Research Article

Bimetallic Pt-Ru Nanoparticle Catalyst for Hydrogen Peroxide Detection

Metini Janyasupab,1 Yuan Zhang,2 Po-Yuan Lin,3 Brandon Bartling,1 Jiaqiang Xu,2 and Chung-Chiun Liu1

1 Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA
2 Department of Chemistry, Shanghai University, Shanghai 200444, China
3 Department of Material Sciences and Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

Correspondence should be addressed to Metini Janyasupab, mxj52@case.edu

Received 10 June 2011; Revised 3 August 2011; Accepted 4 August 2011

Academic Editor: Charles M. Lukehart

Copyright © 2011 Metini Janyasupab et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A bimetallic Pt-Ru nanoparticle catalyst was prepared and characterized for the enhancement of hydrogen peroxide (H2O2) detection in biosensing applications. The particles were synthesized via sodium borohydride reduction, with low heat treatment, and characterized by TEM and HRTEM. The chemical composition analyses were performed by EDX. The bimetallic particle diameters ranged from 2 to 12 nm, with an average of 4.5 nm. The Pt-Ru catalyst exhibited an improved performance at low overpotential (+0.2 V versus Ag/AgCl reference electrode) in H2O2 detection, suggesting a sensitivity value of 78.95 µA · mM−1 (or 402.1 µA · mM−1 · cm−2) which was 30% higher than that for the single Pt catalyst. The major contribution of this enhancement comes from the stronger oxygen adsorption on Ru metal. The Pt-Ru catalyst also showed a more stable signal at the high overpotential (+0.4 V versus Ag/AgCl), providing better accuracy in the detection of H2O2.

1. Introduction

Measuring hydrogen peroxide (H2O2) is important as an indicator in many enzymatic reactions [1–4]. Its deviation from a normal metabolic condition is an indicator of cell function failures. For example, the deficit of insulin is often related to the lower level H2O2, due to a decrease in the glucose conversion process [5, 6]. Clark and Lyons [7] demonstrated the electrochemical oxidation of H2O2 from the glucose oxidase enzymatic reaction that nowadays is commonly used for diabetic diagnosis and management. Furthermore, the other enzymatic reactions that produce H2O2 can also be used to quantify the analytes by the same principle as glucose oxidation. Therefore, the detection of H2O2 by electrochemical oxidation is important.

Metal catalysts such as platinum, palladium, gold, or iridium [8–13] are often used for H2O2 biosensing applications. Based on the theoretical trend and simulation studies [14–18], Ru apparently requires less activation energy than Pt to adsorb OHads as well as Oads. Gsell and coworkers [19, 20] reported that the oxygen adsorption preferably occurred onto the Ru (0001), hcp, surface. This observation may allow the Oads inhibitor to interact with Ru metal, thereby minimizing the side reactions to poison the Pt metal. Consequently, Pt active binding sites may have a higher possibility of interacting with H2O2, enhancing the catalytic activity of the H2O2 detection.

In our research, the Pt-Ru nanoparticles were synthesized by using sodium borohydride reduction. Material characterization was assessed by using TEM and EDX to examine the structural property and verify elemental composition, respectively. For electrochemical performance, the detection of H2O2 was performed on a 5% wt. Pt-Ru catalyst working electrode and experimentally assessed by amperometry. Our study demonstrated that the Pt-Ru catalyst shows a significantly higher sensitivity of amperometric current at an overpotential of +0.2 V versus Ag/AgCl, and a more stable signal at +0.4 V overpotential than that for the single Pt and single Ru.
2. Experimental

2.1. Chemical Materials for the Synthesis. Hydrogen hexachloroplatinate (IV) hexahydrate (H$_2$PtCl$_6$·6H$_2$O, 37.5% Pt basis), ruthenium (III) chloride hydrate (RuCl$_3$·nH$_2$O, 99.8% purity) were used as precursors for the Pt and Ru metal nanoparticles, respectively. Citric acid (99.5 wt.%) and sodium borohydride (NaBH$_4$, 99 wt.%) were prepared as the capping and reducing agent, respectively. The pH of the solution was adjusted by sodium hydroxide solution. All chemicals were purchased from Sigma Aldrich (St. Louis, MO) and used as received without further purification. Vulcan XC 72 carbon black (Cabot, Boston, MA) was used as a supporting material. Nafion solution (LIQUION) was purchased from Ion Power Inc., New Castle, DE.

