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PtAu Nanoparticle as a Catalyst for Ethanol Electrooxidation

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Abstract

In this work, PtAu nanoparticles were successfully synthesized using the electrodeposition technique. The nanoparticles obtained were irregularly spherical in shape and in the size range of 20-200 nm. X-ray diffraction (XRD) confirmed that the formed PtAu nanoparticles were alloys, because they showed a peak of 2θ in the region between Pt and Au metals, namely at 2θ 39.15˚ and 45.53˚. The cyclic voltammetry (CV) test showed that the PtAu catalyst has an ethanol electrooxidation activity of 22.9 mA/cm^2, 11 times higher than the Pt catalyst previously synthesized using the same technique and conditions. In addition, at 300–1000 cycles the ethanol electrooxidation performance is fairly constant, indicating that this catalyst is quite stable. Interestingly alloying Pt with Au also increases the poisoning resistance of the catalyst from CO or other intermediate species. Thus, the use of PtAu catalysts can effectively increase catalytic activity, maintain stability of the catalyst, and reduce the possibility of poisoning by intermediate species.

Keywords: electrodeposition, catalyst, PtAu, ethanol electrooxidation

1. Introduction

Research related to the development of direct ethanol fuel cells (DEFCs) has increased rapidly in the last two decades. This is because DEFCs has the potential to replace traditional fossil fuels [1] thereby reducing the energy crisis and greenhouse gas emissions. However, the development of DEFCs is hampered because the ethanol electro-oxidation, one of the reactions present in the DEFCs component, has relatively slow kinetics [2]. Therefore, an appropriate catalyst is needed to increase the rate of the ethanol electrooxidation reaction.

It is known that platinum (Pt) is one of the most promising nanomaterials as a catalyst for the ethanol electrooxidation [1]. Unfortunately, Pt-based catalysts are very susceptible to carbon monoxide (CO) poisoning [3], and different strategies have been employed to increase tolerance to CO. One strategy is to design Pt nano-structures and combine Pt with other metals [4], such as Ni [5], Ru [6], Rh [7,8], Bi [9,10], Sn [11,12], Cu [13,14], and Au [15,16].

Among other metals, it is known that the ethanol electrooxidation catalytic activity of Au catalyst under alkaline conditions [17] and resistance to poisoning of adsorbed carbon monoxide (CO_{ads}) is quite good [18]. From previous studies it is also known that Au has a very good ability to oxidize carbon monoxide, which is part of the indirect reaction pathway. Its affinity for the oxidation of carbon monoxide encourages the production of bimetallic Au with other metals, for example Pt [19]. By alloying Au to the Pt catalyst, it is expected that the performance of the catalyst and its durability will increase. Therefore, this study aims to synthesize PtAu nanoparticles as a catalyst for the ethanol electrooxidation. In this study, PtAu nanoparticles were synthesized using the electro-deposition technique on FTO-coated glass substrate. This technique was chosen because it provides a simple route to study the surface chemistry involved since FTO-coated glass has no effect on the ethanol electrooxidation.

2. Materials and Method

2.1 Materials

Potassium hexachloroplatinate(IV) (K_2PtCl_6), tetra-chloroauric(III) acid ($HAuCl_4.3H_2O$), sodium hydroxide (NaOH), and potassium chloride (KCl) were analytical grade

chemicals. Sulfuric acid (H_2SO_4) and ethanol (C_2H_5OH) were used without further purification. All chemicals used were solved in freshly distilled water.

2.2 Instruments

Electrodeposition and ethanol electrooxidation measurements of PtAu nanoparticles were carried out using an eDAQ EA163 potentiostat connected to a three-electrode system. Pt wire as a counter electrode, Ag/AgCl (3M) as a reference electrode, and fluorine-doped tin oxide (FTO) coated glass 10 sq/Ω 3 × 10 mm as a working electrode. The electrochemical impedance spectroscopy (EIS) test was carried out with a CorrTest CS310 potentiostat which is also connected to a three-electrode system. Pt plate 8 × 7 mm as the counter electrode, Ag/AgCl (3M) as the reference electrode, and PtAu nanoparticles deposited on the FTO as the working electrode.

