Research Article

Fabrication of Nonenzymatic Glucose Sensors Based on Multiwalled Carbon Nanotubes with Bimetallic Pt-M (M = Ru and Sn) Catalysts by Radiolytic Deposition

Sun-Young Kwon, Hai-Doo Kwen, and Seong-Ho Choi

Department of Chemistry, Hannam University, Daejeon 305-811, Republic of Korea

Correspondence should be addressed to Seong-Ho Choi, shchoi@hnu.kr

Nonenzymatic glucose sensors employing multiwalled carbon nanotubes (MWNTs) with highly dispersed Pt-M (M = Ru and Sn) nanoparticles (Pt-M@PVP-MWNTs) were fabricated by radiolytic deposition. The Pt-M nanoparticles on the MWNTs were characterized by transmittance electron microscopy, elemental analysis, and X-ray diffraction. They were found to be well dispersed and to exhibit alloy properties on the MWNT support. Electrochemical testing showed that these nonenzymatic sensors had larger currents (mA) than that of a bare glassy carbon (GC) electrode and one modified with MWNTs. The sensitivity (A mM^{-1}), linear range (mM), and detection limit (mM) (S/N = 3) of the glucose sensor with the Pt-Ru catalyst in NaOH electrolyte were determined as 18.0, 1.0–2.5, 0.7, respectively. The corresponding data of the sensor with Pt-Sn catalyst were 889.0, 1.00–3.00, and 0.3, respectively. In addition, these non-enzymatic sensors can effectively avoid interference arising from the oxidation of the common interfering species ascorbic acid and uric acid in NaOH electrolyte. The experimental results show that such sensors can be applied in the detection of glucose in commercial red wine samples.

1. Introduction

The measurement of glucose concentrations is important not only to diabetes diagnosis but also to the food and textile industries, wastewater treatment, and environmental monitoring [1–4]. The first enzyme electrode capable of this was reported in 1962 [5]; sensors' sensitivities, selectivities and reliabilities, detection limits, costs, and response times have all seen much improvement since. There have been several improvements in the immobilization of enzymes and designs of redox systems [6, 7]. Glucose oxidase (GOx), an enzyme catalyst, has been widely used in electrochemical biosensors as it has the advantages of high sensitivity and selectivity, simple instrumentation, low production cost, and promising response speed. However, the low stabilities of enzymatic sensors and the interference of some electro-oxidizable species remain problems in its application [8, 9]. To address these issues, nonenzymatic sensors based on the direct electrocatalytic oxidation of glucose are being investigated.

The majority of nonenzymatic electrochemical glucose sensors rely on the current response of glucose oxidation directly at the electrode surface. Therefore, the electrocatalytic activity of the electrode strongly affects both the sensitivity and selectivity of glucose detection. Initial research developing nonenzymatic sensors focused on the use of noble metals, such as Pt and Au, especially Pt-based amperometric electrodes [10, 11]. However, such Pt-based glucose sensors lack sufficient selectivity and sensitivity due to chemisorbed intermediates and electroactive species. The desire for better and cheaper electrocatalysts has resulted in bimetallic systems being developed. Pt-Au [12], Pt-Pb [8, 13–16], and Pt-Ru [17] have all displayed high electrocatalytic activities to glucose oxidation.

Effective fabrication of electrocatalysts also relies on the supporting material [18]. Catalyst dispersion and utilization have been shown to be improved by supporting Pt-Ru nanoparticles on high-surface-area carbon materials, such as carbon nanotubes (CNTs), carbon nanofibers, carbon

nanocoils, and carbon nanohorns [19–22]. A systematic study has shown that multiwalled carbon nanotubes (MWNTs) are the best of the carbon based electrocatalyst supports [23]. In principle, MWNTs are seamless cylinders. However, they often have defects where the attachment of Pt-based alloy nanoparticles most likely occurs.

In a preliminary report, Pt-Ru nanoparticles were deposited on the surfaces of various carbon supports, including Vulcan XC-71, Ketjen-300, Ketjen-600, single-walled carbon nanotubes (SWNTs), and MWNTs for use as fuel cell catalysts using γ-ray irradiation without anchoring agents [24]. The metal (Ag or Pd) and alloy (Pt-Ru) nanoparticles were also deposited on the surfaces of single-walled carbon nanotubes (SWNTs) [25] and porous carbon supports using γ-irradiation without anchoring agents [26]. However, metallic alloy nanoparticles aggregated on the surfaces of the carbon supports due to their hydrophobic nature. This aggregation was overcome by modifying the surface of the carbon support to give it hydrophilic properties. This was done by *in situ* polymerization of β-caprolactone, methacrylate, and pyrrole using oxidizing agents as initiators [27]. Pt-Ru nanoparticles were then deposited on the polymer-wrapped MWNT supports to produce a direct methanol fuel cell (DMFC) anode catalyst.

Pt-Ru nanoparticles have also been deposited on functional polymer (FP)-grafted MWNTs obtained by radiation-induced graft polymerization (RIGP), to produce an anode catalyst for DMFCs [28]. This method involved two steps: grafting the functional polymer onto the MWNTs by RIGP; and then depositing the Pt-Ru nanoparticles onto the MWNTs by radiation-induced reduction. Pt-M nanoparticles on FP-MWNT supports have also been prepared via a one-step process initiated by free radicals and hydrated electrons generated during γ-irradiation in an aqueous solution.

In this study, Pt-M (M = Ru and Sn) catalysts on PVP-MWNTs for detection of glucose were synthesized by a one-step radiation reaction. Their structural and electrochemical properties were characterized by transmittance electron microscopy (TEM), X-ray diffraction (XRD), and elemental analysis. These catalysts were then hand-casted to produce nonenzymatic sensors on GC electrodes with Nafion as binder. The prepared nonenzymatic sensors were tested for their efficiencies of sensing glucose in a phosphate buffer or NaOH solution. Furthermore, the sensors' detection limits were tested and compared with a commercial glucometer in measuring total glucose contents of four commercially available red wines. The prepared nonenzymatic sensors showed remarkably sensitive response currents towards glucose in a NaOH electrolyte. It was also highly stable, produced reproducible results, and was capable of resisting interference.

