O 75.   SENSITIVE HYDROGEN PEROXIDE SENSOR BASED ON BIMETALLIC CATALYSTS

Orhan Alal[1], Rabia Esra Takir[2*], Hilal Kivrak[1], Ozlem Sahin[2]

[1]*Van Yuzuncu Yil University, Faculty of Engineering, Department of Chemical Engineering, Van 65000, Turkey*
[2]*Konya Technical University, Faculty of Engineering, Chemical Engineering Department, 42031 Konya, Turkey*

E-mail: osahin@ktun.edu.tr

ABSTRACT In this study, Pd and PdAu catalysts were synthesized by $NaBH_4$ reduction method and the activity of these catalysts for H_2O_2 reduction has been measured by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. Electrochemical sensitivities of these CNT supported different atomic ratio PdAu bimetallic nanocatalysts were determined in 0.1 M pH 7.4 phosphate buffer solution towards H_2O_2.

Keywords: Hydrogen peroxide, Platinum, Gold, $NaBH_4$ Reduction

1. INTRODUCTION

Hydrogen peroxide (H_2O_2) has importance in many areas such as clinical, food, pharmaceutical, and environmental because of its strong oxidizing and reducing ability (Yang, et al., 2015). Therefore, fast and accurate determination of H_2O_2 is very important. Various methods have been developed for the determination of H_2O_2 such as titrimetry (Hurdis et al., 1956), fluorescence (Cathcart et al., 2015), spectroscopy (Luo et al., 2008), chemiluminescence (Xu et al., 1999), and electrochemical methods (Guascito et al., 2008). Comparing with these methods, electrochemical method is preferred due to its high sensitivity, selectivity, and simplicity. Various chemically modified electrodes, especially enzyme modified electrodes have been widely developed for the detection of hydrogen peroxide (Wang et. all, 2015). However, the main problem is that the activity of enzyme can be easily affected by temperature, pH, humidity, and toxic chemicals. Moreover, the complicated immobilization procedures may also decrease the activity of the enzyme and have influence on the stability and reproducibility of the enzyme based electrodes. Therefore to resolve these problems, numerous studies have focused on developing non-enzymatic electrodes. In this study, Pd and PdAu catalysts were synthesized by $NaBH_4$ reduction method and the activity of these catalysts for H_2O_2 reduction has been measured by cyclic voltammetry (CV) and chronoamperometry (CA) techniques.

2. MATERIAL AND METHOD

2.1. Synthesis of Catalysts

All chemicals used in this study namely carbon Vulcan XC-72, Nafion 117, $AuCl_3$ K_2PdCl_4, CNT were of analytical grade and purchased from Sigma-Aldrich. Electrocatalysts were synthesized via $NaBH_4$ reduction method. CNT was used as the support material, and the percentage of metals loaded on the CNT support was 10 wt%. CNT was dispersed in 10 ml of purified water. Then, Pd and Au salts were transferred to the solution. The content was dispersed with ultrasonic bath and magnetic stirrer for 80 min. After, $NaBH_4$ was added to the catalyst ink, and the mixture was mixed with magnetic stirrer for 40 min. Following this, catalyst ink was dried and filtered. As a result, Pd/CNT and PdAu/C were synthesized at varying atomic ratios.

2.2. Electrochemical Measurements

Electrochemical measurements were performed on Pd/CNT and PdAu/CNT catalysts. H_2O_2 electroreduction measurements were performed via cyclic voltammetry (CV) and chronoamperometry (CA). Electrochemical measurements were performed with CHI 6043d potantiostat, with a three electrode cell system consist of platinum wire as counter electrode, Ag/AgCl as reference electrode and Pd based catalysts modified glassy carbon electrode (GCE, 3 mm diameter) as the working electrode.

Glassy carbon electrodes were polished successively using 1, 0.3, 0.05 µM alumina powder and then thoroughly rinsed with deionized water. All the electrochemical measurements were carried out in 0.1 M phosphate buffer solution (pH 7.4). Prior to measurements, the solution was deoxygenated with nitrogen gas.

3. RESEARCH FINDINGS

Pd/CNT, Au/CNT, $Pd_{70}Au_{30}$/CNT and $Pd_{50}Au_{50}$/CNT catalysts were prepared for detection of H_2O_2. To calculate the electrochemical surface areas of the electrodes, the CVs were carried out in 5.0mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl (Figure 1) at different sweep rates (v) . The electrochemical surface area can be determined using the Randles–Sevcik equation. The calculated electroactive surface area of the $Pd_{70}Au_{30}$/CNT GCE was 0.16 cm^2, which is about 2.0, 1.78 and 1.34 times higher than that of Au/CNT (0.08 cm^2), Pd/CNT (0.09 cm^2) and $Pd_{50}Au_{50}$/CNT (0.12 cm^2) GCEs, respectively. These results indicated that the $Pd_{70}Au_{30}$/CNT catalyst has excellent electrochemical properties to increase the reaction surface area of the electrode and enhance the electron transfer.
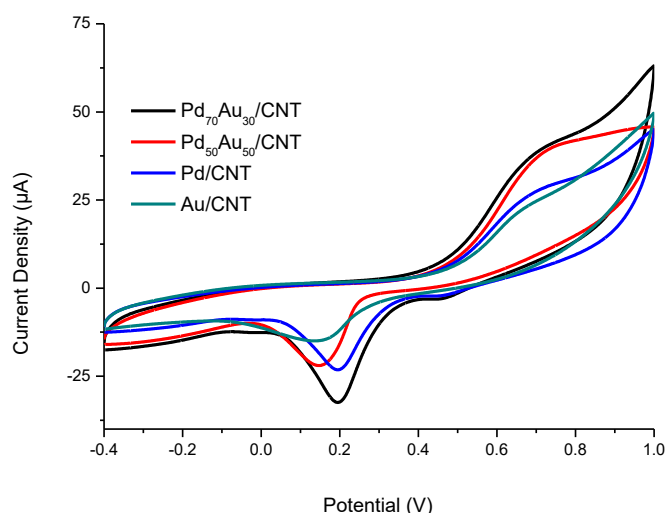