Morphological characterization and the presence of elements in the samples were carried out using a scanning electron microscopy (SEM, FEI Inspect F50) connected to energy dispersive X-ray (EDX, EDAX Apollo X), respectively. Structural characterization was carried out by X-ray Diffraction (XRD, SmartLab Rigaku Co. Ltd., Japan) using Cu-Kα radiation.

2.3 Procedure

Prior to synthesis, the FTO substrate was cleaned with ethanol and distilled water. The electrodeposition of PtAu nanoparticles consist from a mixture of 1 mM K_2PtCl_6 and 0.4 mM $HAuCl_4.3H_2O$ dissolved in 0.5 M H_2SO_4. The technique and parameter used during the synthesis is similar with previous work, that is square-wave pulse electrodeposition with an upper potential limit of 0.6 V, lower potential limit of -0.5 V, pulse duration of 100 ms, and frequency of 1 Hz during 10 minutes [20]. After completion, the samples were rinsed with distilled water and dried.

EIS test were carried out in a solution containing 0.5 M KCl with a frequency range of 50 kHz to 0.1 Hz. The electrooxidation activity of ethanol was determined by cyclic voltammetry (CV) in a solution consisting of 0.1 M NaOH and 1 M ethanol at potential -0.75 to 0.75 V with scan rate 25 mV/s.

3. Results and Discussion

Fig. 1a shown that the PtAu nanoparticles are irregularly spherical and dispersed on the FTO surface. Based on ImageJ analysis, the particle size formed is in the range of 20–200 nm, as illustrated in Fig. 1b. From the EDX results (Fig. 2), elements Au and Pt are evident in the range of ±2.5 keV, while other spectra come from the FTO substrate. The PtAu atomic ratio is closed to 83:17 based on Table 1.

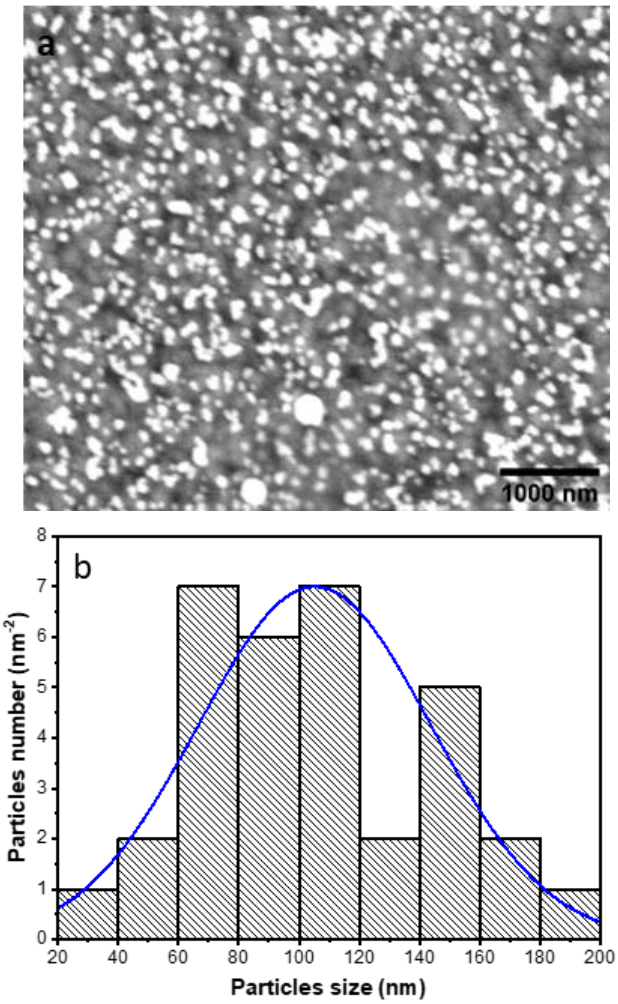

Figure 1. (a) Micrograph and (b) size distribution of PtAu nanoparticles synthesized on FTO-coated glass by electro-deposition technique.