2. Experimental Section

2.1. Chemicals. $H_2PtCl_6 \times H_2O$ (37.5% Pt), $RuCl_3 \times H_2O$ (41.0% Ru), $SnCl_2 \times H_2O$ (52.0% Sn), and vinylpyrrolidone (VP) were of analytical reagent grade (Sigma-Aldrich, USA) and used without further purification. MWNTs (CM-95) were supplied by Hanwha Nanotech Co., Ltd. (Korea).
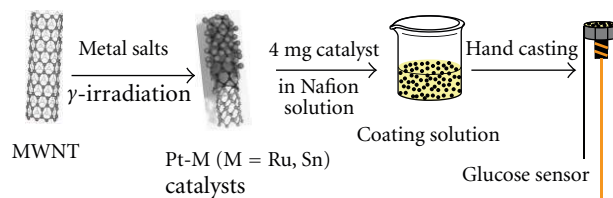

Figure 1: Radiation-induced fabrication of glucose sensors based on Pt-M (M = Ru, Sn) catalysts.

Nafion (perfluorinated ion-exchange resin, 5% (w/v) in 90% aliphatic alcohol/10% water solution) was also purchased from Sigma-Aldrich (USA). Solutions were prepared with water of final resistance 18.2 MΩcm purified in a Milli-Q plus water purification system (Millipore Co. Ltd., USA) and degassed prior to each measurement. Other chemicals were of reagent grade.

2.2. Preparation of the Nonenzymatic Glucose Sensors with Pt-M@PVP-MWNTs Catalysts. Figure 1 outlines the preparation of the nonenzymatic glucose sensors. MWNTs were first purified to remove the catalyst and noncrystallized carbon impurities. They were then treated with phosphoric solution. The purified MWNTs were used as the supporting material for the deposition of the metallic catalysts. The Pt-Ru@PVP-MWNT catalysts were prepared by dissolving $H_2PtCl_6 \times H_2O$ (0.43 g), $RuCl_3 \times H_2O$ (0.41 g), and VP (0.5 g) in deionized water (188 mL). 1.00 g purified MWNT was added to this solution. Nitrogen gas was bubbled for 30 min through the solution to remove oxygen. After which, the solution was irradiated by γ-rays from Co-60 source under atmospheric pressure and ambient temperature. A total irradiation dose of 30 kGy (dose rate = 6.48×10^5/h) was applied. Pt-Ru@PVP-MWNT catalysts were then precipitated after the γ-irradiation. The catalysts were filtered and dried in a vacuum oven at 50°C for 8 hrs. The Pt-Sn@PVP-MWNTs catalysts were prepared similarly.

The nonenzymatic sensors incorporating Pt-M@PVP-MWNTs (M = Ru and Sn) were prepared by mixing a solution of Pt-M@PVP-MWNT (4.0 mg) catalysts in 5.0%-Nafion solution (40 μL), and then coating a portion (10 μL) of this on to the surface of a GC electrode (2 mm in diameter) by hand casting.

2.3. Instrumentation. The catalysts' particle sizes and morphologies were analyzed by HR-TEM (JEOL, JEM-2010, USA). Their metal atom contents were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Jobin-Yvon, Ultima-C, USA). X-ray diffraction (XRD) patterns of the samples were obtained using a Japanese Rigaku D/max-rA X-ray diffractometer equipped with graphite monochromatized Cu Ka radiation (l = 0.15414 nm). The scanning range was 5–80° at a scanning rate of 5°/min.

The catalysts' efficiencies for the electro-oxidation of glucose were tested by their coating on glassy carbon electrodes. This was achieved by catalytic inks being prepared by mixing

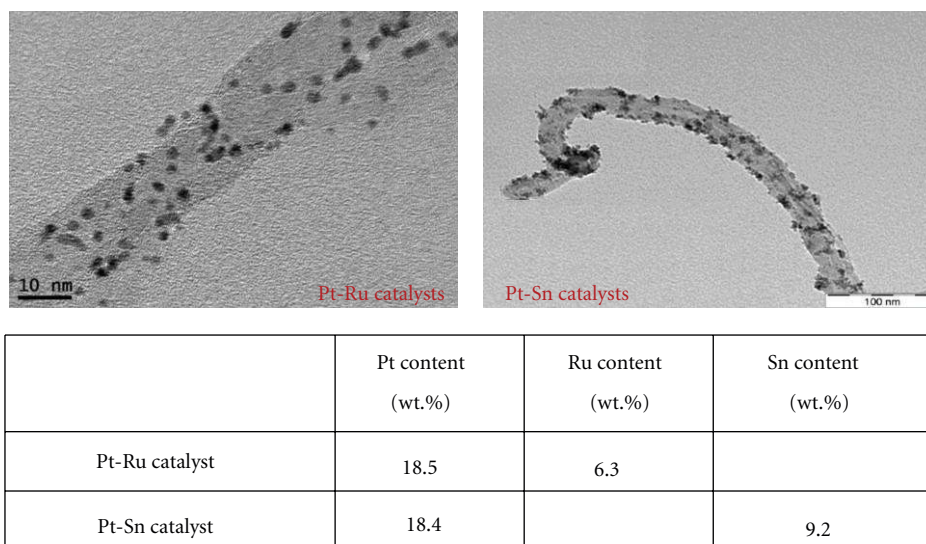|	Pt content (wt.%)	Ru content (wt.%)	Sn content (wt.%)
Pt-Ru catalyst	18.5	6.3	
Pt-Sn catalyst	18.4		9.2

FIGURE 2: TEM images and ICP-AES data of Pt-M (M = Ru, Sn) catalysts prepared by radiation-induced reduction.

the Pt-M@PVP-MWNTs catalysts (4.0 mg) and 5% Nafion solution (0.04 mL) and stirring for 24 hrs. The catalytic inks were then applied on glassy carbon (2 mm diameter) by wet coating and dried in a vacuum oven at 50°C under nitrogen gas. The electro-oxidation of glucose was examined using the Pt-M@FP-MWNTs catalyst electrodes, submerged in PBS buffer or NaOH electrolyte, by cyclic voltammetry (EG&G Instruments, Potentiostat/Galvanostat model 283, USA).

