Can Tho University Journal of Science
website: sj.ctu.edu.vn

DOI: 10.22144/ctu.jen.2017.028

Electrospun CuO/Ag nanofibers for nonenzymatic glucose sensors

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Article info.

Received 15 May 2016
Revised 29 Nov 2016
Accepted 29 Jul 2017

Keywords

Electrospinning, glucose sensor, nonenzyme

ABSTRACT

Nonenzymatic biosensors based on Ag/CuO nanofibers have been successfully investigated. Polyvinylpyrrolidone nanofibers loaded $AgNO_3/Cu(NO_3)_2$ were successfully synthesized by an electrospinning method. The conditions of electrospinning included 8% PVP solution, feed rate of polymer solution of 0.5 mL/h, applied voltage of 20 kV, and the tip-to-collector distance of 8 cm. The nanofibers were carbonized at 300, 450, and 600°C to obtain Ag/CuO nanofibers. The Ag/CuO nanofibers were characterized by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction analyses to confirm the morphology as well as the formation of copper oxide and silver. The Ag/CuO nanofibers were used to construct a nonenzymatic glucose sensor. The Ag/CuO NFs-IGZO electrode was applied to detect glucose by cyclic voltammetry. The direct oxidation of glucose in sodium hydroxide medium at Ag/CuO nanofiber modified electrodes has been investigated.

Cited as: Thien, D.V.H., Toan, H.T., Quyen, T.T.B., Tri, N.M., 2017. Electrospun CuO/Ag nanofibers for nonenzymatic glucose sensors. Can Tho University Journal of Science. Vol 6: 63-68.

1 INTRODUCTION

Diabetes is a health problem that is currently popular worldwide. It is a consequence of insulin deficiency and hyperglycemia (Wang, 2001). The diabetes is resulted by the blood sugar level is higher or lower than normal levels of 70 - 120 $mg.dL^{-1}$ (4 - 8 mM) (Wang, 2008; 2001). Monitoring and controlling of blood glucose levels are simple methods for health care of patients with diabetes today.

Electrochemical glucose sensors can be classified into two types, including enzymatic glucose oxidase (GOX) and nonenzymatic glucose sensor (Ding *et al.*, 2010a; Zheng *et al.*, 2011). GOX with sensitivity and high selectivity has been used extensively for glucose detection (Ahmad *et al.*, 2010; Tang *et al.*, 2010). The disadvantages of GOX are unstable due to using enzyme, easy affected by pH and temperature, and high cost. The nonenzymatic glucose sensors based on direct oxidation of glucose have conveniences to avoid the GOX drawbacks (Sun *et al.*, 2001; Mayorga-Martinez *et al.*, 2012; Singh *et al.*, 2013). Several nanostructured metals (Au, Pt, Ni, Cu) and metal oxides (CuO, NiO, Co_3O_4) have been investigated as a catalyst for oxidation of glucose (Meng *et al.*, 2009; Ding *et al.*, 2010b; Nie *et al.*, 2011; Wang *et al.*, 2012; Li *et al.*, 2013). Among these materials, copper (II) oxide (CuO), a p-type semiconductor with a narrow band gap (1.2 eV), is suitable for sudying of biosensors (Reitz *et al.*, 2008; Anu Prathap *et al.*, 2012; Sahay *et al.*, 2012;). Silver (Ag) having the highest conductivity is often used as a catalyst in many chemical reactions. Thus, CuO/Ag would be a potential catylst for oxidation of glucose.

Electrospinning is a simple method to create polymer nanofibers. Electrospinning is not only applied for pure polymer but also can be applied for blended polymers with the metal, salt, oxide, and gra-

phene to create composite nanofibers owning novel properties. Thus, the fabrication of nanofibers by using an electrospinning method is an interesting topic today. In this study, PVP/$AgNO_3$/$Cu(NO_3)_2$ nanofibers were fabricated by an electrospinning method. The applied voltage and polyvinylpyrrolidone (PVP) concentration that are strong effects on the morphology of electrospun nanofibers were studied. Then, the nanofibers were carbonized to obtain Ag/CuO nanofibers that were applied for glucose sensors.

2 MATERIALS AND METHODS

2.1 Materials

Ethanol, silver nitrate ($AgNO_3$), glucose, PVP, and nafion, copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), isopropanol ($CH_3CH(CH_3)OH$), and glucose were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) was purchased from Merck.

2.2 Methods

2.2.1 Electrospinning of PVP

Three major components of an electrospinning setup are a high-voltage power supply using direct current (DC) and generating a voltage up to 20 kV, a 3 mL syringe with a metallic needle of 0.65 mm inner diameter, which can control the flow rate by a K.D Scientific pump, and a collector using an aluminum foil.

