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Square Wave Pulse Deposition of Gold Nanoparticles for Ethanol Electrooxidation Performance and Its Electrochemical Properties Investigation

Amir Mahmud[1,]*, Bimo Tri Goutomo[2]

[1]Division of Chemical Convergence Engineering, Pukyong National University, Yongso-ro, Busan, Korea

[2]Department of Enviromental Engineering, Pukyong National University, Yongso-ro, Busan, Korea

*Corresponding author: amirmahmud@pukyong.ac.kr

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Abstract

In this study, gold nanoparticles (Au NPs) were successfully synthesized using square wave pulse deposition. The synthesis process involved applying a lower potential of -0.1 V and an upper potential of 0 V for 25 minutes. Characterization of the synthesized Au NPs was conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The XRD analysis confirmed the formation of the Au phase on the FTO substrate. The SEM images revealed a nanopyramid-like morphology, with an average particle size ranging from 20 to 200 nm. The EIS measurements indicated low resistance values for the Au NPs. During the CV test for ethanol electrooxidation, a stable electric current of 4.28 mA/cm² was achieved, demonstrating good stability in the electrochemical process.

Keywords: gold nanoparticle, electrodeposition, ethanol electrooxidation.

1. Introduction

Petroleum is the main source of energy. Unfortunately, energy from petroleum is non-renewable energy and its sources become limited over time. This development finally ended the search for the newest renewable fuel and the energy yield was large. One fuel that can be a substitute for conventional fuel is ethanol, often known as the Direct Ethanol Fuel Cell (DEFC) [1,2].

More attention is paid to change conventional fuel to DEFC, but there are still more problems, including the catalyst used for the DEFC process. Catalysts that have been widely studied for the DEFC process start from several base metals, such as Sn, Bi, Co, and Ni [3–5]. Unfortunately, this metal cannot maintain its stability in the DEFC process and other metals like CoNi [6], are added. To improve the catalytic process and reduce operational costs during DEFC, precious metals were researched to solve these problems. The metal that is often used is platinum (Pt) [7–9].

Platinum metal is used because it has very high catalytic activity in DEFC, but Pt cannot maintain its stability due to the active site can be inhibited by intermediate phases (CO_{ads}) during ethanol electrooxidation. Another noble metal that can retain its active side from carbon monoxide (CO_{ads}) is gold (Au) [10–12]. Gold metal has been proven to be a catalyst for the oxidation processes of methanol and formaldehyde, which has excellent potential [13–16].

Catalysts from Au metal need to be developed because they have the potential to improve the DEFC process. This development includes the morphology or structure of the synthesized Au. Morphological manipulation has many advantages, one of which is that it can increase the surface area for performing DEFC [17,18]. The morphological manipulation process can be achieved by utilizing a deposition process. The process of manipulation morphology includes chemical vapor deposition, hydrothermal deposition, and electrodeposition [19,20]. Electrodeposition provides several benefits, including being cheaper, being able to control several parameters to get the desired results, simple process, and faster process [6,21].

This research aims to synthesize Au catalysts using the electrodeposition method. Important parameters in manipulating morphology are potential, additives, and time. In this research, the focus will be on the synthesis of an Au catalyst using a certain potential in a 0.5 M H2SO4 electrolyte within 25 minutes.

2. Materials and Method

The synthesis of the Au catalyst in this research used a solution of HAuCl4 from the $HAuCl_4.3H_2O$ salt (Sigma-Aldrich) in a 0.5 M H_2SO_4 (Merck) solution. Other materials needed in this research were C_2H_5OH (Merck), NaOH (Merck), and KCl (Merck). The sample will be deposited on fluorine-doped thin oxide (FTO) measuring 1.5 cm x 1 cm x 0.5 cm. Electrodeposition will be carried out using the square-wave pulse deposition method at an upper potential (E_U) 0 V and a lower potential (E_L) -0.1 V and a frequency of 1 Hz. The synthesis time was 25 minutes at room temperature. The synthesis process starts with the FTO cleaning process with distilled water and 96% ethanol until clean. Electrodeposition will be carried out on a potentiostat (eDAQ ER466) with a three-electrode system consisting of a working electrode containing FTO, an Ag/AgCl (KCl 3M) reference electrode, and a Pt sheet counter electrode. After the electrodeposition process, the electrodeposition results are washed until clean.