3. Results and Discussion

3.1. One-Step Preparation of Pt-M@PVP-MWNTs Catalysts (M = Ru and Sn) by γ-Irradiation and Their Characterization. When γ-ray irradiated in aqueous solutions, two active species, free radicals, and solvated electrons (eaq−) were generated, as shown in the following equation:

$$H_2O \longrightarrow eaq^-, H^+, H^\bullet, OH^\bullet, H_2O_2, H_2 \qquad (1)$$
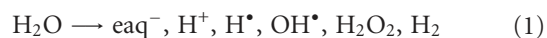
Metallic nanoparticles can be prepared by the solvated electrons, which induce the reduction of aqueous metallic ions and then grafted onto polymer subtracts by the induced free radicals as initiators. Metallic nanoparticles have been prepared using the solvated electrons, eaq−, induced during γ-irradiation, in aqueous solution for use as antibacterial materials and catalysts in fuel cells and chemical reactions [24, 29, 30]. The metallic nanoparticles were then successfully grafted on to the surfaces of the MWNTs by free radicals induced during γ-irradiation [28, 31, 32]. However, little study has been made on the preparation of metallic catalysts on polymer-grafted MWNTs using both the solvated electrons and free radicals induced during γ-irradiation in aqueous solution. The reaction mixture was initiated by vinyl pyrrolidone as an anchoring agent, metallic salts, and MWNT as supporting material in order to prepare the catalysts (Figure 1).

Figure 2 shows the TEM images and ICP-AES data of the catalysts prepared by γ-irradiation. They show that the Pt-M catalysts were successfully deposited on to the MWNTs surfaces when vinyl pyrrolidone was used as an anchoring agent. Without the anchoring agent, the Pt-M nanoparticles aggregated on carbon surface due to the hydrophobic nature of the carbon surface [24]. The mean particle size of the Pt-M nanoparticles (M = Ru and Sn) was between 7.5 and 15 nm. As the TEM images show, the Pt-M nanoparticles were well dispersed on the surface of PVP-MWNT supports. Thus, these catalysts are expected to have good efficiencies of glucose oxidation.

Metal content is very important in determining catalytic efficiency. It was measured using ICP-AES (Figure 2). The Pt content (%) in the Pt-M catalysts was higher than the other metal's content for both the Ru and Sn catalysts, despite the catalysts being prepared with the same molar amounts of Pt ion to M ion. This is because the standard reduction potential of the Pt ion is higher than that of other metal ions, leading to quicker reduction of the Pt ions compared with the other metals. The total metal content (%) of the Pt-M@PVP-MWNT catalysts was in the range of 24–26%.

The crystalline nature of the Pt-M nanostructures was confirmed by XRD (Figure 3). All samples show the peak associated with the MWNT supporting material at approximately 26°. The crystallinity of Pt-Ru catalysts was confirmed by the presence of peaks around 39.9°, 46.2°, and 67.4°. These peaks are assigned as Pt (111), (200) planes, and (220), respectively, of the face centered cubic (fcc) structure of platinum and platinum alloy particles [33]. The XRD peaks corresponding to metallic ruthenium with hexagonal structure were not detected for these samples. Figure 3(b) shows the XRD pattern obtained after the oxidizing pretreatment; this technique showed an almost full transformation of the Pt-Sn alloy present after the reduction to the Pt₃Sn alloy. New reflections appearing at 39°, 45.5°, 66°, and 79.5° are characteristic of this cubic phase; small
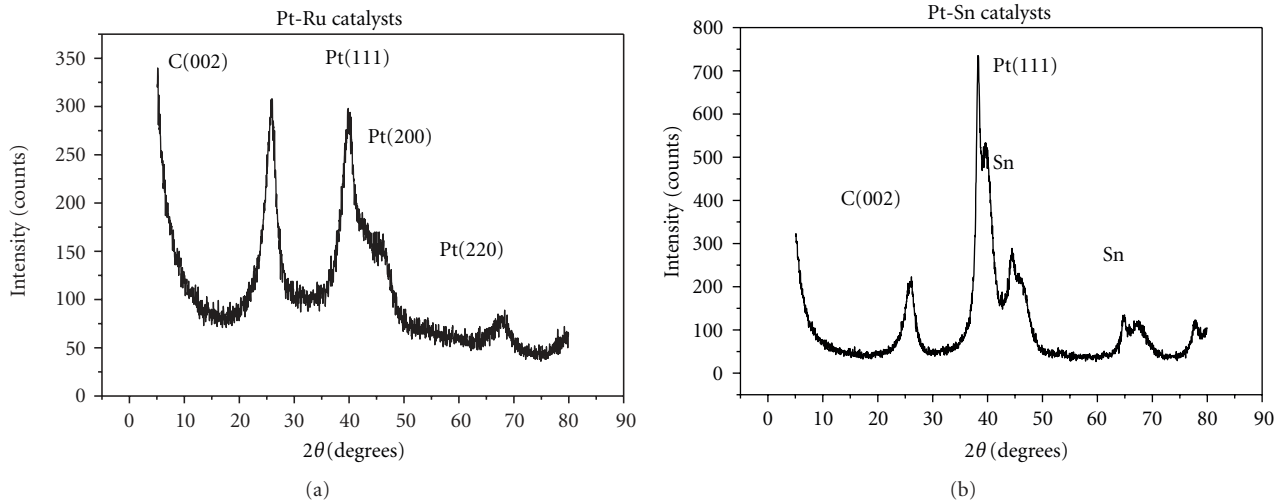
(a)

