

Electrochemical sensor applications of Pt supported porous gold electrode prepared using cellulose-filter

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(Received 16 June 2015 • accepted 19 August 2015)

Abstract—A facile and rapid method for the synthesis of porous gold (PAu) electrodes on cellulose-filters is proposed. Morphology and active surface area of the electrode greatly influence the electrochemical properties of sensor. Compared to smooth electrode and glassy carbon, PAu and Pt/PAu electrode showed high roughness due to porous structure, which is helpful in electrochemical sensing of target molecules. The electrochemical sensing performance of Pt/PAu electrode was evaluated to detect hydrogen peroxide, glucose, and perchloric acid. The amperometric results with various concentrations of target molecules showed potential applications of Pt/PAu electrode in sensitive and effective chemical sensors.

Keywords: Porous Gold, Syringe Filter, Hydrogen Peroxide, Electrochemical Sensor

INTRODUCTION

A great deal of interest has developed for electrochemical sensors using several modified electrodes, such as immobilization of nano/bio-materials [1] and hierarchical re-structuring [2]. Gold nanoparticles (AuNPs) with high surface area have attracted interest as catalysts or sensors due to excellent biocompatibility and electrochemical response [3]. However, the immobilization of AuNPs on a foreign substrate with weak adsorption may reduce the catalytic or sensing properties due to low roughness and slow electron transport [4]. To overcome these drawbacks, porous gold (PAu) nanostructures were developed that showed excellent performance in catalytic and sensing applications, due to higher surface area and better electron transport phenomena [5-10].

As compared with AuNPs-based electrodes, PAu electrodes not only allow fast mass transport of ions through the electrolyte/electrode interface, but also rapid electrochemical reactivity due to short diffusion length and large active surface activation area. Therefore, the porous structure of gold electrodes offers many active sites for biomaterials, which would make PAu attractive for use in nano/biosensors [6]. Erlebach et al. first proposed a facile synthesis of PAu through dealloying sacrifice metal (Ag) from a binary Au/Ag alloy [7,8]. This dealloying process is normally used for preparing PAu electrodes, while a templating approach was applied to prepare PAu. The metal is deposited onto the artificial templates with different sizes, followed by removal of the templates to form a porous structure with adjustable pore size [9]. In our previous reports [5,10-12], coral-like PAu, prepared by templating method using polystyrene beads and nanoporous alumina, was shown to be very effective and promising electrochemical and biological sensor. Pt nano-

particle-deposited PAu-pellet electrode also exhibits an extremely low working potential, a detection limit of 50 μM of H_2O_2 , and a fast response time within 10 s-20 s [5,10]. Thiol functionalized PAu electrodes have been successfully applied to the detection of mercury ion at very low concentration and display high linearity from 7 ppb to 150 ppb [11,12]. However, this templating method, combined with an etching process, is very time-consuming and complicated, which includes templating, calcination, dealloying, and sintering [11]. Therefore, we suggest a facile and fast synthesis method to produce paper-based PAu and uses AuNPs with a syringe-filter paper. Paper has many interesting properties such as durability, cost-effectiveness, light weight, and environmental friendly material, but also PAu electrodes exhibit competitive nanostructure and are easy to control in a lab. To evaluate the electrochemical activity of a paper-based PAu electrode, platinum (Pt) electrodeposited PAu electrode (Pt/PAu) was prepared using a potentiostat. Small dots of deposited Pt not only play a role as electrocatalytic active sites but also impart rough surfaces on the electrode. The electrochemical sensing properties of PAu and Pt/PAu were evaluated by detecting the three different chemicals (H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4) for securing various applications.