2.2. Preparation of Pt-Ru Nanoparticle Catalyst. The Pt-Ru was synthesized via the borohydride reduction as published by Shimazaki et al. [21] with the following modifications: the Pt and Ru precursors were dissolved separately in deionized (DI) water achieving a 1.8 mM metal solution. 5.55 mL of both Pt and Ru solution (for Pt-Ru, 1:1 ratio) was added together to obtain a 0.01 M bimetallic Pt-Ru solution. The citric acid was added to prevent particle agglomeration at a molar ratio of citric acid to the metal solution of 0.42. The bimetallic Pt-Ru solution was then adjusted to pH = 7.0 by 0.1 M NaOH solution. Finally, the nanoparticle solution was then added dropwise by the amount of NaBH$_4$ 1.4-times the theoretical value of the number of electron required to reduce the metal solution. The solution was stirred overnight for the completion of the chemical reduction. For nanoparticle carbon-paste catalyst preparation, the Pt-Ru solution was sonicated for 30 minutes, and the active carbon black powder Vulcan XC was then added. The catalyst solution was stirred overnight, removing the liquid by centrifugation and was then dried at 50°C in vacuum for 12–20 hours.

2.3. Material Characterization. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained by Techai F30 FEI with the high accelerating voltage of 300 keV. The TEM samples of Pt, Pt-Ru, and Ru nanoparticle solution had initially undergone sonication for 3 hours. A droplet of the solution was deposited onto an ultrathin carbon-copper grid (Ted Pella, Inc., Redding CA) and dried at room temperature. The chemical composition and elemental mapping were performed in the same sample by energy dispersive X-ray spectroscopy (EDX).

2.4. Electrochemical Testing. Amperometric studies were carried out. A glassy carbon rotational disk electrode (RDE, diameter of 5 mm.) and the Electrochemical Workstation, Model 660 C, CH Instrument (Austin, TX) were used. 8 mg of 5% wt. Pt-Ru nanoparticle catalyst was grounded and mixed with ethanol (200 μL). Then, 4 μL of this catalytic solution was deposited onto a glassy carbon electrode and dried at room temperature for 10 minutes. Finally, a 4 μL of 5 wt.% Nafion solution was then deposited on top of the electrode and dried for another 10 minutes in open air. Prior to the experiment, the electrode was washed thoroughly with isopropanol and acetone in sequence, then polished by 0.05 μm aluminum powder solution and sonicated for 10 minutes to remove any remaining residue. A three-electrode system of a Pt counter electrode, an Ag/AgCl reference electrode, and a glassy carbon working electrode was employed for the amperometric studies. The working electrode was operated at a rotational speed 900 rpm, which was determined to adequately maintain the hydraulic effect. Testing samples were performed in 0.1 M PBS at pH 7.2 with 0.15 M KCl as supporting electrolyte.

3. Results and Discussion

3.1. Structure and Cluster Size. Figures 1–3 show typical TEM images of Pt-Ru, Pt, and Ru nanoparticles in aqueous solution. The structural formation and cluster size of the Pt-Ru appeared different from both the single Pt and the single Ru. As shown in Figure 1(a), the bimetallic cluster appeared highly dispersed. On the other hand, each single Pt cluster connected to its neighboring cluster, forming a
branch-like network as seen in Figure 2(a). In spite of the different structural formation, the single Pt had a similar particle size to that of Pt-Ru. Both of them ranged from 2 to 12 nm, with an average diameter of 4.0 and 4.5 nm for the Pt and the Pt-Ru, respectively.

Furthermore, at a higher resolution of the TEM image (Figure 1(b)), the phase contrast lattice fringes of the Pt-Ru are nearly unnoticeable. In contrast, those lattice fringes found in the single Pt are highly visible as shown in Figure 2(b). More interestingly, the Ru appeared amorphous in Figure 3, suggesting that the less crystalline structure of the Pt-Ru could be contributed to the incorporation of Ru metal in this synthesis.

### 3.2. Chemical Composition

Chemical compositions of the samples in Figures 1–3 were performed by EDX analysis. As illustrated by Figure 4, the bimetallic nanoparticles revealed all of the peaks that were found in the single Pt and the single Ru at the exact same location. Thus, the elemental mapping of the Pt-Ru confirmed the presence of both metals in the bimetallic sample. In addition to those peaks, there are other elements that are commonly found in this synthesis and preparation. For example, the Na peak and the O peak were caused by the remaining residues in NaBH₄ reduction. Also, the Cu and Fe peaks were part of the copper grid and TEM instrument.

