleneck of fuel cells is still the sluggish kinetic of ORR at their cathodes [3,4]. Most of the studies have been devoted into the pursuit of ORR catalysts with high activity and long-term stability. To design highly active Pt electrocatalysts, a strategy is to tune relevant structural parameters and create architectural alternatives to standard, spherical Pt nanoparticles [5]. It has been reported that platinum nanocrystals (Pt NCs) or alloyed truncated octahedral Pt_3Ni and PtNi NCs have excellent catalytic activity toward ORR [6–10].

Pt NCs with cubic-, tetrahedral-, or octahedral-like shapes have been synthesized using a colloidal method [7,11–13]. Usually they present a face-centered cubic (fcc) crystal structure defined as (111), (100), and (110) for the three basal planes [14]. The catalytic properties of a particular material are evaluated from the size or surface composition [15–17]. But the shape-dependency of NCs has been demonstrated to be a crucial factor in ORR [14,18–20]. The low-coordination sites at edges, kinks and defects of Pt NCs play an important role in ORR [21]. Because the low-coordination

sites are easily degraded, the long-term performance of Pt NCs is still far from being optimized. It has been reported that Br^- adsorption/desorption reduced surface roughness of NCs and increased the durability of the catalyst dramatically for ORR [21,22].

For heterogeneous catalysis, both metal and metal support interactions are crucial in determining catalytic properties [23–25], the thermal stability and shape evolution of active metal nanoparticles supported on different substrates at elevated temperatures have been studied [23,26,27]. Polymer was usually used to help synthesize Pt NCs. Capping polymer adsorbed at NCs can be removed through heat treatment, and then expose the active sites for ORR process. However, heat treatment of Pt NCs may result in the facet transformation and tuning of the surface atomic configuration, which will influence the activity and long-term durability of Pt NCs. It has been reported that the core-shell structure of Pt catalysts transformed from a Pt-skeleton surface to smoother multilayered Pt skin surface structure by heat treatment, which exhibited an improvement factor of more than 1 order of magnitude in activity versus conventional Pt catalysts [28]. Heat treatment at 800 °C improved the ORR activity of $PtCo_3$ by 2.4 times compared with the common PtCo alloy catalysts [29]. Because heat condition will change the morphology (*e.g.* size, facet, shape) of Pt NCs, it is interesting to study the relation between the variation of ORR activities with Pt NCs morphology.

In this work, ORR activity of Pt NCs supported on carbon nanotubes (Pt NCs@CNTs) was studied in acidic medium. As one-dimensional carbon material, CNTs with huge specific surface has

* Corresponding author. Tel./fax: +86 635 8239001.

E-mail address: liujifeng111@gmail.com (J. Liu).

recently been used in fuel cells as catalyst supports [30,31]. Here, Pt NCs were synthesized via a homogeneous aqueous chemical reduction method [32] and then dispersed and adsorbed onto CNTs support. Pt NCs@CNTs were heated in tubular quartz furnace under pure Ar or 20% H_2 –80%Ar (V:V) atmosphere. The catalysts were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and electrochemistry. The effects of heat temperature and atmosphere on the ORR activities were studied in acidic solutions. This work presented a new strategy to finely mediate the surface atomic configuration of Pt NCs and may help to design Pt NCs with high catalytic activity and long-term durability for ORR.

2. Experimental section

2.1. Chemicals and apparatus

Dihydrogen hexachloroplatinatate ($H_2PtCl_6 \cdot 6H_2O$, 99.9%) was purchased from Alfa Aesar. Silver nitrate ($AgNO_3$, 99%), poly(vinylpyrrolidone) (PVP, Mw 58,000) and carbon nanotube (SSA > 60 m^2/g , –COOH content 0.73 wt%, Length ~20 μm , OD 30–50 nm, Purity > 95 wt%) were obtained from Sigma–Aldrich. Ethylene glycol (EG) and other solvents were purchased from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in this paper were analytical grade and used without further purification. Water used in this work was prepared from Milli-Q water purification system ($\geq 18 M\Omega$).

TEM or HRTEM images were obtained with a JEM-2010 microscope at an acceleration voltage of 200 kV. Specimens were prepared for TEM by making suspensions of the catalyst powders in H_2O , using an ultrasonic bath. These suspensions were dropped onto carbon-coated copper grid for TEM and HRTEM.

The electronic structures of Pt NCs@CNTs were performed on an ESCLAB MKII (VG Co., United Kingdom). The XPS data were collected with monochromatic Al K radiation. The binding energy scale of the spectra was aligned through the C(1s) peak at 284.6 eV. Peak fit analysis was done using the program XPS PEAK version 4.0.

2.2. Synthesis of Pt nanocrystals and preparation of Pt NCs@CNTs

Pt NCs were prepared from chemical reduction method as previously reported by Yang's group [11]. The obtained Pt NCs suspension was then ultrasonically mixed with CNTs for 20 min and then filtered, washed several times. Finally the precipitation of CNTs support adsorbed with 20 wt% Pt NCs (Pt NCs@CNTs) was dried in vacuum drier for further heat treatment.

