



# Activity and stability of supported gold nano- and submicro-particles toward the electrocatalytic oxidation of carbon monoxide



Dafeng Zhang<sup>a,b</sup>, Peng Diao<sup>a,\*</sup>

<sup>a</sup> Department of Materials Chemistry, School of Materials Science and Engineering, Beihang University, Beijing 100191, China

<sup>b</sup> Department of Chemistry, Henan Polytechnic University, Jiaozuo 454000, China

## ARTICLE INFO

### Article history:

Received 9 May 2013

Received in revised form 30 August 2013

Accepted 21 September 2013

Available online 30 September 2013

### Keywords:

Gold particles

CO oxidation

Electrocatalysis

Electrocatalytic activity and stability

## ABSTRACT

Gold nano- and submicro-particles were prepared on indium tin oxide (ITO) substrate by methods of sputtering deposition (SD), self-assembly (SA) and electrochemical deposition (ECD). The electrocatalytic activity of these gold particles toward CO oxidation was systematically studied using cyclic voltammetric (CV) technique. It was found that the method used to prepare gold catalysts had great effect on their catalytic activity and stability for CO electrooxidation. Electrodeposited Au particles exhibited a higher activity and better stability than particles prepared by SD and SA methods. The distinct activity and stability of gold particles prepared by ECD was believed to be due to the strong “support effect” arising from the intense interaction between gold particles and the substrate. An electrochemical dissolution process of gold was revealed on all kinds of gold particles after long-term CO electrooxidation. The dissolution of Au in alkaline solution was proposed as the primary origin for the deactivation of gold catalysts.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The extraordinary catalytic activity of gold nanoparticles (AuNPs) dispersed on metal oxide supports has attracted great interest and been extensively studied over the past two decades [1–12]. In both the solid–gas reaction systems [1–9] and the electrochemical systems [10–15], the highly dispersed gold catalysts exhibit high catalytic activity toward a number of reactions, among which the oxidation of CO at the low temperatures has generated the most interest due to its theoretical and practical significance [1–3,7–12]. The high catalytic activity of AuNPs toward CO oxidation provides an efficient strategy to selectively eliminate CO and its related species [16–18]. In the field of fuel cells, this means that the supported AuNPs may serve as a potential candidate to prevent the anodic catalysts from being poisoned, since the poisoning of platinum metals by CO during anodic oxidation of fuels is one of crucial problems in the development of low temperature fuel cells [19]. The electrocatalytic activity of AuNPs supported by metal oxides has been less intensively investigated [10–12,20–22], in spite that the ability of bulk gold to oxidize CO at high positive potentials has been known for many years in electrochemistry [23–28]. Recent work from McFarland and co-workers [11,21] and our group [12] demonstrated that the supported AuNPs also possessed a size- and support-dependent catalytic activity toward

electrooxidation of CO, providing direct evidence that the inherent electrocatalytic activity of supported AuNPs is greatly different from that of bulk gold. A large CO oxidation current was detected on AuNPs electrodes in the positive potential sweep during CV measurements [11,12]. Besides, in the negative potential sweep, both groups also found a complete replacement of the reduction peak of gold oxides by an AuNP-catalyzed new CO oxidation peak [11,12]. This oxidation peak current greatly depended on the particle size and the nature of the support [12,21]. The smaller the particle size, the higher the catalytic activity of supported gold particles. Recently, we have further demonstrated that the perimeters of the gold-support interface, where the CO-containing solution can contact both the AuNPs and the ITO substrate, are the primary active sites for the gold catalyzed electrooxidation of CO [20]. We also demonstrated that the high activity of AuNPs made them a good candidate for the development of CO electrochemical sensor with wide detection concentration range [29].

The size of AuNPs and the nature of the supports have been confirmed as two crucial factors controlling the catalytic activity of supported AuNPs in solid–gas systems [1,2,5,7,30]. Therefore, to produce highly active AuNPs, it is highly desirable to both decrease the particle size and strengthen the particle-support interaction in one simple preparation method. What's more, creating a stronger interaction may bring more profits in electrochemical systems, as the strong particle-support interaction not only enhances the support effect but also benefits the electronic contact between the particles and the support, and then greatly promotes the electron transfer between the electrode and reactants in solution.

\* Corresponding author. Tel.: +86 10 82339562.

E-mail addresses: [pdiao@buaa.edu.cn](mailto:pdiao@buaa.edu.cn), [pdiao@126.com](mailto:pdiao@126.com) (P. Diao).

Compared with studies on the activity, the catalytic stability of gold particles has not caught much attention [4,18,31–35] though the stability is another key issue for their commercial applications. In fact, the surprisingly high initial catalytic activity is ready to lose during catalytic reaction [4,18,31–35], which serves as the main reason for their rare use in commerce. The deactivation reported was primarily caused by the agglomerating of gold particles [4,31,32] and the loss of catalytic active sites [18,32–35]. The small particles, which are highly active but weakly anchored on the support, prefer moving on the surface to produce large particles with poor activity in reaction. The loss of active sites was suggested arising from the adsorption of some carbonate intermediates on them [18,32–35]. All of these findings are obtained in the solid–gas reaction system, whereas in electrochemical system, no work has been reported on the catalytic stability of gold particles during electrochemical oxidation of CO in solution. As the reaction condition in electrochemical system is quite different from those in solid–gas system, for example the applied potential and the aqueous solution, the catalytic behavior should vary in a different way. The purpose of this work is to clarify the influence of preparation methods on the catalytic activity and stability of gold particles toward CO electrooxidation, and the origin of the deactivation in the electrochemical system.