The next process is the characterization of the sample. The sample morphology will be characterized by field emission scanning electron microscopy (FE-SEM, Thermo Scientific Quattro S). The elemental composition was analysed by energy dispersive X-ray (EDAX Ametek). Electrochemical characterization was carried out using electrochemical impedance spectroscopy (EIS Corrtest CS350). This characterization was done with a 0.5 M KCl solution and a 50 kHz – 0.1 Hz frequency range. Ethanol electrooxidation was carried out using the cyclic voltammetry (CV) method in 1 M ethanol and 0.1 M NaOH.

3. Results and Discussion

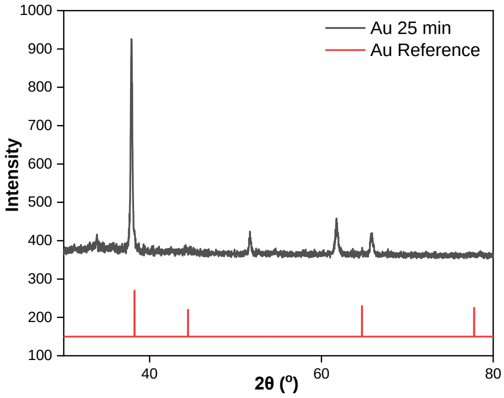

Figure 1. XRD pattern of Au NPs synthesized in lower potential -0.1 V, upper potential 0 V, and time deposition 25 min.

Figure 1 shows XRD patterns of Au that are synthesized using square-wave pulse deposition. The synthesized Au sample produced peaks at 26.5°, 37.8°, 51.6°, 61.7°, and 65.9°. These peaks confirm that Au formation occurred at 37.8° and 65.9° in accordance with the previous study [22], while there is a peak that confirms the presence of FTO-substrate at 51.6° [23]. The attributed planes of the Au at (1 1 1) and (2 2 0) respectively at the peak of 37.8° and 65.9° [24]. The characteristic of Au is face-centered cubic (fcc) structure in agreement with Geraldes et.al [25].

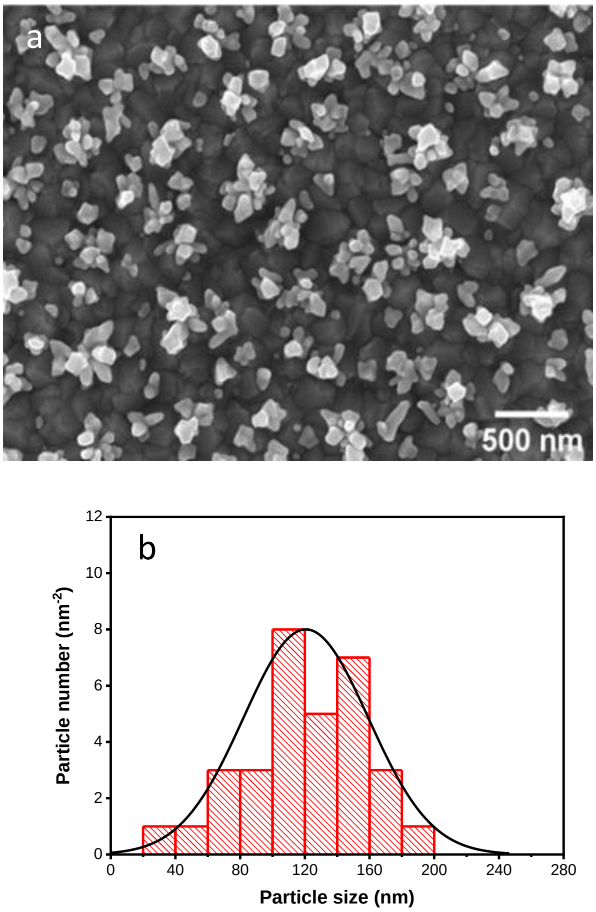

Figure 2. (a) FESEM micrograph and (b) particle size distribution of the Au NPs synthesized in lower potential -0.1 V, upper potential 0 V, and time deposition 25 min.