EXPERIMENTAL

1. Preparation of PAu and Pt/PAu

Colloidal AuNPs were prepared by traditional reduction method following a previous report [13]. The prepared AuNPs were characterized by UV/vis spectroscopy (UV-1800, Shimadzu), and transmission electron microscopy (TEM, JEM1010, JEOL). A syringe-filter (Advantech) with 200 nm pore size, prepared from cellulose, was used as physical template. As shown in Fig. 1, 100 mL of 60 ppm AuNPs was filtered five times by syringe using a filter, then dried overnight in an oven at 60 °C. The dried filter paper was sintered at 350 °C-500 °C for 90 min to remove the cellulose of the filter

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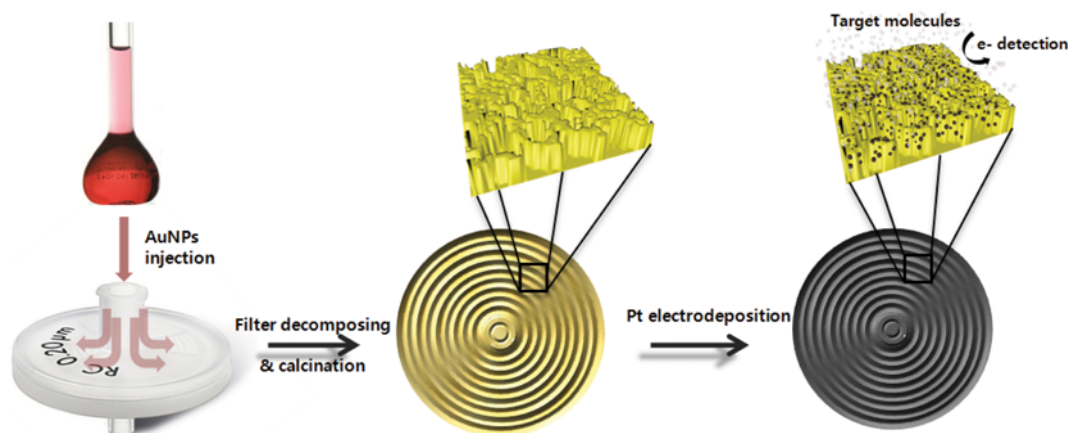


Fig. 1. Preparation procedure of porous gold using cellulose syringe-filter paper.

paper and further sinter AuNPs. Obtained PAu was attached on the edge of glassy carbon electrode (GCE) using silver glue. Pt dots were loaded on PAu by electroplating via simple redox reaction using battery (1.5 V). After PAu (anode) and Pt plate (cathode) were immersed in 0.2 mM K_2PtCl_6 electrolyte, redox reaction time was adjusted from 5 s to 60 s. Surface morphology and composition of the paper-based PAu was investigated by scanning electron microscopy (SEM, S-4700, Hitachi) and energy dispersive X-ray spectroscopy (EDX, 7200-H, Horiba).

2. Electrochemical Sensing of H_2O_2 , $C_6H_{12}O_6$, and $HClO_4$

All electrochemical analysis was performed using a potentiostat (263A, EG&G Parc). A three-electrode cell was used. Pt plate, PAu and Ag/AgCl (saturated NaCl) were used as the counter, working

and reference electrodes, respectively. The cyclic voltammetric (CV) behavior of as-made electrodes was tested in a mixture of 0.1 M PBS and 0.1 M KCl containing various concentrations of hydrogen peroxide (H_2O_2), glucose ($C_6H_{12}O_6$), and perchloric acid ($HClO_4$) to find applied potential for sensing target chemicals. In addition, amperometric testing of PAu and Pt/PAu electrodes at fixed potential (-0.3 or 0.3 V) was conducted with successive addition of H_2O_2 , glucose, and $HClO_4$ (from 0.1 to 60 mM with time intervals of 60 to 120 s) while continuously stirring.

