Codeposition of AuPd bimetallic nanoparticles on to ITO and their electrocatalytic properties for ethanol oxidation

Jing Tang,*, Xiao-Chun Tian, Wen-Hui Pang, Yue-Qiang Liu, Jian-Hang Lin

A R T I C L E   I N F O

Article history:
Received 24 May 2012
Received in revised form 12 July 2012
Accepted 13 July 2012
Available online 20 July 2012

Keywords:
Bimetallic nanoparticles
ITO
Electrocatalysis
Ethanol
Electrodeposition

A B S T R A C T

Gold–palladium nanoparticles (AuPd NPs) were prepared on an indium tin oxide (ITO) surface by poten-
tiostatic electrodeposition from a mixture of two metal salts. The bulk compositions of the prepared
AuPd NPs were studied by means of energy-dispersive X-ray analysis (EDX) and X-ray diffraction (XRD).
The electrochemical behavior of the AuPd NPs in the sulfuric acid showed that the atomic ratio between
Au and Pd could be adjusted by the composition of electrolyte and the applied potential. Field emission
scanning electron microscopy (FE-SEM) images of the electrodeposits show that the morphology of the
AuPd NPs was affected by the electrochemical deposition potential and deposition period. In addition,
the AuPd NPs displayed good electro-catalytic activity for ethanol electro-oxidation in alkaline solution.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Bimetallic nanoparticles (NPs) have been used as catalysts in chemical industry. It has been shown that the catalytic activity and selectivity of metals could be enhanced by the synergetic effect of bimetallic electrocatalysts [1–4]. In recent years, research into gold–palladium NPs has attracted considerable attention due to their special catalytic activities for several reactions including CO oxidation at low temperature [5,6], hydrogen electro-sorption [7,8], the growth of ZnO nanowires [9] and the oxidation of alcohols [10,11] and carboxylic acids [12]. For many applications, it is desirable to fabricate supported bimetallic NPs for heterogeneous catalysis. In particular, the catalytic oxidation of ethanol has been the topic of numerous research papers, since ethanol is a more attractive fuel for low-temperature fuel cells and it is much less toxic than methanol [13–16]. Moreover, ethanol can be produced in large quantities from agricultural products or biomass. The recent researches demonstrated that the anodic oxidation of ethanol in alkaline media becomes faster than acidic media, which makes it possible to use Pd and Pd-based catalysts as an alternative to Pt-based catalysts for the alcohol oxidation reaction [17–19].

The traditional synthetic techniques typically involve depositing metal precursors onto high surface area supports followed by thermal activation treatments [11,20] and entrapping presynthesized NPs into inorganic matrix by the sol–gel method [21]. The former method has a poor control over the composition and structures of NPs and the NPs prepared by the latter one often coalesced with each other after removing the stabilizer by calcination. Among the methods of alloy preparation, the direct electrochemical codeposition from a mixture of several metal salts is an interesting route which has been investigated by other groups [12,22,23]. This offers great advantages due to the possibility of controlling the process in a simple way [24]. In the deposition process, it is easy to adjust the composition of two metals by varying the electrolysis conditions, for instance the electrolyte composition, current density and applied potential [25]. For electrodeposition, a conductive solid support is necessary. ITO has been employed as a cheap substitute for traditional electrode (e.g. the gold electrode and the glassy carbon electrode), since it has a very low background current and large electrochemical potential window [23]. Moreover, it has been used as an ideal substrate for electrocatalytic research into nanoparticles due to its rather high chemical and thermal stability. For example, a modified ITO electrode with binary metallic NPs has been extensively used for the electro-catalytic oxidation of glucose [26] even though ITO has no catalytic activity for this reaction.

In this report, the direct electrochemical deposition is controlled at a certain potential, therefore the potentiostatic deposition was used as a powerful tool to modify the ITO with AuPd metallic NPs. By changing the composition of the electrolyte, the deposition potential and the deposition time, the morphology and the...
bulk composition of deposits have been varied and studied. The size and morphology of the AuPd NPs were characterized by FE-SEM images, and their bulk composition and structure were also studied by means of energy-dispersive X-ray analysis (EDX) and X-ray diffraction (XRD), respectively. The electrochemical behavior of the ITO electrode modified with AuPd NPs was investigated by using cyclic voltammetry in sulfuric acid and the preliminary studies of the catalytic activity for ethanol oxidation in alkaline solution carried out.