PVP was dissolved in ethanol at a PVP concentration of 8%. A PVP solution was placed into a syringe for electrospinning with a tip-to-collector distance of 8 cm, a feeding rate of 0.5 mL/h. The electrospinning experiments were carried out at room temperature. Electrospun nanofibers were deposited on glasses with an area of 1×1 cm^2.

2.2.2 Synthesis of Ag/CuO nanofibers

Ag/CuO nanofibers were prepared by an electrospinning method. Briefly, PVP was dissolved in ethanol and stirred for 3 hours at room temperature to obtain a PVP solution of 8%. 50 mg $Cu(NO_3)_2$ and 50 mg of $AgNO_3$ were added in 5 mL of the PVP solution. The solution was stirred for 2 hours to disperse the salts in the polymer solution. The polymer solution was placed into a 3-mL syringe with 0.65 mm inner diameter of metallic needle which can be controlled the flow rate by a K.D Scientific pump. The flow rate of polymer solution was 0.5 mL/h. The other conditions for electrospinning include a collector using an aluminum foil, 15 kV of applied voltage, and 15 cm of the tip-to-collector distance. After electrospinning, Ag-NO_3/$Cu(NO_3)_2$/PVP nanofibers were obtained. Then, the nanofibers were carbonized at 300, 450, and 500ºC to convert to Ag/CuO nanofibers.

2.2.3 Characterization of nanofibers

The surface morphology of the scaffolds was observed by scanning electron microscopy (S4800, JEOL, Japan) at an accelerating voltage of 15 kV after gold coating. Transmission electron microscopy (TEM) was performed on a EP070 microscope with an accelerating voltage of 80 kV. The crystalline phase of Ag/CuO was investigated by X-ray diffraction (D8 Phaser, Bruker, Germany) over the 2 theta (2θ) range from 20 to 75º with a scanning speed of 0.05º/min using CuKα radiation (λ = 1.5406 Å) operating at an accelerating voltage of 40 kV and a current at 40 mA.

2.2.4 Electrochemical measurements

Cyclic voltammetry measurements were performed on a Model VMP3B-5 BioLogic. All experiments were carried out using a three-electrode electrochemical cell (working volume of 5 mL) with a working electrode (Ag/CuO nanofibers), an Ag/AgCl reference electrode, and a platinum disc counter electrode. A solution of 50 mM NaOH was used as the supporting electrolyte. The effective surface of the working electrode for glucose detection was 75 × 25 mm.

3 RESULTS AND DISCUSSION

3.1 Electrospinning of PVP

Effects of PVP concentration

Figure 1 shows the effects of PVP concentration on the electrospun nanofibers. PVP concentrations of 4%, 6%, 8%, and 10% were used with an applied voltage of 20 kV, a tip-to-collector distance of 8 cm, a flow rate of 0.5 mL/h, and an ambient temperature of 30ºC. From Figure 1, the appearance of beads decreased with the increase of PVP concentration. At PVP concentrations of 4% and 6%, nanofibers were obtained with some of beads. At PVP concentrations of 8% and 10%, the uniform nanofibers were obtained. The chain entanglement is sufficient to keep continuous jet during the electrospinning process when concentration was high enough. However, the morphology of PVP nanofibers at the 8% PVP concentration was better than that of 10% PVP concentration. Thus, 8% of PVP concentration was chosen for further experiments.

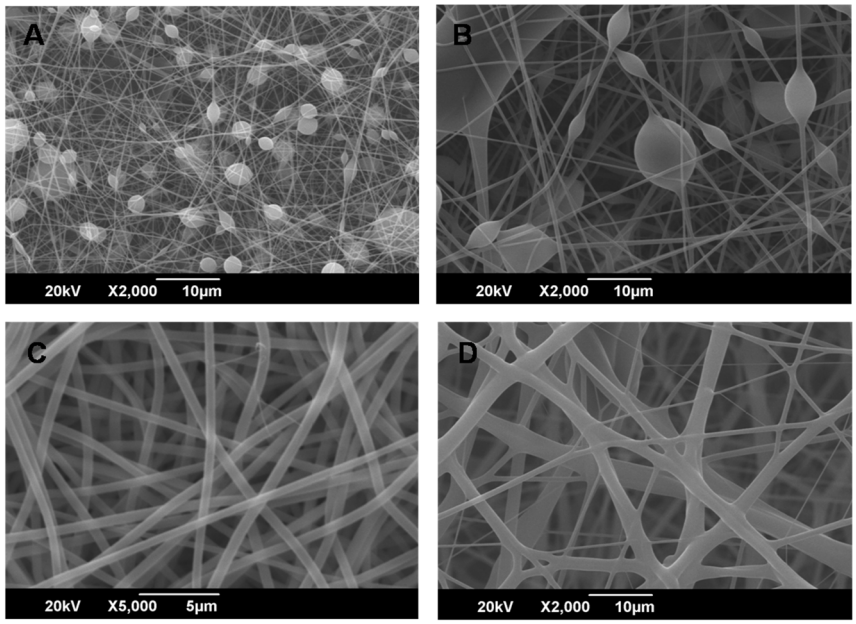

Fig. 1: Effect of PVP concentration on electrospinning of PVP with feeding rate of 0.5 mL/h, tip-to-collector distance of 8 cm, applied voltage of 20 kV: (A) PVP 4%; (B) PVP 6%; (C) PVP 8%; (D) PVP 10%