RESULTS AND DISCUSSION

To synthesize porous gold electrode, AuNPs were used as a pre-

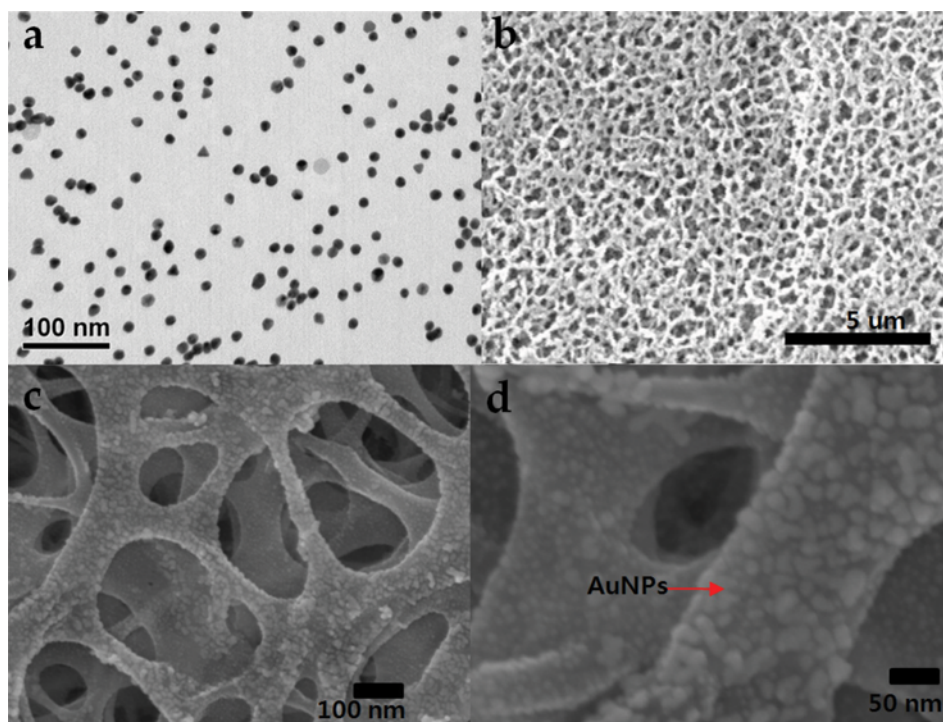


Fig. 2. (a) TEM image of as-synthesized AuNPs, and SEM image of (b) bare and ((c) and (d)) AuNPs loaded syringe filter.

cursor material for the backbone. In our previous works [11,12], the gold ion was directly mixed with an aluminum precursor and formed a bicontinuous structure, followed by sintering and forming gold network. In this paper-based synthesis method, gold ion was not adsorbed but rather formed metallic particles on the cellulose paper. Therefore, pre-synthesized AuNPs, readily prepared by reduction of gold ion using citrate as the reductant, were used in the filtering process. As shown in Fig. 2(a), AuNPs with ca. 15 nm–20 nm measured by TEM analysis showed mainly spherical and partially triangular shape. The resulting solutions have a dark red color and showed the representative peak (520 nm) of spherical AuNPs in UV-vis spectra. Cellulose filters have porous structures with 200 nm pore (Fig. 2(b)), and small AuNPs were adsorbed on the surface of cellulose substrate while not filling the pore. After injection of AuNPs solutions into the syringe-filter, the color of the

filter paper changed from white to dark red, indicating that AuNPs were physical or chemical loaded on the cellulose substrate, which has many OH moieties. After five sequential filterings, the resulting filter incorporating AuNPs (Fig. 2(d)) were thermally treated to remove cellulose template and sintered for neighboring AuNPs to form a gold network as free-standing backbone structure.

To find the optimum temperature for heat treatment, calcination temperature was adjusted as 350 °C, 450 °C, and 500 °C. At heat treatment of 350 °C, the resulting material showed a dark color, indicating incomplete removal of the cellulose template. The cellulose has a degradation temperature as 365 °C with ca. 10% residue [14]. To completely remove, the filter was treated at 500 °C. However, severe sintering collapses the pore structure, as shown in Fig. 3(b). Namely, evolution of necks between AuNPs eliminated pores in substrate. Therefore, cellulose filter with AuNPs was treated at