2. Experimental

Chlorauric acid tetrahydrate (HAuCl₄·4H₂O) and palladium chloride (PdCl₂) were purchased from Sinopharm Chemical Reagent Co., Ltd. ITO (1.1 mm thickness, less than 30 Ω·cm⁻¹) was obtained from Xiamen ITO Photoelectricity Ind. Co., Ltd. (Xiamen, China). All other chemicals in this study are of analytical grade. Ultrapure water was used throughout. All electrochemical measurements were carried out with a CHI614D or CHB842B electrochemistry workstation (Shanghai Chenhua Apparatus Corporation, China) with a standard three-electrode cell. A saturated calomel electrode (SCE) and a Pt slice were used as the reference electrode and auxiliary electrode, respectively. ITO (about 1 cm × 1 cm) was ultrasonically cleaned with acetone, alcohol, ultrapure water in sequence then used as the working electrode. The sample solutions were purged with high-purity nitrogen for at least 10 min to remove oxygen prior to starting a series of experiments.

The electrolyte consisted of chlorauric acid and chloropalladate acid, and 0.1 mol L⁻¹ KCl was selected as the supporting electrolyte. Chloropalladate acid was prepared by heating a mixture of palladium chloride and hydrochloric acid (PdCl₄^2⁻ : HCl = 1 : 2). According to the cyclic voltammetric curves, the appropriate deposition potential was determined. The electrochemical deposition at a certain potential was used to deposit the AuPd NPs on to ITO. A series of values of potential and time of deposition were chosen to investigate the morphology and composition of the AuPd NPs. Three kinds of electrolyte containing mixed salts were employed in the experiments. The simplified forms were shown as follows. 0.75 mM HAuCl₄ + 0.25 mM H₂PdCl₄ + 0.1 M KCl (C(HAuCl₄) : C(H₂PdCl₄) : C(KCl) = 3 : 1) is simplified as Au₄Pd₁, 0.5 mM HAuCl₄ + 0.5 mM H₂PdCl₄ + 0.1 M KCl (C(HAuCl₄) : C(H₂PdCl₄) = 1 : 1) as Au₃Pd₂ and 0.25 mM HAuCl₄ + 0.75 mM H₂PdCl₄ + 0.1 M KCl (C(HAuCl₄) : C(H₂PdCl₄) = 1 : 1) as Au₅Pd₃. Furthermore, the simplified forms Au₄ and Pd₃ stand for the solution of 1 mM HAuCl₄ + 0.1 M KCl and 1 mM H₂PdCl₄ + 0.1 M KCl, respectively.

Then cyclic voltammograms of AuPd NPs/ITO in 0.5 mol L⁻¹ H₂SO₄ were used to confirm the composition of electrodeposits. The size and morphology of the synthesized particles on the ITO substrate were observed by using a field emission scanning electron microscope (FE-SEM, NOVA NANO SEM230), and the composition and structure of the nanoparticles were analyzed by energy-dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). The X-ray diffraction (XRD) patterns of the AuPd NPs on ITO were obtained with a Philips powder diffraction system X’Pert Pro MPD (Holland) using Cu Kα radiation with a 2θ step size of 0.02° over the range of 10°–90°. The accelerating voltage was set at 40 kV.

The AuPd NPs/ITO obtained were used for the electrocatalytic oxidation of ethanol in alkaline solution.

3. Results and discussion

3.1. Electrochemical deposition of AuPd NPs onto ITO

The mechanism of the deposition of AuPd NPs on to the ITO electrode surface was studied by cyclic voltammetry in the electrolyte with different concentrations of HAuCl₄ and H₂PdCl₄. When the potential was scanned negatively Au and Pd did not deposit simultaneously [23]. The standard redox potentials (E°) of AuCl₄⁻ → Au and PdCl₄²⁻ → Pd are 0.99 V and 0.64 V, respectively which are relative to the normal hydrogen electrode (NHE). Thus, AuCl₄⁻ tends to be reduced at more positive potential than PdCl₄²⁻. Therefore, the first reduction peak in the three curves (a)–(c) of Fig. 1 corresponds to the reduction of gold, and the second one at more negative potential corresponds to the reduction of palladium. When the concentration of HAuCl₄ was increased from 0.25 mM (curve a) to 0.75 mM (curve b), the peak corresponding to the reduction of AuCl₄⁻ increased, hence the peak potential of Pd deposition is moving positively despite the decrease in the concentration of H₂PdCl₄. This can be explained by the easier nucleation of Pd on Au than on the ITO substrate [27,28].