Figure 1. Cyclic voltammograms of the of Pd/CNT, Au/CNT, $Pd_{70}Au_{30}$/CNT and $Pd_{50}Au_{50}$/CNT GCEs in 5.0 mM $Fe(CN)_6^{3-/4-}$ +0.1 M KCl. Scan rate: 100 mVs^{-1}

The electroreduction of H_2O_2 measurements on these catalysts were carried out by cyclic voltammetry (CV) in 0.1 M pH 7.4 phosphate buffer solution (Figure 2a). The electro-reduction of H_2O_2 occurs at around -0.4 V. The sensitivity of the catalysts towards H_2O_2 (Fig. 2b) increases in the order of Au/CNT<Pd/CNT<$Pd_{50}Au_{50}$/CNT<$Pd_{70}Au_{30}$/CNT. Obviously, $Pd_{70}Au_{30}$/CNT showed the highest oxidation current among all the other catalysts. Pd_xAu_y/CNT bimetallic catalysts exhibit an enhanced remarkable catalytic current peak greater than the current peaks of Pd/CNT and Au/CNT catalysts. This result showed that alloying Pd with Au enhanced the electrocatalytic performance towards H_2O_2 detection due to the synergistic effect between Pd and Au.
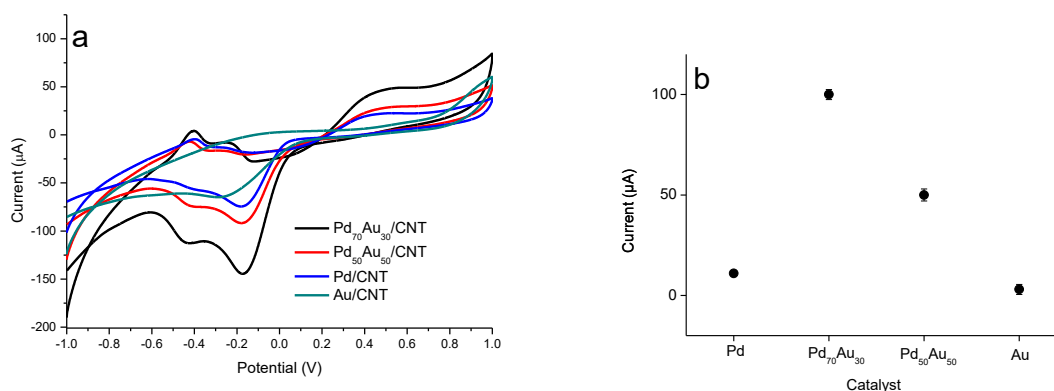
Figure 2. **(a)** Cyclic voltommograms, **(b)** sensitivity values for Pd/CNT, Au/CNT, $Pd_{70}Au_{30}$/CNT and $Pd_{50}Au_{50}$/CNT catalysts to the addition of 5 mM H_2O_2 in N_2 saturated 0.1 M phosphate buffer solution at pH 7.4, scan rate: 100 mV/s.

Figure 3 shows typical amperometric response of the Pd/CNT, Au/CNT, $Pd_{70}Au_{30}$/CNT and $Pd_{50}Au_{50}$/CNT GCEs to the successive additions of H_2O_2 at an applied potential of -0.4 V. Compared with the other catalysts modified GCEs, the response of $Pd_{70}Au_{30}$/CNT modified GCE possesses wider linear range and higher sensitivity.
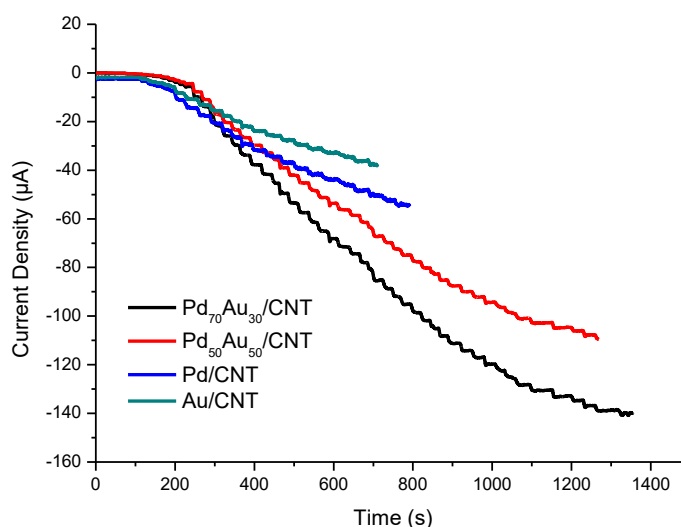
Figure 3. Amperometric response of the Pd/CNT, Au/CNT, $Pd_{70}Au_{30}$/CNT and $Pd_{50}Au_{50}$/CNT GCEs for the successive addition of different concentration of H_2O_2 into constantly stirred 0.1 M phosphate buffer solution, pH 7.4 . Applied potential: -0.4 V.

4. CONCLUSIONS AND DISCUSSION

The new H_2O_2sensor was constructed by Pd/CNT, Au/CNT, $Pd_{70}Au_{30}$/CNT and $Pd_{50}Au_{50}$/CNT catalysts. Electrochemical experiments were conducted to examine the effect of second metal addition to electrochemical sensing ability. These experiments indicated that the prepared $Pd_{70}Au_{30}$/CNT sensor displayed good performance for H2O2 detection with low working potential and high sensitivity.

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