Effects of applied voltage

Figure 2 shows the effects of applied voltage on electrospun PVP nanofibers. The applied voltages were chosen from 5 to 20 kV. Other crucial parameters of electrospinning were kept as constant including the PVP concentration of 8%, the tip-to-collector distance of 8 cm, the flow rate of 0.5 mL/h, and the temperature of 30 ^{o}C. At the applied voltage of 20 kV, the PVP nanofibers with uniform diameters were obtained. At applied voltages of 5, 10, and 15 kV, some large beads coexisted with nanofibers because the Columbic forces are not enough to stretch electropun fibers into nanoscale. Accordingly, over-low applied voltages resulted in bead-in-string structures. An applied voltage must be high enough to overcome the surface tension of a polymer solution. Thus, the applied voltage of 20 kV was chosen for further experiments.

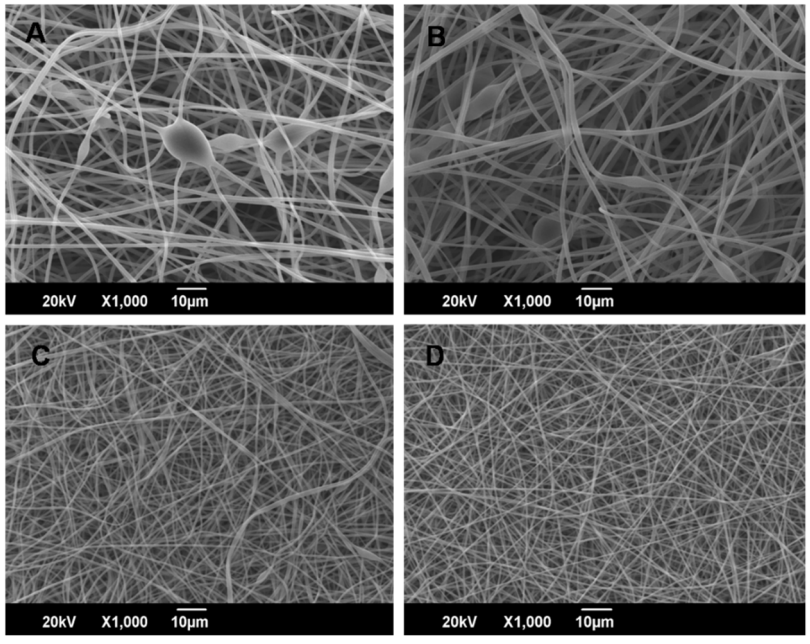

Fig. 2: Effects of applied voltage on electrospinning of PVP with PVP concentration of 8%, feeding rate of 0.5 mL/h, tip-to-collector distance of 8 cm: (A) 5 kV; (B) 10 kV; (C) 15 kV; (D) 20 kV

3.2 Electrospun nanofibers of Ag/CuO

Figure 3 shows the scanning electron microscopy (SEM) images of electrospun nanofibers and TEM image of Ag/CuO nanofibers after carbonization of the nanofibers at 450ºC. The nanofibers were homogeneous, and the diameter of electrospun nanofibers was from 70 nm to 1000 nm (Figure 3A and 3B). After carbonization, the nanofibers kept the morphology. However, the diameter of nanofibers was slightly decreased (Figure 3C). The nanofibers contained Ag and CuO nanoparticles are displayed in TEM image (Figure 3D). The particle sizes were about 5 to 10 nm that would be suitable for using in catalytic reactions.