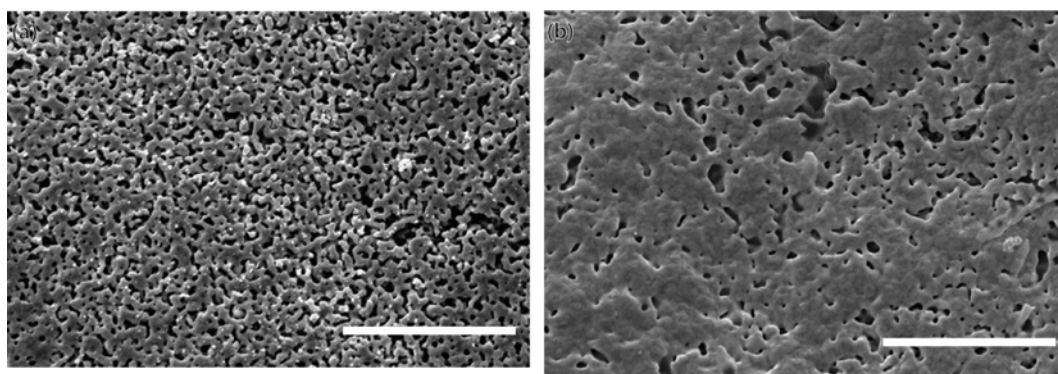


Fig. 3. SEM images of calcined PAu at (a) 450 °C and (b) 500 °C (scale bar=20 μm).

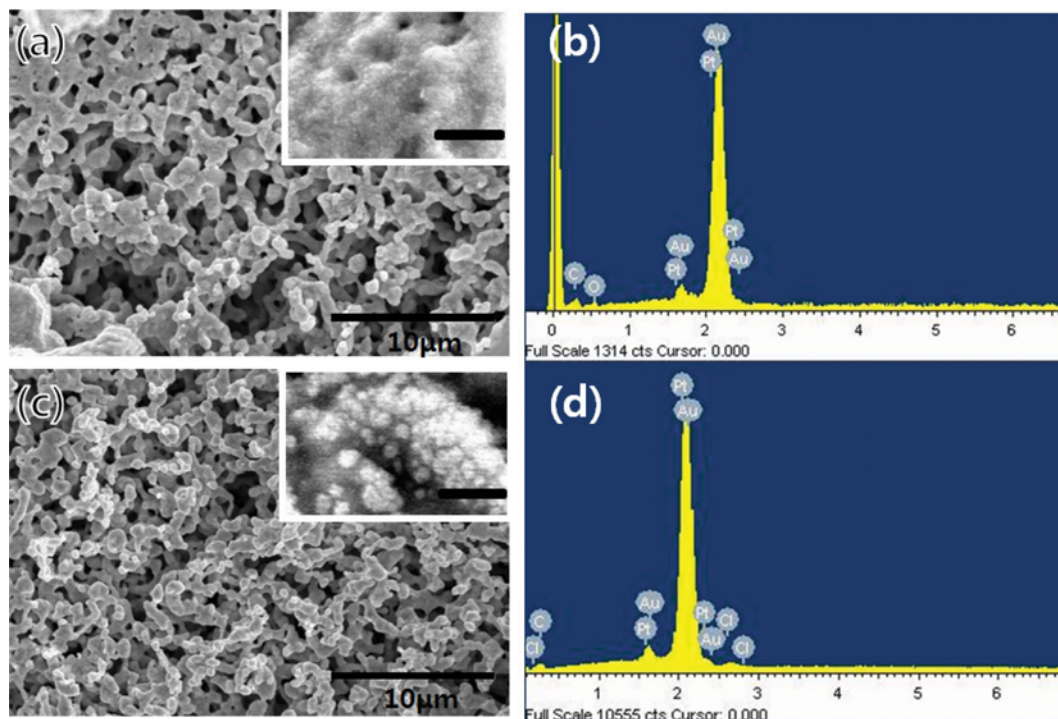


Fig. 4. SEM images of Pt/PAu electrodeposited for (a) 20 sec and (c) 60 min, and ((b) and (d)) EDX spectrum of (a) and (c), respectively. Inset is magnification image of (a) and (c), and scale bar in inset is 200 nm.

450 °C as optimum temperature, free-standing porous gold with bulk gold color was obtained (Fig. 3(a)). The surface morphology of PAu was a coral-like structure and showed a window pore of 100 nm-400 nm. As compared with our previous reports [5,10-12], this proposed approach for paper-based synthesis of PAu was a very simple and time-saving process.