3.2. The bulk structure composition characterized by XRD and EDX

To determine whether the bimetallic NPs are aggregated metal particles or consist of an alloy of the two metals, XRD analysis of AuPd NPs with different compositions was performed [17,22]. XRD is used as a strong method to investigate the solid structure of metal nanoparticles and the presence of the alloy particles rather than the physical mixtures can be demonstrated. In Fig. 2 curve (a) of the XRD pattern of the pure Au NPs/ITO showed that an overwhelmingly intense diffraction peak was located at 44.7° in the samples, which corresponds to the (1 1 1) lattice plane of the gold. In addition, curve (c) shows the X-ray powder diffraction pattern of pure Pd NPs on ITO. The peak at 47.1° corresponds to the (1 1 1) lattice plane of the palladium.

Curves (b)–(d) show the XRD patterns for various compositions of AuPd NPs, and only one diffraction peak could be observed for each lattice plane of AuPd NPs. For the AuPd NPs obtained from the different electrolytes, both the intensity and position of the Bragg peaks (1 1 1) (2 0 0) (2 2 0) changed, and the peaks were located far from those of pure Au and pure Pd NPs. In contrary, the diffraction pattern of the physical mixtures consists of overlapping lines of the two individual monometallic nanoparticles. Here, these results as shown in Fig. 2 indicated that the AuPd NPs were alloys rather than a mixture of mono–metallic or core–shelled nanoparticles [23]. Peaks with an asterisk were from the diffraction of ITO and the position of these peaks did not shift for different AuPd NPs.
Table 1
The area of AuPd NPs and pure metals on ITO was deposited in different solution at the potential of −0.2 V for 600 s.

<table>
<thead>
<tr>
<th>Deposition solution</th>
<th>The atomic compositions of Pd (EDX)</th>
<th>The atomic compositions of Pd (XRD)</th>
<th>Charge of surface oxide reduction of Au (×10−4 C)</th>
<th>Area of Au (cm²)</th>
<th>Charge of surface oxide reduction of Pd (×10−4 C)</th>
<th>Area of Pd (cm²)</th>
<th>Total area of cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₁</td>
<td>100%</td>
<td>100%</td>
<td>0</td>
<td>0</td>
<td>202.2</td>
<td>4.8143</td>
<td>4.81</td>
</tr>
<tr>
<td>Auᵢ₋₃Pd₃</td>
<td>60.7%</td>
<td>69.2%</td>
<td>3.533</td>
<td>0.9059</td>
<td>126.5</td>
<td>3.0119</td>
<td>3.92</td>
</tr>
<tr>
<td>Auᵢ₋₃Pd₁</td>
<td>32.6%</td>
<td>46.3%</td>
<td>8.524</td>
<td>2.1856</td>
<td>11.15</td>
<td>0.2655</td>
<td>2.45</td>
</tr>
<tr>
<td>Auᵢ₋₃Pd₁</td>
<td>16.1%</td>
<td>23.1%</td>
<td>4.102</td>
<td>1.0564</td>
<td>2.299</td>
<td>0.0547</td>
<td>1.11</td>
</tr>
<tr>
<td>Au₁</td>
<td>0%</td>
<td>0%</td>
<td>1.867</td>
<td>0.4787</td>
<td>0</td>
<td>0</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Concerning the bulk composition of Pd and Au in the alloyed NPs, the EDX also proved to be a useful tool. The EDX spectra (seen in Supporting information Figs. S1 and S2) demonstrates that the atomic percentage of Au in the bimetallic particles is 70.1%, 69.8%, 67.4% and 65.6%, when the deposition potential is negatively shifting from 0.2 V to −0.4 V in the solution of Auᵢ₋₃Pd₁. The decrease of Au atomic percentage occurs because the negative shift of the deposition potential resulted in the increase of Pd deposition. In comparison with the influence of deposition potential, the concentration of the electrolyte had a much bigger influence on the composition. For example, when the deposition electrolytes were Auᵢ₋₃Pd₁, Auᵢ₋₃Pd₁ and Auᵢ₋₃Pd₃ separately and the deposition potential was set at the same potential −0.2 V for 600 s, the atomic composition of Pd in AuPd NPs was significantly different with values 16.1%, 32.6% and 60.7%, respectively. Therefore, higher concentrations of Pd ions can lead to Pd rich alloy NPs and higher concentrations of Au ions can make Au rich NPs. In our experiments, all the NPs measured using EDX were measured again by XRD, and the Pd content was calculated according to Vegard’s law [29,30]. Although the different values obtained from the EDX and XRD, the trend is the same as shown in Table 1. For example, when the values for Pd in AuPd NPs were 16.1%, 32.6% and 60.7% measured from EDX, the corresponding values calculated from the XRD spectra are 23.1%, 46.3% and 69.2%.