### 3.3. Electrochemical Characterization

Amperometry was used to evaluate electrochemical performance on three metallic working electrodes. Prior to an experiment, an open circuit potential was measured to determine the equilibrium potential. Among these three metals, the Pt-Ru working electrode has the open circuit potential of +0.25 V, which was higher than that of the Ru (0.00 V), but lower than the single Pt (+0.30 V) versus Ag/AgCl reference electrode. Because each metal has a different equilibrium potential, overpotential is considered to quantify the actual performance of the metals in the H₂O₂ detection [22]. Thus, two overpotentials of +0.2 and +0.4 V versus Ag/AgCl were arbitrarily selected based on H₂O₂ detecting scheme in physiological fluid. Furthermore, in order to directly relate the contribution of H₂O₂ to the current response, the electrode was operated at 900 rpm to control the diffusion limiting current. Thus, only the catalytic reaction from H₂O₂ contributed to a change of current.

Figure 5 shows the amperometric response of each metallic catalyst at the low overpotential of +0.2 V, and each increasing step of current corresponds to 0, 0.5, 1, 2, 3, 5, 7,
and 9 mM H₂O₂. The sensitivity of each metal is evaluated by the steady-state current calibration curve as shown in the insert plot. In particular, the sensitivity of the Pt-Ru was estimated to be 78.95 μA·mM⁻¹ or 402.1 μA·mM⁻¹·cm⁻² (based on the geometric area) whereas the single Pt and the single Ru have the sensitivity of 59.93 and 11.67 μA·mM⁻¹, respectively. Therefore, the Pt-Ru catalyst showed superior performance and improved the sensor’s sensitivity by 31.7–57.6% when compared to single metallic catalysts.

Figure 6 shows the testing results of the electrode materials shown in Figure 5 but at a higher overpotential of +0.4 V. The sensor sensitivity of the Pt-Ru working electrode was 105.7 μA·mM⁻¹. Unlike at low overpotential, the bimetallic sensitivity was lower than that of the single Pt by 13.2%. Nevertheless, the Pt-Ru had the smaller standard deviation, indicating a good stability of the electrode at this higher overpotential.

In practical applications, a low oxidation potential to H₂O₂ is preferred for the detection of H₂O₂ to minimize the oxidation of any other chemical species, and our experimental results show that at the low overpotential of +0.2 V, the Pt-Ru working electrode is preferred to detect H₂O₂. According to the bifunctional theory by Watanabe et al. [23], the incorporation of the bimetallic Pt-Ru could minimize the side reactions [24, 25] on Pt catalyst sites. Because Ru required less adsorption energy than Pt, oxygen and proton would be preferably adsorbed by Ru(OH)₂. As a result, more H₂O₂ interacted with the Pt active binding sites [26–30], which led to a favorable condition for the oxidation of the H₂O₂ in this case. Hence, the bimetallic catalyst could provide a higher oxidation current output from the H₂O₂ detection, translating to higher sensitivity. However, at a high overpotential of +0.4 V, the adsorption of O species in both metals could increase and form Pt(OH)₂·O₂ and Ru(OH)₂·O₂ poisoning the surface of the electrode. Therefore, the bimetallic catalyst might not be as sensitive as the single Pt metal. Nonetheless, its stability was very good and was favored at this overpotential.
4. Conclusion

The electrochemical performance of the bimetallic Pt-Ru catalyst was investigated for \( \text{H}_2\text{O}_2 \) detection. In our study, we found that the sensitivity of the Pt-Ru was enhanced by 30% when compared to the single Pt. Not only did the Pt-Ru improve the catalytic performance, the smaller concentration of the expensive Pt metal could provide benefits to sensor manufacturing and lead to practical applications in enzymatic determination related to many other \( \text{H}_2\text{O}_2 \)-related reactions.

Acknowledgments

This paper study is financially supported by Royal Thai Government Scholar Fellowship, China Scholarship Council and a research grant from the Delta Environmental Government Scholar Fellowship, China Scholarship Council. Special thanks to Amir Avishai for an enlightening discussion in the TEM and HRTEM analysis assistance.

References