Pt dots were electroplated on the PAu substrate using a simple redox reaction. Pt^{2+} ion dissolved from Pt plate was electroplated on the PAu to form Pt dots through reduction. Electroplating time of Pt was adjusted from 5 s to 60 s, and the surface morphology and composition of resulting Pt/PAu was analyzed with SEM and EDX, respectively (Fig. 4). Increasing the electroplating time from 5 s to 20 s, the size of the Pt dots increased from 11 nm to 20 nm, and the weight ratio of Pt to Au on PAu increased from 7.2 wt% to 29 wt%. Pt dots were successfully immobilized on the surface of PAu electrode with increased electroplating time. However, when electroplating time reached 60 s, the Pt/PAu electrode showed excessive growth of Pt dots (over 130 nm) and loading (43 wt%), as shown in Fig. 4(b). Therefore, we selected Pt/PAu electrode electroplating at 20 s and used it for all subsequent experiments.

To check the oxidation/reduction feature of the prepared electrode, CV data of PAu and Pt/PAu were measured in 0.1 M PBS

and 0.1 M KCl. As shown in Fig. 5(a), CV of electrode showed different features with dependence on the presence of Pt dots. The hydrogen oxidation and reduction peaks of PAu were found at ca. -0.4 V and 0.3 V, respectively. Pt/PAu electrode showed significantly large current and shift of potential as compared to PAu. Pt dots on the PAu electrode enhanced the electroactivity for hydrogen oxidation/reduction.

To calculate the roughness factor (RF) of the three electrodes, CV was measured in acidic solution (0.5 M H_2SO_4). The electrochemically active area was calculated from the H_{UPD} method with assumption of the charge densities for H_{UPD} as 0.240 mC/cm² [15]. The RF was calculated by dividing the electrochemical active area by the geometry area (0.20 cm²). The RF of PAu and Pt/PAu electrodes were ca. 55 and 101, respectively. As compared to our previous reports [5,10], RF value of paper-based synthesized PAu was larger than (40-70) of PAu prepared by templating method using porous alumina. Therefore, the increased surface roughness of Pt/PAu electrode may be helpful in enhancing the electrochemical activity. This enhanced current response could be found at several porous electrodes [10,16,17]. CV analysis of GCE, Au foil, and PAu was conducted in ferricyanide solution. The pristine GCE and Au foil showed typical oxidation-reduction curve, with the current being slightly less than ± 0.3 and ± 0.5 mA, respectively. The three-