## 2. Materials and methods

### 2.1. Sputtering deposition (SD) of gold nanoparticles on ITO substrates

The indium tin oxides (ITO) film coated glass slides were employed as the substrates for the deposition of all three different gold particles to minimize the influence of the nature of support. Before use, the ITO substrates were successively sonicated in acetone, water, and methanol, and then dried with high purity N<sub>2</sub>. The sputtering deposition of AuNPs was performed on a traditional sputter-coater (SBC-12, Beijing KYKY Co., China) on the ITO substrates. Previous reports showed that while controlling the sputtering procedure in a short time, most of the produced particles were still isolated on the surface. In the experiment, 2.0 ± 0.5 nm AuNPs in diameter have been deposited on ITO substrates by shortening the sputtering time to 2 s. The average size of the particles was determined by transmission electron microscopy (TEM). The samples, prepared by SD method, were referred as AuNPs(SD)/ITO in this work.

### 2.2. Self-assembly (SA) of citrate-capped gold nanoparticles on ITO substrates

The citrate-capped gold nanoparticles colloids were prepared by Frens method [36]. Briefly, 3.5 mL of 1 wt% aqueous solution of sodium citrate was added into a boiling HAuCl<sub>4</sub> aqueous solution (100 mL, 2.4 × 10<sup>-4</sup> M) under vigorous stirring. The average diameter of particles, determined by TEM, was 13 ± 1.0 nm. The cleaned ITO substrates were immersed in a 5 mM 1,12-dodecanediamine (DDA) solution of absolute methanol for 48 h to form a DDA monolayer on the surface [12]. The resulting DDA-coated ITO substrates were rinsed with copious absolute methanol and water, respectively, and then dried in a stream of high-purity N<sub>2</sub>. The assembly of AuNPs on ITO substrates was carried out by immersing the DDA-coated ITO substrates in the gold colloids for 12 h. The pH value of gold colloids was adjusted to 3.8–4.0 to ensure that the amino groups of DDA were protonated and positively charged. The strong electrostatic interaction between the positively charged DDA monolayer and the negatively charged AuNPs will lead to the

immobilization of AuNPs on ITO substrates. The samples, prepared by SA method, were referred as AuNPs(SA)/ITO in this work.

### 2.3. Electrochemical deposition (ECD) of gold submicro-particles (AuSMPs) on ITO substrates

The carefully cleaned ITO substrates were used as the working electrode in the procedure of the electrochemical deposition of AuSMPs. The deposition was carried out at 0 V (vs. SCE) in 10<sup>-4</sup> M HAuCl<sub>4</sub> solution with 1 M KCl as the supporting electrolyte. The size of the AuSMPs can be controlled by varying the electrodeposition time. Herein, the deposition time, 15 s and 300 s, were selected. The samples, prepared by ECD method, were referred as AuSMPs(ECD)/ITO in this work.

The morphologies and size distribution of AuNPs and AuSMPs were characterized using SEM (Philips FEI XL30 SFEG) and TEM (JEOL JEM-2100F). The atomic absorption spectroscopic measurements were performed on an AAS8000 atomic absorption spectrometer (Skyray Instrument Co.).

### 2.4. Electrocatalytic oxidation of CO

The electrocatalytic activity and stability of gold particles were investigated in a CO saturated 0.5 M KOH solution by CV technique within a potential range of -0.4 V to 0.7 V (vs. SCE) under a scan rate of 100 mV s<sup>-1</sup>. Before electrochemical measurements, the KOH solution was deoxygenated with high-purity N<sub>2</sub> for at least 25 min. Three cycles of CV potential sweep (from -0.4 V to 0.7 V) was first performed for each sample in this CO absent solution. The first cycle was to activate gold particles, and the followed two stable cycles were used to obtain the total active surfaces areas of particles. The deaerated solution was then saturated with CO for 45 min for the CO oxidation measurements. Two different CO bubbling procedures were adopted for the purpose of evaluating the catalytic stability of gold catalysts. The first one was a continuous bubbling to maintain a saturation of CO in solution, and the second one was a cyclic alternating bubbling procedure during which CO and N<sub>2</sub> were alternately introduced into the solution. Because of the high toxic nature of CO, all electrocatalytic oxidation measurements were carried out in a gas-sealed box with an inlet gas tube reaching to the bottom of the electrochemical cell.

All of the electrochemical experiments mentioned above were performed on a CHI 660A electrochemical workstation (CH Instruments, USA) using a conventional three-electrode cell at room temperature. A saturated calomel electrode (SCE) and a platinum foil were used as reference and counter electrodes, respectively. All potentials are reported with respect to SCE.

## 3. Results and discussion

### 3.1. Electrocatalytic activity of gold particles prepared by different methods

As an active support for gold particles, the ITO substrate itself was inert for the CO oxidation [12,20]. The particles prepared on ITO substrates by different methods usually varied in morphology, surface structure, and especially the particle-support interaction, thus exhibiting different catalytic activity and stability for CO electrooxidation. Fig. 1a–c show the SEM micrographs of gold particles deposited on ITO substrates prepared by SD, SA, and ECD methods, respectively. Clearly, all gold particles were dispersed uniformly on ITO surface, but differ largely in both diameter and surface density. From the higher magnification inset images in Fig. 1 and the statistic results shown in Table 1, we found the particles deposited on ITO by SD, SA

Download English Version:

<https://daneshyari.com/en/article/40151>

Download Persian Version:

<https://daneshyari.com/article/40151>

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