3.3. The morphology and bulk composition of AuPd bimetallic nanoparticles deposited on ITO

Following the voltammetric profiles, the following deposition potentials in the solution of Auᵢ₋₃Pd₃ were examined: 0.2 V (diffusion controlled reduction potential of AuCl₄⁻), 0 V (onset of PdCl₂− deposition), −0.2 V and −0.4 V (diffusion controlled reduction of PdCl₂−). Fig. 3 shows FE-SEM images of AuPd NPs deposited on the ITO electrodes. The deposition potential was held at the above mentioned potentials for 10 s. The formation of large particles was observed, yielding a sparse coverage of NPs on the substrate at 0.2 V. The average size of NPs was determined by the controlled potential in the potentiostatic deposition; this decreased from 400 nm at 0.2 V to 17 nm at −0.4 V (Fig. 3(d)). Moreover, when the deposition potential was moving negatively, the density of the small particles increased simultaneously [31]. It was noteworthy that when the potential was controlled at −0.2 V, two different sized particles was observed, as shown in Fig. 3(c). The average diameter of the larger particles was around 41 nm, while that of the smaller particles was around 15 nm. Since the cyclic voltammetric curves in Fig. 1(b) showed the growth of Pd on the substrate has begun at −0.2 V, the larger NPs might arise from the growth of metal alloy on an Au rich nucleus, while the smaller ones might be new nuclei forming on the ITO. When the deposition time at −0.2 V was prolonged to 60 s, as shown in Fig. 3(e) and 600 s, as in Fig. 3(f), the two different sized particles could still be observed on the ITO. However, when the potential was moved to −0.4 V for 10 s, as shown in Fig. 3(d), the AuPd NPs showed a much more uniform distribution of size, at around 20 nm, which might result from the co-deposition of two metals from the mixed metal salts at a large over-potential. A similar morphology for AuPd NPs was observed when the electrolyte was changed to Auᵢ₋₃Pd₁, as displayed in Fig. 4. However, the average size of the NPs in Fig. 4(a) is 28 nm, which is two times larger than the particles in Fig. 3(c) due to a higher concentration of H₂PdCl₄.

3.4. The electrochemical behavior of AuPd NPs in H₂SO₄

The voltammogram is characteristic of the individual noble metal and hence it is used as an electrochemical “fingerprint” of the binary noble metal [32]. The AuPd NPs on ITO were investigated by cyclic voltammetry in 0.5 mol L⁻¹ sulphuric acid [32,33]. Fig. 5(a) and (b) are the CVs of AuPd NPs which were deposited from the solution of Auᵢ₋₃Pd₁ and Auᵢ₋₃Pd₃ for 60 s, respectively. As mentioned above, the Pd rich NPs can be fabricated on ITO using an electrolyte with a higher concentration of H₂PdCl₄.

By virtue of surface oxide formation and reduction, the reduction of palladium oxide occurred at about 0.4 V, while that of Au is at 0.75 V. The peak current for the surface oxide reduction changes significantly with different AuPd compositions, but the reductive potentials remain largely unchanged. In Fig. 5(a) and (b), the reduction peaks at 0.4 V corresponding to Pd appeared only for the AuPd alloy NPs for which the deposition potential is more negative than −0.2 V. The reductive peak current at 0.4 V in Fig. 5(b) was bigger than the current shown in Fig. 5(a). It is attributed to the larger proportion of Pd in the alloy NPs that were deposited from the solutions with higher concentrations of Pd ions (Auᵢ₋₃Pd₃). In addition, the excessive quantity of Pd also resulted in the obvious appearance of hydrogen adsorption and desorption at −0.2 V in Fig. 5(b) [7]. For example, in Fig. 5(b), the NPs (curve c) prepared in Auᵢ₋₃Pd₃
Fig. 3. FE-SEM images of electrodeposited AuPd NPs at (a) 0.2 V, (b) 0 V, (c) −0.2 V and (d) −0.4 V on bare ITO for 10 s and at −0.2 V for (e) 60 s and (f) 600 s. The electrolyte consisted of 0.25 mM HAuCl₄ + 0.75 mM H₂PdCl₄ + 0.1 M KCl (Au₁Pd₃).

at −0.2 V for 600 s have a larger reductive peak at 0.4 V compared with those (curve c) prepared in Au₁Pd₁. EDX measurement results in Table 1 has shown that the atomic composition of Pd in curve (c) is 60.7%, while the latter in curve (c') is 32.6%.