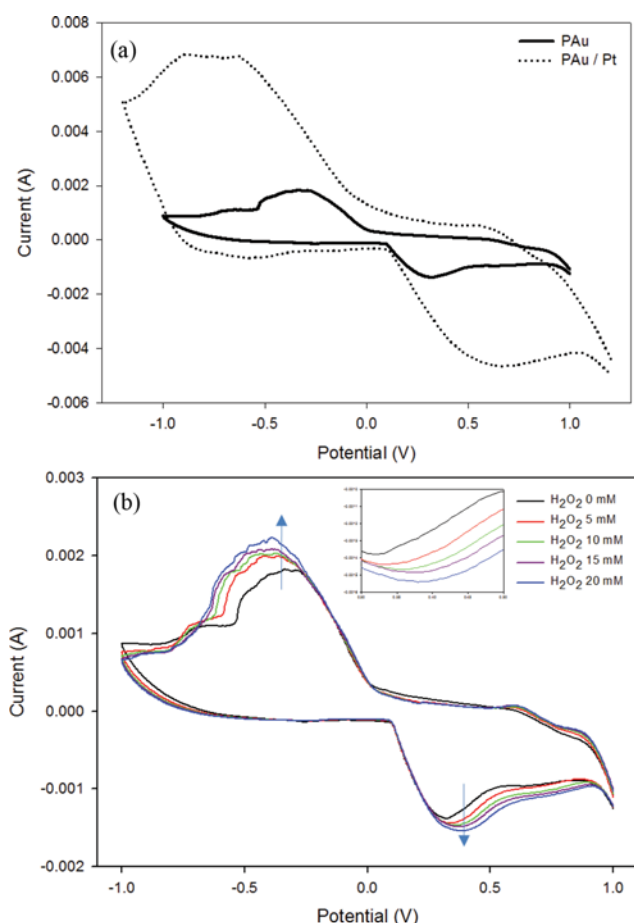


Fig. 5. CV curve of (a) PAu and Pt/PAu electrodes in 0.1 M PBS+ 0.1 M KCl solutions at a scan rate of 50 mV. (b) CV curves depended on the concentration of H_2O_2 solutions using electrode in 0.1 M PBS+0.1 M KCl solutions.

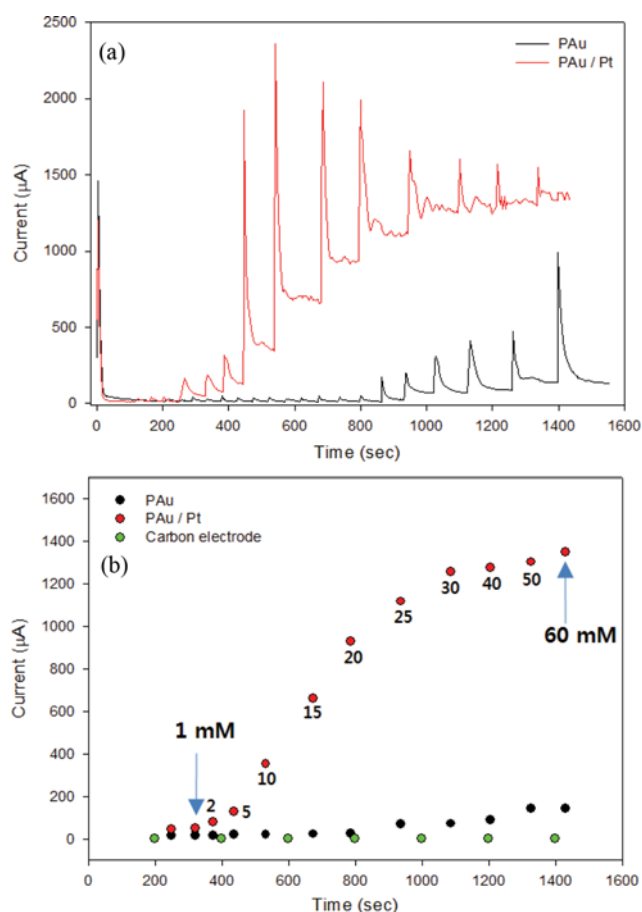


Fig. 6. Amperometric responses of PAu and Pt/PAu electrodes for successive additions of H_2O_2 at applied working potential of -0.3 V vs. Ag/AgCl.

dimensional porous gold structure exhibited high electroactivity compared to two-dimensional smooth gold substrate.

To demonstrate applicability of electrochemical sensing of prepared electrodes, sensing tests for three different chemicals (H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4) were conducted. Hydrogen peroxide and glucose are representative target chemicals in food and healthcare field, and perchloric acid salt is an environmental pollutant usually found in aqueous environments. The voltammetric behavior of Pt/PAu electrode was obtained in 0.1 M PBS and 0.1 M KCl solution contained in the various concentrations of H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4 . As concentration of H_2O_2 increased, the redox current increased (Fig. 5(b)). The oxidation peak at -0.3 V with the direction of negative-sweep increased to 20 mM H_2O_2 and the potential value of oxidation peak also shifted to the negative direction, indicating the surface reaction of H_2O_2 molecule on the electrode increased. CV data of HClO_4 were similar to that of H_2O_2 , and the static applied potential of the two chemicals for amperometric measurement was fixed at -0.3 V.

