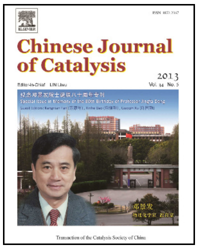
Chinese Journal of Catalysis 34 (2013) 942–948

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc



Article (Special Issue in Memory of the 80th Birthday of Professor Jingfa Deng)

# Nano-size effect of Au catalyst for electrochemical reduction of oxygen in alkaline electrolyte

ZHANG Gui-Rong, XU Bo-Qing *

*Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China*

ARTICLE INFO

*Article history:*
Received 11 January 2013
Accepted 15 February 2013
Published 20 May 2013

*Keywords:*
Au nanoparticle
Size effect
Oxygen reduction reaction
Surface electronic structure
Alkaline electrolyte

ABSTRACT

Oxygen reduction reaction (ORR) in alkaline electrolyte (0.5 mol/L KOH) was studied on a series of carbon supported Au nanoparticles (NPs) with average sizes ranging from 3 to 14 nm, using the rotating disk electrode methods. Downsizing the Au NPs from 14 to 3 nm resulted in continued enhancement in both the intrinsic and mass-specific activity of Au for ORR but produced no influence on the reaction mechanism or number of transferred electrons per $O_2$-reduction. Careful analyses of the particle shapes of Au NPs with varied sizes by using high-resolution transmission electron microscopy enabled us to estimate the fraction of surface Au atoms at different positions or coordination (energy) state. Correlating the fraction of high energy surface atoms with the Au activity for ORR disclosed the importance of high energy surface atoms in enhancing the intrinsic activity of Au. Fundamental correlation between the Au intrinsic activity for ORR and the experimentally determined surface electronic structure of Au NPs was also established.

## 1. Introduction

The electrochemical reduction of oxygen (oxygen reduction reaction, ORR) is a reaction of tremendous interest both for basic and applied research [1–5]. It constitutes the cathode reaction in polymer electrolyte membrane fuel cells as well as in chlorine electrolysis using oxygen depolarized cathodes, and is of importance to the corrosion phenomena [1–3]. Gold was found reasonably active for ORR in alkaline electrolyte [6–9]. The use of Au nanoparticles (NPs) for ORR has attracted increasing attention in recent years due to their distinctly different catalytic properties from bulk Au [8,10–15]. One of the intensively debated issues in this field is concerned with the size-dependent catalytic activity of Au NPs for ORR, especially when the size or diameter of Au NPs is reduced to the sub-10 nanometer region where the Au NPs are theoretically predicted to have enhanced electron density near the Fermi level, narrowed d-band and higher-lying d-band center energy relative to bulk Au [16–18]. Besides, the coordination state of surface atoms and the fractions of surface atoms at different locations (corners, edges, (111) and (100) facets) would also change with the Au particle sizes [16]. As ORR features a strongly structure-sensitive chemistry, uncovering how the size-dependent surface electronic/geometric structure of Au could affect its catalysis towards ORR would have significant implications not only for better understanding the size effect of Au in electrocatalysis but also for the design and optimization of new cathode catalysts.

Previous studies on electrocatalysis of Au NPs for ORR in alkaline electrolyte were documented with inconsistent obser-

---

* Corresponding author. Tel: +86-10-62792122; Fax: +86-10-62771149; E-mail: bqxu@mail.tsinghua.edu.cn

This work was supported by the National Natural Science Foundation of China (21033004) and the National Basic Research Program of China (2013CB933103).

DOI: 10.1016/S1872-2067(12)60546-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 5, May 2013

vations on the Au nanosize effect [8,11,12,19]. Smaller Au NPs showed higher activity for ORR in Refs. [8] and [11] but were found less active in Refs. [12] and [19]. In these previous reports, Au NPs with varied sizes were synthesized via colloidal methods by varying the nature and/or dosage of the stabilizer molecules. The variations in the stabilizers (nature and dosage) could heavily distort the size-dependent catalytic behavior of Au NPs [20,21]. We also showed earlier that a change in the nature of the stabilizer molecules could cause an influence that even significantly outweighs the Au nano-size effect in electrocatalysis [15]. The discrepancy in previous literature on the size-dependent activity of Au NPs for ORR may therefore arise from an ignored effect of the stabilizers involved in the colloidal synthesis of the Au NPs. To better address the size-dependent catalytic activity of Au NPs, it would be essential to prepare differently sized Au NPs without varying the nature of the stabilizer molecules.