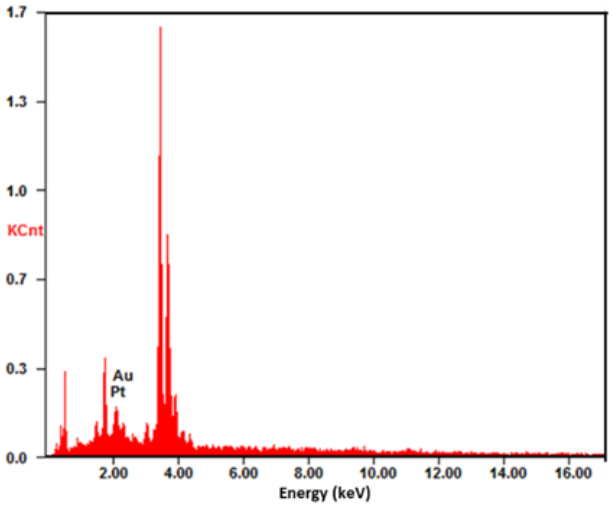

Figure 2. EDX spectrum of PtAu nanoparticles synthesized on FTO-coated glass by electrodeposition technique.

Table 1. Weight and atomic percentage of PtAu nanoparticles synthesized on FTO-coated glass by electrodeposition technique.

Element	Wt%	At%
Pt	83.13	83.27
Au	16.87	16.73

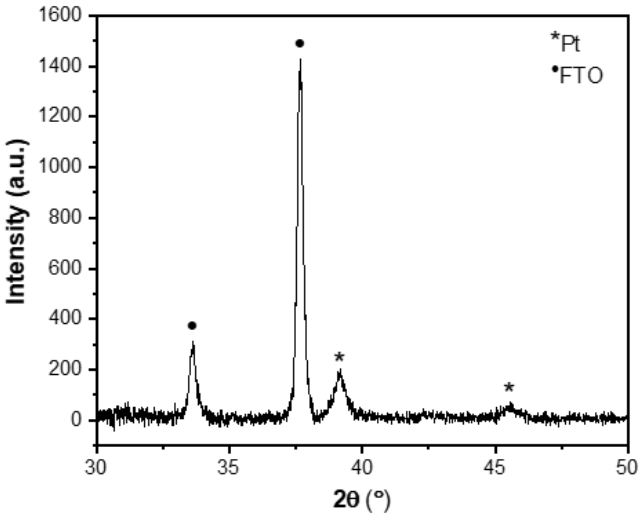

Figure 3. X-ray diffraction of PtAu nanoparticles synthesized on FTO-coated glass by electrodeposition technique.

Based on the XRD results (Fig. 3), the peak at 39.15˚ lies between 2θ Au(111) at 38.25˚ and Pt(111) at 39.76˚. Meanwhile the peak of 45.53˚ is located between Au(200) at 44.46˚ and Pt(200) at 46.23˚ [19]. These results indicate that the PtAu formed is an alloy (references Pt and Au used respectively ICDD 01-071-3756 and ICDD 03-065-8601). To investigate the electrochemical properties of the sample, the PtAu 0.6 V was tested by EIS, the result is as shown in Fig. 4. This sample has a fairly low R_{ct}, which is 41.671 Ω. In the Nyquist plot, the lower the R_{ct} value indicates the relatively fast electron transfer kinetics. This indicates that the PtAu sample has relatively fast electron transfer kinetics, thus enabling high catalytic performance.