3 mg of the obtained Pt NCs @CNTs was put inside a quartz vessel and then was put in a tubular quartz furnace to be heated. Under pure Ar or 20% H_2 –80%Ar stream (flow rate, 100 ml/min), Pt NCs@CNTs was heated from room temperature to different temperatures ranged from 100 to 800 °C (increasing rate, 10 °C/min) and treated at the temperature for 1 h. And then the furnace was cooled to room temperature and the final black product was collected.

2.3. Electrochemical measurements

Electrochemical measurements were conducted in a standard three-compartment electrochemical cell with a Pt wire and a mercury sulfate electrode (Hg/Hg_2SO_4 , MSE) used as the counter and the reference electrodes, respectively. All potentials in this work were given versus MSE. Glassy carbon electrodes (GCE, 3 mm in diameter, Shanghai Chenhua Co.) or commercial rotating Pt

ring-GC disk electrodes (RRDEs, 4 mm in diameter of disk, ALS Co. Ltd., Japan) was used as working electrode with a collection efficiency (N) of 0.49. For RRDEs, ring and disk potential were controlled with a bipotentiostat CHI 832B electrochemical workstation (Shanghai Chenhua Co., China). Typically, the GCE or RRDEs were polished with 0.05 μm Al_2O_3 slurry and washed ultrasonically with ethanol and water separately. An aliquot of 1.0 μL (1 mg mL^{-1}) well-dispersed Pt NCs@CNTs catalyst suspension was dropped onto the GCE disk. After drying, 0.5 μL of 0.5 wt% Nafion (in ethanol) was placed immediately onto the electrode surface to cover the catalyst. Nafion loading was very thin, within the range where the resulting Nafion diffusion limitation was considered to be negligible [33,34]. The electrolyte solution was 0.1 M H_2SO_4 .

The ORR measurements were carried out in the same 0.1 M H_2SO_4 solution. All electrochemical experiments were recorded at room temperature. Cyclic voltammetry (CV) were measured from –0.7 to 0.5 V in air-saturated 0.1 M H_2SO_4 at a scan rate of 50 mV/s. RRDE experiments were conducted in air-saturated 0.1 M H_2SO_4 from –0.5 to 0.5 V at a scan rate of 10 mV/s under different rotating rate.

Accelerated durability testing (ADT) was performed with cycling the potential from –0.7 to 0.5 V at a scan rate of 500 mV/s in air-saturated 0.1 M H_2SO_4 .

3. Results and discussion

3.1. Morphology of Pt NCs@CNTs

TEM and HRTEM of the Pt NCs and Pt NCs@CNTs before or after heat treatment are shown in Fig. 1. Low-magnification images illustrate a highly dispersed and remarkably uniform cubic Pt NCs. The HRTEM images show that the obtained samples mainly contain (200) and (111) facets, which agree with the interplanar lattice of 0.196 nm and 0.226 nm (Fig. 1A and B). It has been reported that the shape of Pt nanoparticle changed up to 300 °C, surface diffusion or surface premelting took place and the particle shapes experienced a dramatic transformation into spherical-like shapes as the temperature was raised above 400 °C. Surface melting and coalescence of neighboring particles occurred as the annealing temperature above 600 °C [26].

For Pt NCs prepared at room temperature, the size distribution was uniform and the mean size was about 6.2 nm for Pt NCs. TEM analysis indicated that both the shape and the particle size of the NCs changed after heat treatment. Standard ruler was used in the iTEM software to measure the nanoparticles' sizes. About 100 nanoparticles were chosen to calculate average size. The decreased size of Pt NCs from 6.2 nm to 5.8 nm may result from the removal of the capping polymer when heating temperature was ranged from room temperature to 300 °C (Pt NCs@CNT₃₀₀, Fig. 1B–E, Table 1), which means that Pt NCs will be able to move along CNT surface and aggregate during heat treatment process. However, the size of Pt NCs increased from 8.84 nm to larger size as Pt NCs@CNTs was heated above 400 °C (Fig. 1F–H, Table 1). The interface between NCs disappeared partially after heating at 400 °C and then resulted in the aggregation. The size variation of Pt NCs was summarized in Table 1 for catalysts heated at different temperatures.

When Pt NCs@CNTs was heated above 300 °C, the cubic shape of Pt NCs also changed (Fig. 1E and F). Pt NCs aggregated to form larger particles and the dominate facets was not easily observed via TEM when Pt NCs@CNTs was heated above 400 °C, especially at 800 °C (Fig. 1G and H). Because the aggregation of Pt atoms on the surface can be activated by thermal energy, NCs usually become more spherical-like at high temperatures to lower the surface energy due to the atom rearrangement on the NCs surface [35]. Fig. 1I shows the same catalysts heated at 300 °C under pure

Download English Version:

<https://daneshyari.com/en/article/218701>

Download Persian Version:

<https://daneshyari.com/article/218701>

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