(b)

FIGURE 3: XRD spectra of the Pt-Ru and Pt-Sn catalysts prepared by radiation-induced reduction.
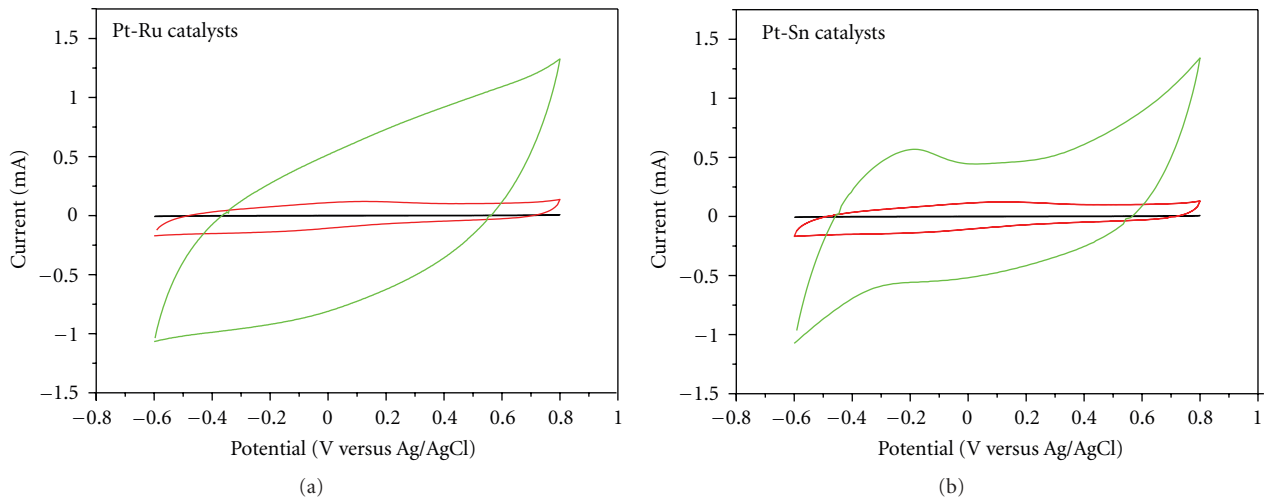

(a)

(b)

FIGURE 4: Cyclic voltammograms of the glassy carbon electrode (black line), MWNT electrode (red line), and glucose sensor (green line) prepared by Pt-Ru (a) and Pt-Sn (b) catalysts in 0.1 M PBS. Scan rate: 50 mV/s.

peaks corresponding to the presence of Pt-Sn phase can be yet observed in the X-ray diffraction pattern at 41.5° and 44° [34]. The crystallinities of the catalysts were also assigned, as shown in Figure 3, showing that crystalline metallic alloy nanoparticles were successfully synthesized by the solvated electrons and the free radicals induced during γ-irradiation. This γ-irradiation method is very useful for preparing well-dispersed metallic nanoparticles on support materials for the detection of glucose.

3.2. Nonenzymatic Sensors and Their Determination of Glucose in Commercial Red Wines. Electrochemical experiments were performed to test the fabricated nonenzymatic sensors with Pt-Ru or Pt-Sn catalysts in 0.1 M PBS buffer solution. Figure 4 shows the cyclic voltammograms of a GC electrode, a MWNT electrode, and the nonenzymatic biosensors at a scan rate of 50 mV/s. The results demonstrate that the nonenzymatic sensors had larger currents (mA) than the

bare GC electrode and the MWNT electrode due to the high electrical conductivities of the metallic alloy nanoparticles.

Figure 5 shows cyclic voltammograms of glucose oxidation on the nonenzymatic sensor with the Pt-Ru catalyst in a 0.1 M phosphate buffer solution (PBS) (pH = 7.0), as a function of glucose concentration. The sensor had a sensing range of glucose concentrations between 5.0–100 mM, as shown in Figure 5(b). Figure 6 shows the calibration curves of the Pt-Sn containing biosensor to glucose concentration in PBS. The detection response range for glucose was found to be 5.0–100 mM in PBS electrolyte. However, the oxidation peak for glucose hardly shifted indicating that the prepared nonenzymatic sensors cannot be used for the determination of glucose concentrations in real samples.

The electro-oxidation of glucose on platinum electrodes in alkaline solutions using cyclic voltammetry and the modulated potential-time waveform technique have been investigated previously [35]. Figure 7 shows the calibration
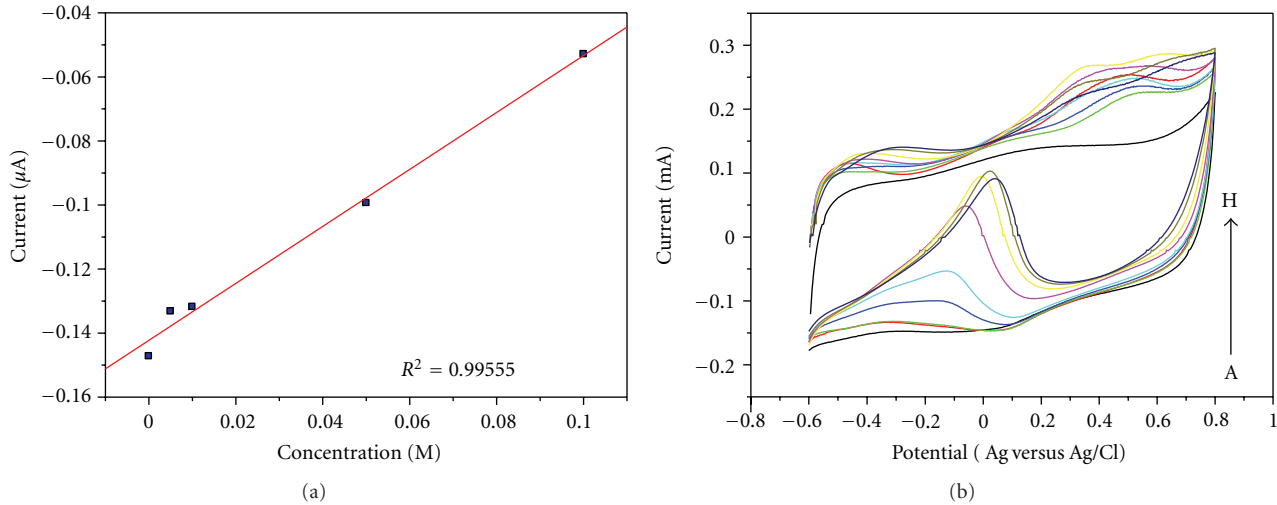
(a)