The morphology of the synthesized Au catalyst is shown in Figure 2a. The morphology shown is nanopyramid-like. This morphology was formed at E_L -0.1 V with a deposition time of 25 minutes. A study from Tian et.al stated that using a potential of -0.08 V produced a clear nanopyramid-like morphology. If a negative overpotential is applied, it will form an imperfect spherical morphology on the sample [26]. Based on figure 2a, Au NPs have been shown good distribution and dispersed on the substrate, but the size of Au particles varies widely. This is because Au agglomerates very easily on the substrate and can influence its catalytic property [27]The size of the nanopyramid-like morphology is shown in Figure 2b, which has a size range of 20 – 200 nm.

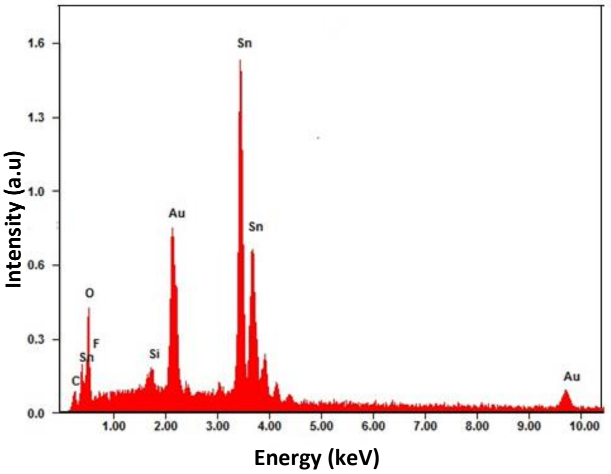

Figure 3. EDX spectrum of Au NPs synthesized in lower potential -0.1 V, upper potential 0 V, and time deposition 25 min.

The EDX characterization is carried out to determine the sample's elemental composition. Au elements are formed in Au NP samples synthesized using the electrodeposition method. In addition, other elements such as Sn, F, and O were detected originating from the FTO substrate.

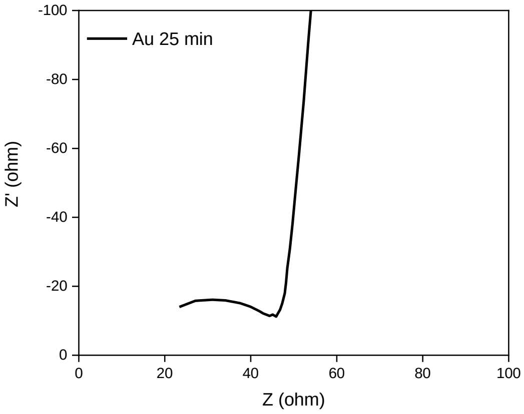

Figure 4. Nyquist plot of Au NPs synthesized in lower potential -0.1 V, upper potential 0 V, and time deposition 25 min.

The Au-NPs catalyst was characterized by EIS for resistance testing. The results from EIS stated that the addition of Au can increase the electrical conductivity of the substrate. A study by Aulia stated that the electrical conductivity of AuNPs deposited on the FTO substrate increases compared to the only substrate [12,28].