Fig. 6 shows an amperometric response of PAu and Pt/PAu electrodes at -0.3 V as a result of successive addition of H_2O_2 , and a distinct response to the change of H_2O_2 concentration was observed (Fig. 6(a)). The current response caused by PAu electrode is relatively small compared to the Pt/PAu electrode, indicating the Pt dots electroplated on PAu have good electrochemical activity for H_2O_2 detection. In addition, pristine GCE showed no current change with the addition of H_2O_2 (Fig. 6(b)) and the current response of Pt/PAu loaded GCE can be judged as similar to the Pt/PAu electrode. The enhanced electrooxidation current for H_2O_2 on the Pt/PAu may be influenced by the coral-like Au structures and larger roughness factor, compared to PAu and GCE.

Based on the amperometric response of Pt/PAu electrode for the three chemicals, a calibration curve plot was obtained as shown in Fig. 7. To compare the sensitivity of three chemicals, current response was normalized. The excellent electrochemical sensing properties of Pt/PAu were clearly demonstrated. The detecting range for H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4 was 0.1–60 mM, 5–40 mM, and 5–50 mM, respectively. For higher concentrations, amperometric re-

sponses were saturated in Langmuir type fashion. In addition, Pt/PAu electrode exhibited an extremely high sensitivity of $114 \mu\text{Acm}^{-2} \text{mM}^{-1}$, $14 \mu\text{Acm}^{-2} \text{mM}^{-1}$, and $25 \mu\text{Acm}^{-2} \text{mM}^{-1}$ for H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4 , respectively. In literature reports, nonenzymatic glucose sensor using PAu showed a linear range from 2 mM to 10 mM with a sensitivity of $11.8 \mu\text{Acm}^{-2} \text{mM}^{-1}$ [18], and hydrogen peroxide sensor using carbon nanotube/NP hybrid showed $1.4 \mu\text{Acm}^{-2} \text{mM}^{-1}$ [19]. Pt/PAu prepared by paper-based method has excellent sensitivity for the target molecules and may be applicable to various nano/bio-sensors.

CONCLUSIONS

PAu and Pt/PAu electrode with porous structure and high roughness were easily prepared by a paper-based synthetic method. Cellulose-filter and AgNPs were used as physical templates and backbone material, respectively. Through thermal treatments at 450°C , cellulose was removed and sintered AuNPs formed the backbone, and the free-standing PAu was readily obtained. The Pt-electroplated PAu electrode was used for sensing test of H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4 , demonstrating applicability as an electrochemical sensor. The excellent electrochemical sensing properties of Pt/PAu were clearly demonstrated with high sensitivity compared to literature values. Three-dimensional porous structures may be helpful to increase current response through the enhancement of electron transport. This study showed paper-based PAu with Pt-dot electrodes may have potential application such as electrochemical sensors and catalyst.

ACKNOWLEDGEMENTS

This work is supported by the National Research Foundation of Korea (NRF-2013R1A1A2A10004353).

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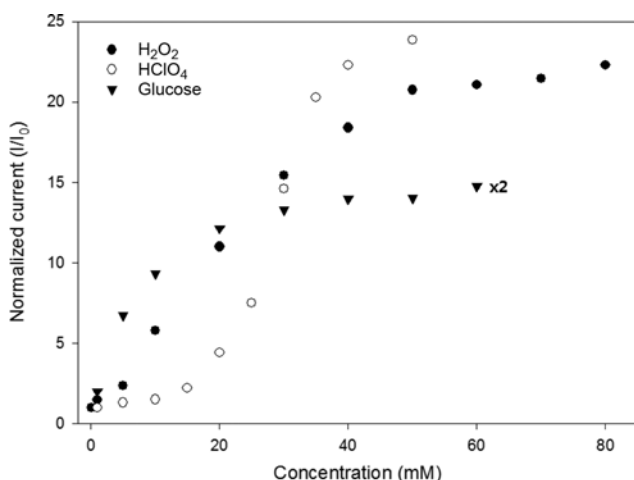


Fig. 7. Calibration curve plots for H_2O_2 , $\text{C}_6\text{H}_{12}\text{O}_6$, and HClO_4 responses of Pt/PAu electrode.

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