(b)

FIGURE 5: (a) Calibration curve of glucose sensor based on Pt-Ru catalyst according to glucose concentration in 0.1 M PBS at room temperature. (b) Cyclic voltammograms of the sensor. 0.1 M PBS (A), containing 5 mM (B), 10 mM (C), 50 mM (D), 0.1 M (E), 0.5 M (F), 1 M (G), 1.5 M (H), and 2 M glucose (I). Scan rate: 50 mV/s.
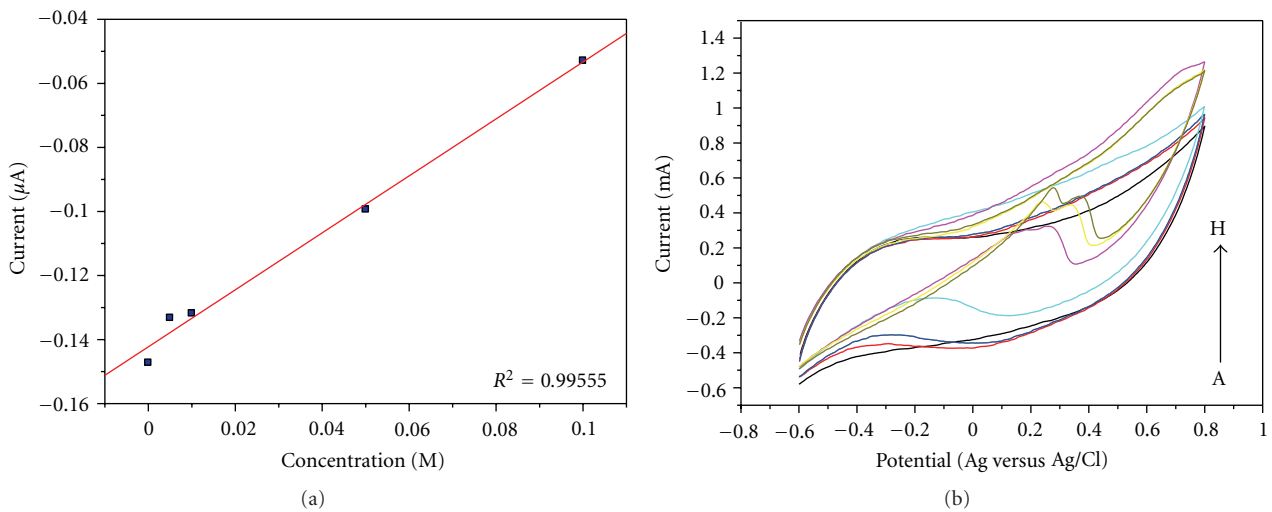

(a)

(b)

FIGURE 6: (a) Calibration curve of glucose sensor based on Pt-Sn catalyst according to glucose concentration in 0.1 M PBS at room temperature. (b) Cyclic voltammograms of the sensor. 0.1 M PBS (A), containing 5 mM (B), 10 mM (C), 50 mM (D), 0.1 M (E), 0.5 M (F), 1 M (G), 1.5 M (H), and 2 M glucose (I). Scan rate: 50 mV/s.

curves for glucose concentration on the Pt-Sn catalyst containing sensor in 0.1 M NaOH electrolyte. Three oxidation peaks (upper), due to D-glucose, D-gluconic acid, and a cathodic peak (down in Figure 7(b)) appeared in the positive scan. They are consistent with the literature data [35], where the observations were carried out at a high glucose concentration of 12 mM. This sensor's response sensing range at -0.1 V is 1.0–3.0 mM in alkaline solution.

Table 1 compares the sensitivities of the fabricated glucose sensors in the two electrolytes. They exhibited higher sensitivities and lower detection limits in the alkaline solution when compared with the PBS. Abbadi and van Bekkum examined the oxidation of glucose on Pt electrodes between pH 2 and 9 [36]. They found that at pH = 9, D-gluconic acid

with high yield and high selectivity from D-glucose on the Pt/C catalyst was obtained at 50°C.

The interferences of ascorbic and uric acids with the glucose assays of the Pt-Sn sensor were observed. All the compounds tested were present at a concentration of 10 mM with a glucose concentration of 10 mM. As shown in Figure 8, the response signals of the acids were negligible or below 0.314%. This implies that the electrode has good selectivity and can be used as a stable sensor for glucose detection.