Fig. 5 shows the result of ethanol electrooxidation reaction test using CV technique. On the forward scan, an oxidation peak appears at a potential of 0.12 V, indicating the ethanol electrooxidation activity of the PtAu nanoparticles. The voltammogram also showed that PtAu 0.6 V has the highest anodic current of 22.9 mA/cm^2 which appeared in the first cycle. The resulting anodic current is 11 times higher than the Pt catalyst in previous work [20] that was synthesized with the similar techniques and conditions, as shown in Table 2.

Table 2. The comparison between Pt and PtAu current density.

Sample	Current density (mA/cm^2)
Pt 0.6 V (previous work)	2.06
PtAu 0.6 V (this work)	22.9

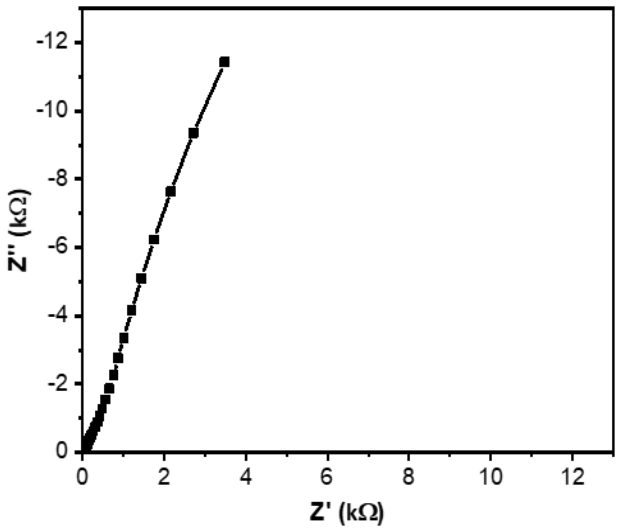

Figure 4. Nyquist plot of PtAu nanoparticles synthesized on FTO-coated glass.

With the formation of the PtAu alloy, the Pt d-band center is modified and results in a change in the electronic structure that promotes higher catalytic activity [19]. If we look at the consistency, the more cycles the lower the anodic current. However, when it reaches 300 cycles, the anodic current tends to be stable up to 1000 cycles. This shows that alloying Au with Pt is also able to maintain the stability of the catalyst. In addition, the presence of Au reduces the buildup of CO and surface oxide in Pt, so that the resistance to poisoning of the catalyst on the PtAu surface increases [19,21].

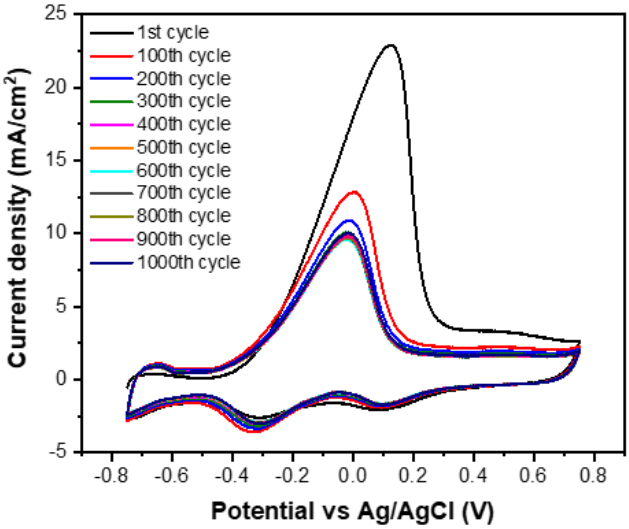

Figure 5. Cyclic voltammogram of PtAu nanoparticles synthesized on FTO-coated glass.

4. Conclusion

In this work, PtAu nanoparticles were successfully synthesized using the electrodeposition technique. Cyclic voltammogram shows that alloying Au with Pt could

effectively increase the current density of the catalyst. In addition, the consistency of the catalyst also tends to be constant since 300–1000 cycles, indicating that the catalyst formed is quite stable. The presence of Au also reduces the poisoning effect of the catalyst by CO or other intermediate species. These results prove that alloying Pt with Au can effectively improve catalytic activity, consistency of catalyst performance, and catalyst poisoning resistance.

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