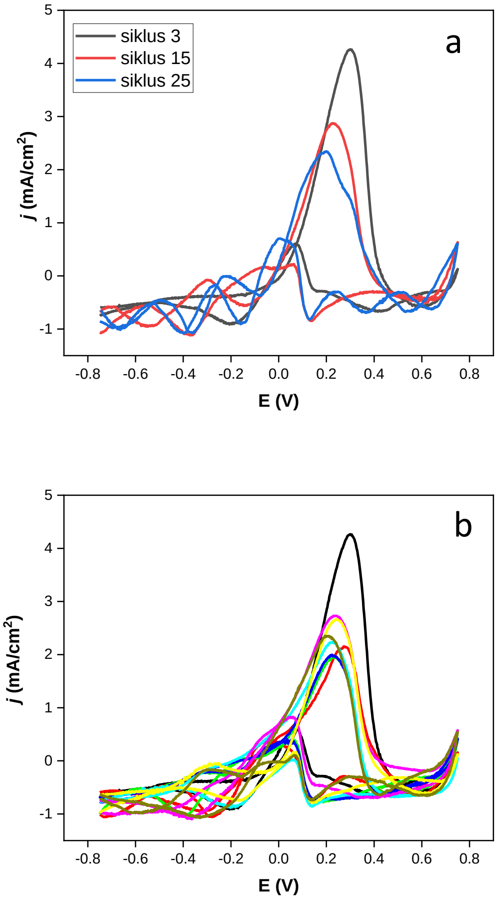

Figure 5. (a) Cyclic voltammogram of Au NPs measured in an alkaline solution containing 1 M ethanol and 0.1 M NaOH (b) ethanol electrooxidation from cycle 3 to cycle 25.

The Au-NPs catalyst was tested to a CV test for ethanol electrooxidation. The electrooxidation of ethanol produces a voltammogram graph in Figure 5. The CV results produce a current density or forward scan (*j*f) of 4.28 mA/cm^2 with E_{onset} at -0.026 V. In addition, the *j*b/*j*f values were reviewed to determine the stability of the CV for Au NPs. Value of forward scan and backward (*j*b/*j*f) shows good stability of its electrode[28,29] The backward scan value for Au NPs exhibited a small peak. It is because Au stabilizes the system by releasing intermediate phases [30,31]. Additionally, ethanol electrooxidation on the Au sample exhibited a slight decrease in figures 5a and 5b, indicating good stability and resistance to poisoning by intermediate phases like COads. According to a previous study, the addition of Au to the ethanol electrooxidation process can increase its stability because the intermediate phase (CO_{ads}) produced during the ethanol electrooxidation process is oxidized to CO_2, so it will reduce the obstruction by the intermediate phase[11,32]. It can be seen in figure 5b that the peak of oxidation is slightly reduced in 25th cycle. The kinetic behaviour of Au NPs for ethanol electrooxidation is recorded in Table 1. The Tafel slope of Au NPs recorded was 108 mV/dec, indicating that Au NPs require less energy for ethanol electrooxidation to occur in the 3rd cycle. This is attributed to the abundant concentrations of ethanol and NaOH still present in the system.

Table 1. Interpretation CV data of Au NPs measured in an alkaline solution (0.1 M NaOH) and containing 1 M ethanol.

Cycle	Measurement			
	jb/jf	Eonset (V vs RHE)	Current density (mA/cm^2)	Tafel slope (mV/dec)
3	0.214	0.032	4.28	108
15	0.028	0.012	2.92	132
25	0.290	-0.030	2.33	146

4. Conclusion

The Au NPs catalyst was successfully synthesized using square wave pulse deposition. X-ray diffraction (XRD) tests confirmed the formation of the Au NPs phase on the FTO substrate. The morphology of the Au NPs exhibited a nanopyramid-like structure with an average size ranging from 20 to 200 nm. Electrochemical impedance spectroscopy (EIS) measurements of the Au NPs indicated low resistance values, highlighting their good catalytic activity. During ethanol electrooxidation tests, the sample demonstrated a current density of 4.28 mA/cm^2 and excellent stability, characterized by a low jf/jb value.

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