The commercial red wines Amor (Vina Francisco de Aguirre, Chile), Song Blue (Ginestet, France), Blue Nun (Langguth, Germany), and Carlo Rossi (E&J Gallo, USA) were tested for their glucose contents using the nonenzymatic sensor with Pt-Sn catalyst and a commercial glucometer (Table 2). Glucose levels were determined to be
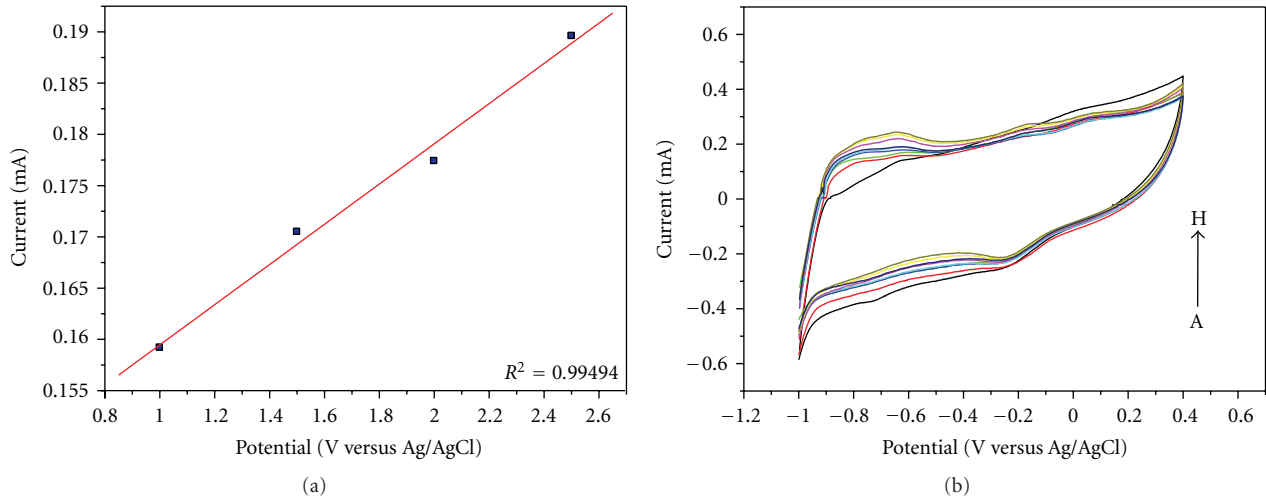
(a)

(b)

FIGURE 7: (a) Calibration curve of glucose sensor based on Pt-Ru catalyst according to glucose concentration in 0.1 M NaOH solution at a scan rate 100 mV/s. (b) Cyclic voltammograms of the sensor at a scan rate 100 mV/s.
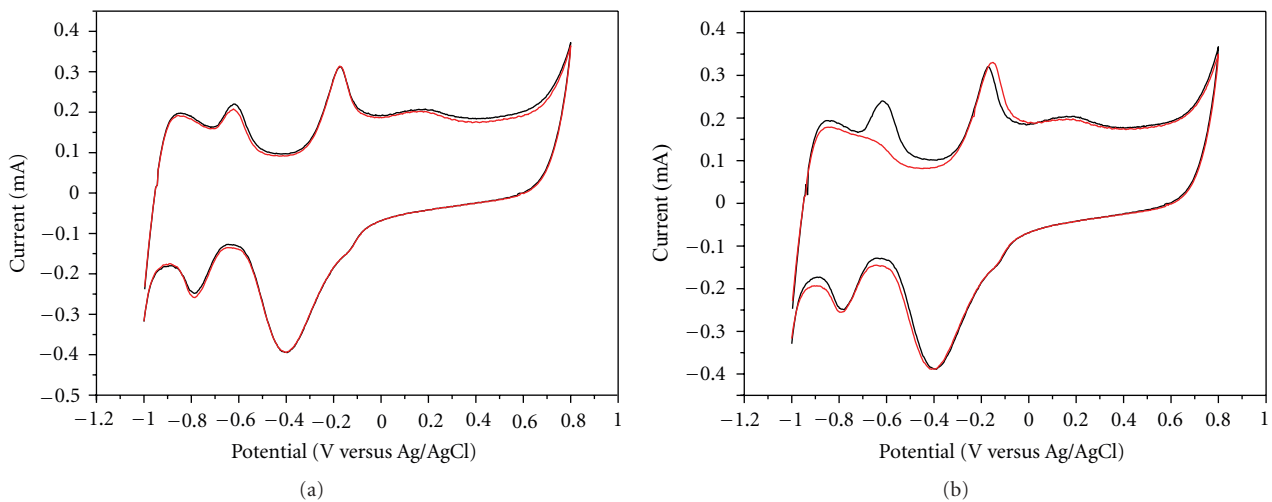

(a)

(b)

FIGURE 8: Cyclic voltammograms of the glucose sensor based on Pt-Sn catalyst in 0.1 M NaOH solution with 10 mM glucose and 10 mM ascorbic acid (a); with 10 mM glucose and 10 mM uric acid (b). The black line indicates tests with solely glucose. The red line indicates tests in the presence of ascorbic acid and uric acid.

TABLE 1: Comparison sensitivity of glucose sensor based on Pt-M catalysts in different electrolyte.

Solution	Catalyst	Sensitivity	Linear range	Detection limit
PBS	Pt-Ru catalyst	$0.810\,\mu A\,mM^{-1}$	5.00–100 mM	5.0 mM
	Pt-Sn catalyst	$0.810\,\mu A\,mM^{-1}$	3.00–100 mM	3.0 mM
NaOH	Pt-Ru catalyst	$889.0\,\mu A\,mM^{-1}$	1.00–3.00 mM	0.3 mM

TABLE 2: Glucose assays for commercial red wines using glucose sensor based on Pt-Sn catalyst and glucometer.

	Amor	Song Blue	Blue nun	Carlo Rossi
Glucose sensor (mg/dL)	40.5	32.1	46.5	45.2
Glucometer (mg/dL)	178	64.0	209	201

The sample (20 μL) was taken from wine solution.

in the range of 32.1–46.5 mg/dL using the nonenzymatic sensor with Pt-Sn catalysts. They did not agree with results from the commercial glucometer (i-Sens, Korea). However, these results show that nonenzymatic sensors with Pt-M catalysts can be used in determining glucose amounts in food chemistry.