This work aims to clarify how the catalytic activity of Au NPs for ORR would change with variations in their particle size and surface structure by carefully measuring the Au NPs using transmission electron microscopy/high-resolution transmission electron microscopy (TEM/HRTEM) and valence band X-ray photoelectron spectroscopy (XPS). We report the size effect on the electrocatalytic properties of nearly monodisperse Au NPs, with the data obtained on a series of Au NP samples whose average sizes range from 3.4 to 14.0 nm. Our samples of Au NPs were synthesized by using polyvinylpyrrolidone (PVP) as the only stabilizer in order to exclude possible interferences from using different stabilizers. We show that smaller Au NPs are intrinsically more active for ORR in alkaline electrolyte. Moreover, for the first time, we disclose that Au activity for ORR correlates well with the experimentally determined surface electronic structure (d-band center energy).

## 2. Experimental

### 2.1. Synthesis of Au-d and carbon supported Au-d (Au-d/C) samples

Nearly monodisperse Au-*d* (*d* = 3.2–14.0 nm, which denotes the average particle diameter) NPs were synthesized by using a seed-mediated growth method using Au NPs in diameters of 1.9 ± 0.4 nm as the primary seeds, as documented previously [22,23]. Au-*d*/C samples were prepared by mixing a desired amount of Vulcan XC-72 carbon black (BET surface area: 240 $m^2/g$, Cabot Company) with as-synthesized Au-*d* hydrosols, followed by a careful adjustment of solution acidity to pH = 1.5 with 1 mol/L $HNO_3$ solution. The suspension was then refluxed for 2 h under vigorous stirring. The solid was separated by filtration, followed by intensively washing with deionized water and air-drying at 110 °C for 2 h to give Au-*d*/C samples.

### 2.2. Structural analysis

TEM images were captured using a JEOL JEM-2010 microscope operated at 120 kV. HRTEM images were obtained on a FEI Tecnai G2 F20 U-TWIN microscope at 200 kV accelerating voltage. The samples were prepared by placing a drop of catalyst powder in deionized water on a Formvar/carbon film coated Cu grid (3 mm, 300 mesh), followed by drying under ambient conditions. High resolution valence band XPS measurements were carried out on an ESCALAB 250 (VG Thermo™) high performance electron spectrometer equipped with a monochromated Al $K_\alpha$ 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 loading amount of Au was set at 5 wt% for all Au-*d*/C samples and was later determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS Intrepid II XSP, ThermoFisher).

### 2.3. Electrochemical characterization

Electrochemical measurements were performed on a potentiostat/galvanostat model 263A (PAR) controlled by PowerSuite software [24–26]. A saturated calomel electrode (SCE) and a Pt wire (diameter: 0.5 mm) were used as the reference and counter electrodes, respectively. All potentials reported in this work are given with respect to SCE. Unless otherwise specified, the ORR measurements were performed in $O_2$-saturated 0.5 mol/L KOH (Au-*d*/C) electrolyte using a glassy carbon rotating disk electrode (GC-RDE, 0.196 $cm^2$, Pine Research Instrumentation) at a rotation rate of 1600 r/min. The linear sweeping voltammetry (LSV) measurement was conducted at room temperature at a scanning rate of 10 mV/s. Before the preparation of the working electrode, the GC-RDE was polished to a mirror finish using 0.5 and 0.05 μm alumina powder. A catalyst ink was prepared by sonicating a suspension of the catalyst (5.0 mg) in isopropanol (1.0 ml), and then 10 μl of the suspension was transferred onto the GC-RDE electrode. After solvent evaporation, 10 μl of Nafion solution (0.05 wt%, DuPont Company) was cast on the disk to attach the catalyst. Prior to each measurement, the electrolyte was purged by bubbling with high purity nitrogen or oxygen for 15 min. A gentle nitrogen or oxygen flow was then kept to avoid disturbance from ambient atmosphere during the measurement.

The kinetic current was used to compare the catalytic activity of the Au-*d*/C catalysts, which was obtained according to the Koutecky-Levich (K-L) equation [27]. The mass-transport corrected kinetic current ($i_k$) was calculated based on the equation $i_k = i \times i_d/(i_d - i)$, where $i$ is the experimentally measured current, and $i_d$ is the diffusion-limiting current.

To compare the size-dependent catalytic activity of Au-*d*/C catalysts, the kinetic currents were normalized according to both the Au loadings to obtain the mass-specific activity (MSA) and the electrochemically active Au surface areas (EAS) to measure the intrinsic activity (IA). The electrochemically active Au surface areas were determined by using the method of Trasatti and Petrii [28].

## 3. Results and discussion

Six samples of nearly monodisperse Au NPs, 1.9 ± 0.4, 3.2 ± 0.5, 4.7 ± 0.7, 8.0 ± 1.3, 10.3 ± 0.8, and 14.0 ± 1.9 nm, were syn-