3.5. Electrocatalytic properties of the AuPd NPs for the oxidation of ethanol

Catalysis is the most important chemical application of metal nanoparticles and transition metals show very high catalytic abilities for many organic reactions. Since the Pd-based catalysts are emerging as an alternative to Pt-based metal catalysts for the alcohol oxidation reaction, the electrocatalytic properties of the AuPd NPs/ITO were evaluated using CV measurements in 1.0 mol L⁻¹ CH₃CH₂OH + 1.0 mol L⁻¹ KOH solution at room temperature.

In order to examine the activity of the catalyst, the current was normalized by the real surface area that was calculated from the CVs of NPs in the sulfuric acid [34]. Many factors (e.g. potential limit [35] and the composition of AuPd alloy [36]) will influence the electrochemical behavior of AuPd alloy NPs and hence the calculation of the real surface area. The extent of oxidation of AuPd NPs is dependent on the potential, for instance, in curves (a) and (b) of Fig. 5(a),
the potential of 1.4 V vs. SCE is still not high enough to complete the oxidation of AuPd NPs. Therefore, the potential upper limit in our experiments was increased to 1.6 V vs. SCE in order to investigate the surface redox behavior of the alloys. Herein, according to the pure polycrystalline metal, the charge values of 420 µC cm⁻² and 390 µC cm⁻² are theoretical values for Pd and Au, respectively [37]. In Table 1 calculated results were summarized according to the metal and bimetallic NPs deposited in different solutions. It should be pointed out that 1.6 V vs. SCE as the upper limit potential in CV characterization is relatively high concerning the AuPd NPs with a high ratio of Pd composition and the fact that Pd can be dissolved at high potential [35] and high potential limit also affects the coverage of oxide [36] should be considered in the future research.

In Fig. 6(a) bare ITO shows no catalytic activity for the oxidation of ethanol. However, the oxidation peak for ethanol can be clearly observed in the CV curves for the ITO electrode modified with AuPd NPs and pure metal NPs. It is worthwhile paying attention to the effect of ITO at the boundary of nanoparticles, where the oxide support might help to oxidize poisoning species resulting from the dissociative adsorption of ethanol. The electro-oxidation of ethanol was observed during the forward and reverse scans in curves (a)-(d) of Fig. 6(a). The pure Pd NPs on ITO (curve a) showed the typical behavior of Pd metal in the presence of ethanol. In the forward scan, the oxidation peak corresponded to the oxidation of the freshly chemisorbed carbon species rising from ethanol adsorption. The reverse scan peak is primarily associated with the removal of various carbonaceous species, which are not completely oxidized in the forward scan [11]. The three curves (curves b-d) for the AuPd NPs are significantly different from those of Au and Pd NPs (curves a and e). In Fig. 6(a), the Au NPs on ITO show much smaller catalytic ability than AuPd NPs and Pd NPs for the oxidation of ethanol. It can be seen that the addition of Pd to the Au catalyst produced an increased activity for the oxidation of ethanol compared with pure Au NPs. In curve (d) of Fig. 6(a), AuPd NPs with the Pd atomic composition about 16.1% were deposited from Au₄Pd₃ solution and the NPs showed a much higher oxidation current density than the other alloy NPs.

Although lower potentials could be more reliable for fuel cell anode operation, in order to discuss the influence of different composition of AuPd NPs on the catalytic ability, we choose 0.2 V vs. SCE in the chronoamperometric measurements to show the difference of catalysis between different AuPd NPs. In Fig. 6(b), chronoamperograms recorded in 1.0 M CH₃CH₂OH + 1.0 M KOH solution at 0.2 V showed that AuPd NPs had a much higher current density than pure metals at the initial stage. At longer reaction times, the differences between the activities of AuPd become minor, but the current density of AuPd (16.1% Pd) is still kept higher current density than the others.

The AuPd NPs with a comparatively low atomic composition of Pd seems to have higher ability to catalyze the ethanol. A similar phenomenon has been observed in the maximum HER activity at a surface concentration of ca. 20% Pd for AuPd surface alloy [38]. The electronic interaction between Au and Pd results in a narrowing and downward shift of the d-band, which increased the rate of reaction on AuPd over Au. This work also hints the importance of properly tailoring the activity of surface atoms in order to achieve desired
electro-catalytic activities for the oxidation of ethanol in alkaline solution. We believe that these findings will benefit research on other alloy nanoparticles whose size and topography can be controlled by electrochemical deposition.

**Acknowledgement**

This work was supported by the National Science Foundation of China (21173048, 21073038).

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2012.07.048.

**References**