4. Conclusion

Nonenzymatic glucose sensors with Pt-M catalysts (M = Ru and Sn) were fabricated by a one-step radiation reaction. Poly(vinyl pyrrolidone) (PVP) was used as an anchoring agent for the deposition of metallic nanoparticles. The sensors' efficiencies were investigated. The one-step radiation fabrication of catalysts based on multiwalled carbon nanotubes with Pt-M (M = Ru and Sn) nanoparticles was successful. The sensitivities (A mM^{-1}), and detection limits (mM) (S/N = 3) of nonenzymatic glucose sensors with Pt-Ru and Pt-Sn catalysts in NaOH electrolyte were determined as 889.0, 18.00, and, 0.3, 0.7, respectively. The sensors effectively avoided interference from ascorbic and uric acids in NaOH electrolyte. They have potential for the determination of glucose in the food industry.

Acknowledgment

References

[1] J. H. Yu, S. Q. Liu, and H. X. Ju, "Glucose sensor for flow injection analysis of serum glucose based on immobilization of glucose oxidase in titania sol-gel membrane," *Biosensors and Bioelectronics*, vol. 19, no. 4, pp. 401–409, 2003.

[2] S. R. Lee, Y. T. Lee, K. Sawada, H. Takao, and M. Ishida, "Development of a disposable glucose biosensor using electroless-plated Au/Ni/copper low electrical resistance electrodes," *Biosensors and Bioelectronics*, vol. 24, no. 3, pp. 410–414, 2008.

[3] J. D. Newman and A. P. F. Turner, "Home blood glucose biosensors: a commercial perspective," *Biosensors and Bioelectronics*, vol. 20, no. 12, pp. 2435–2453, 2005.

[4] Y. M. Uang and T. C. Chou, "Fabrication of glucose oxidase/polypyrrole biosensor by galvanostatic method in various pH aqueous solutions," *Biosensors and Bioelectronics*, vol. 19, no. 3, pp. 141–147, 2003.

[5] L. C. Clark and C. Lyons, "Electrode systems for continuous monitoring in cardiovascular surgery," *Annals of the New York Academy of Sciences*, vol. 102, pp. 29–45, 1962.

[6] B. Wang, B. Li, Q. Deng, and S. Dong, "Amperometric glucose biosensor based on Sol-Gel organic-inorganic hybrid material," *Analytical Chemistry*, vol. 70, no. 15, pp. 3170–3174, 1998.

[7] M. H. Yang, Y. H. Yang, Y. L. Liu, G. L. Shen, and R. Q. Yu, "Platinum nanoparticles-doped sol-gel/carbon nanotubes composite electrochemical sensors and biosensors," *Biosensors and Bioelectronics*, vol. 21, no. 7, pp. 1125–1131, 2006.

[8] H. F. Cui, J. S. Ye, X. Liu, W. D. Zhang, and F. S. Sheu, "Pt-Pb alloy nanoparticle/carbon nanotube nanocomposite: a strong electrocatalyst for glucose oxidation," *Nanotechnology*, vol. 17, no. 9, pp. 2334–2339, 2006.

[9] Z. Dai, G. Shao, J. Hong, J. Bao, and J. Shen, "Immobilization and direct electrochemistry of glucose oxidase on a tetragonal pyramid-shaped porous ZnO nanostructure for a glucose biosensor," *Biosensors and Bioelectronics*, vol. 24, no. 5, pp. 1286–1291, 2009.

[10] S. J. Park, T. D. Chung, and H. C. Kim, "Nonenzymatic glucose detection using mesoporous platinum," *Analytical Chemistry*, vol. 75, no. 13, pp. 3046–3049, 2003.

[11] Y. Y. Song, D. Zhang, W. Gao, and X. H. Xia, "Nonenzymatic glucose detection by using a three-dimensionally ordered, macroporous platinum template," *Chemistry*, vol. 11, no. 7, pp. 2177–2182, 2005.

[12] A. Habrioux, E. Sibert, K. Servat, W. Vogel, K. B. Kokoh, and N. Alonso-Vante, "Activity of platinum-gold alloys for glucose electrooxidation in biofuel cells," *Journal of Physical Chemistry B*, vol. 111, no. 34, pp. 10329–10333, 2007.

[13] Y. Bai, Y. Sun, and C. Sun, "Pt-Pb nanowire array electrode for enzyme-free glucose detection," *Biosensors and Bioelectronics*, vol. 24, no. 4, pp. 579–585, 2008.

[14] H. F. Cui, J. S. Ye, W. D. Zhang, C. M. Li, J. H. T. Luong, and F. S. Sheu, "Selective and sensitive electrochemical detection of glucose in neutral solution using platinum-lead alloy nanoparticle/carbon nanotube nanocomposites," *Analytica Chimica Acta*, vol. 594, no. 2, pp. 175–183, 2007.

[15] J. Wang, D. F. Thomas, and A. Chen, "Nonenzymatic electrochemical glucose sensor based on nanoporous PtPb networks," *Analytical Chemistry*, vol. 80, no. 4, pp. 997–1004, 2008.

[16] Y. Sun, H. Buck, and T. E. Mallouk, "Combinatorial discovery of alloy electrocatalysts for amperometric glucose sensors," *Analytical Chemistry*, vol. 73, no. 7, pp. 1599–1604, 2001.

[17] F. Xiao, F. Zhao, Y. Zhang, G. Guo, and B. Zeng, "Ultrasonic electrodeposition of gold - platinum alloy nanoparticles on ionic liquid—chitosan composite film and their application in fabricating nonenzyme hydrogen peroxide sensors," *Journal of Physical Chemistry C*, vol. 113, no. 3, pp. 849–855, 2009.

[18] N. Y. Hsu, C. C. Chien, and K. T. Jeng, "Characterization and enhancement of carbon nanotube-supported PtRu electrocatalyst for direct methanol fuel cell applications," *Applied Catalysis B*, vol. 84, no. 1-2, pp. 196–203, 2008.

[19] E. S. Steigerwalt, G. A. Deluga, and C. M. Lukehart, "Pt-Ru/carbon fiber nanocomposites: synthesis, characterization, and performance as anode catalysts of direct methanol fuel cells. A search for exceptional performance," *Journal of Physical Chemistry B*, vol. 106, no. 4, pp. 760–766, 2002.

[20] T. Hyeon, S. Han, Y. E. Sung, K. W. Park, and Y. W. Kim, "High-performance direct methanol fuel cell electrodes using solid-phase-synthesized carbon nanocoils," *Angewandte Chemie*, vol. 42, no. 36, pp. 4352–4356, 2003.

[21] K. W. Park, J. H. Choi, K. S. Ahn, and Y. E. Sung, "PtRu alloy and PtRu-WO$_3$ nanocomposite electrodes for methanol electrooxidation fabricated by a sputtering deposition method," *Journal of Physical Chemistry B*, vol. 108, no. 19, pp. 5989–5994, 2004.

[22] R. Yang, X. Qiu, H. Zhang et al., "Monodispersed hard carbon spherules as a catalyst support for the electrooxidation of methanol," *Carbon*, vol. 43, no. 1, pp. 11–16, 2005.

[23] A. L. M. Reddy and S. Ramaprabhu, "Pt/SWNT-Pt/C nanocomposite electrocatalysts for proton-exchange membrane fuel cells," *Journal of Physical Chemistry C*, vol. 111, no. 44, pp. 16138–16146, 2007.

[24] S. D. Oh, K. R. Yoon, S. H. Choi et al., "Dispersion of Pt-Ru alloys onto various carbons using γ-irradiation," *Journal of Non-Crystalline Solids*, vol. 352, no. 4, pp. 355–360, 2006.

[25] S. D. Oh, B. K. So, S. H. Choi et al., "Dispersing of Ag, Pd, and Pt-Ru alloy nanoparticles on single-walled carbon nanotubes by γ-irradiation," *Materials Letters*, vol. 59, no. 10, pp. 1121–1124, 2005.

[26] K. D. Seo, S. D. Oh, S. H. Choi, S. H. Kim, H. G. Park, and Y. P. Zhang, "Radiolytic loading of the Pt-Ru nanoparticles onto the porous carbons," *Colloids and Surfaces A*, vol. 313-314, pp. 393–397, 2008.

[27] H. B. Bae, J. H. Ryu, B. S. Byun, S. H. Jung, and S. H. Choi, "Facile synthesis of novel Pt-Ru@PPy-MWNT electrocatalysts for direct methanol fuel cells," *Current Applied Physics*, vol. 10, no. 2, pp. S44–S50, 2010.

[28] D. S. Yang, D. J. Jung, and S. H. Choi, "One-step functionalization of multi-walled carbon nanotubes by radiation-induced graft polymerization and their application as enzyme-free biosensors," *Radiation Physics and Chemistry*, vol. 79, no. 4, pp. 434–440, 2010.

[29] S. H. Choi, S. Lee, S. J. Kim et al., "Preparation of polymer-stabilized palladium-silver bimetallic nanoparticles by γ-irradiation and their catalytic properties for hydrogenation of cis,cis-1,3-cyclooctadiene," *Catalysis Letters*, vol. 105, no. 1-2, pp. 59–65, 2005.

[30] Y. O. Kang, S. H. Choi, A. Gopalan, K. P. Lee, H. D. Kang, and Y. S. Song, "One-pot synthesis of a few nanocomposites with poly(N-vinylcarbazole) and CdS, Ag, Pd50-Ag50, and Pt50-Ru50 nanoparticles with γ irradiation," *Journal of Applied Polymer Science*, vol. 100, no. 3, pp. 1809–1815, 2006.

[31] M. H. Piao, D. S. Yang, K. R. Yoon, S. H. Lee, and S. H. Choi, "Development of an electrogenerated chemiluminescence biosensor using carboxylic acid-functionalized MWCNT and Au Nanoparticles," *Sensors*, vol. 9, no. 3, pp. 1662–1677, 2009.

[32] K. I. Kim, H. Y. Kang, J. C. Lee, and S. H. Choi, "Fabrication of a multi-walled nanotube (MWNT) ionic liquid electrode and its application for sensing phenolics in red wines," *Sensors*, vol. 9, no. 9, pp. 6701–6714, 2009.

[33] M. Tsuji, M. Kubokawa, R. Yano et al., "Fast preparation of PtRu catalysts supported on carbon nanofibers by the microwave-polyol method and their application to fuel cells," *Langmuir*, vol. 23, no. 2, pp. 387–390, 2007.

[34] J. Araña, P. Ramirez de la Piscina, J. Llorca, J. Sales, N. Homs, and J. L. G. Fierro, "Bimetallic silica-supported catalysts based on Ni-Sn, Pd-Sn, and Pt-Sn as materials in the CO oxidation reaction," *Chemistry of Materials*, vol. 10, no. 5, pp. 1333–1342, 1998.

[35] H. W. Lei, B. Wu, C. S. Cha, and H. Kita, "Electro-oxidation of glucose on platinum in alkaline solution and selective oxidation in the presence of additives," *Journal of Electroanalytical Chemistry*, vol. 382, no. 1-2, pp. 103–110, 1995.

[36] A. Abbadi and H. van Bekkum, "Effect of pH in the Pt-catalyzed oxidation of d-glucose to d-gluconic acid," *Journal of Molecular Catalysis A*, vol. 97, no. 2, pp. 111–118, 1995.