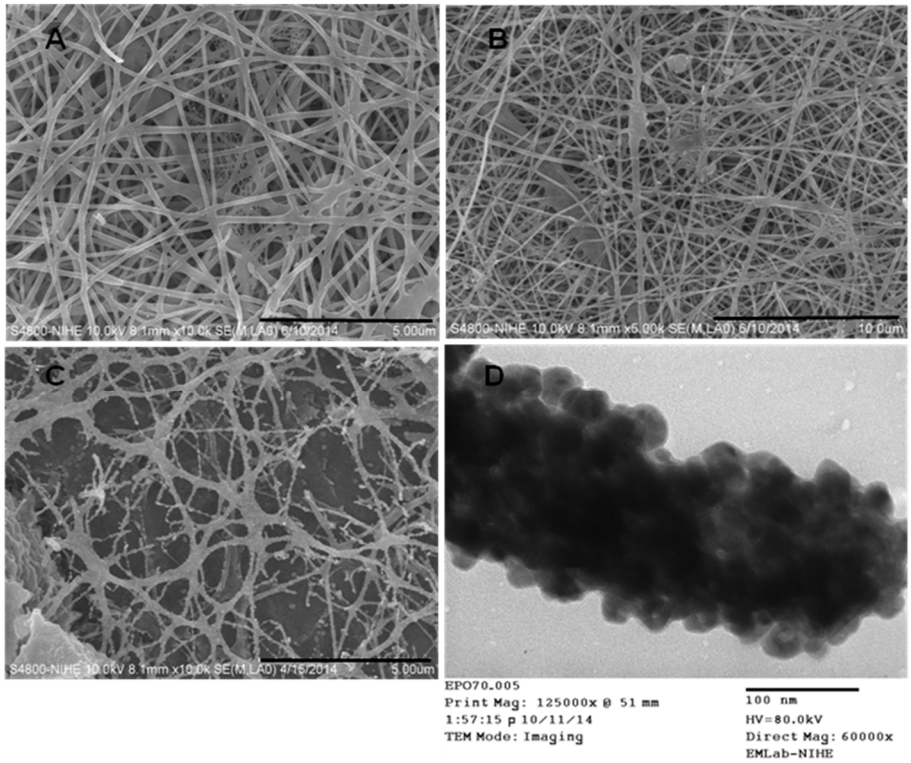

Fig. 3: SEM images of $AgNO_3/Cu(NO_3)_2$/PVP (A, B), Ag/CuO nanofibers (C); TEM image of $AgNO_3/Cu(NO_3)_2$/PVP (D)

3.3 The effect of temperature for synthesis of Ag/CuO nanofibers

Figure 4 shows X-ray diffraction patterns of Ag/CuO nanofibers obtained from carbonization of $PVP/AgNO_3/Cu(NO_3)_2$ nanofibers at 300, 450, and 600ºC. An increase in the temperature from 300 to 600ºC, the characteristic peaks of the samples at 450ºC and 600ºC were the same. The existence of 2θ peaks at 35.4°, 38º, 58°, and 65° confirmed the formation of CuO crystalline structure, and the existence of 2θ peaks at 38°, 44°, and 64° confirmed the formation of Ag crystalline structure. Thus, the temperature of 450ºC was chosen for synthesis of Ag/CuO nanofibers.

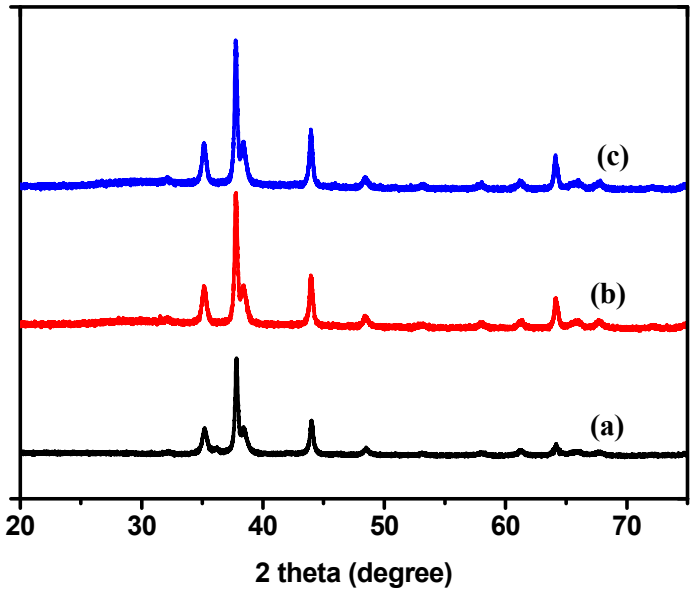

Fig. 4: X-ray diffraction patterns of Ag /CuO nanofibers with carbonization at various temperatures: (a) 300°C; (b) 450°C; (c) 600°C

3.4 Electrochemical performance of different electrodes

The cyclic voltammogram method was used to investigate the catalytic activity of the oxidation of glucose in alkaline medium by using the Ag/CuO NFs-IGZO electrode. Figure 5 shows that the Ag/CuO NFs-ITO electrode exhibits a redox peak between -0.6 and 0.60 mV. On the Ag/CuO nanofibers modified electrode, there appears a pair of redox peaks. An increase in the glucose concentration, the oxidation peak increased because of the direct oxidation of glucose at the Ag/CuO NFs-IGZO electrode. The anodic oxidation peak at 0.40 V indicates the catalytic effect of the Ag/CuO NFs-IGZO on direct oxidation of glucose.

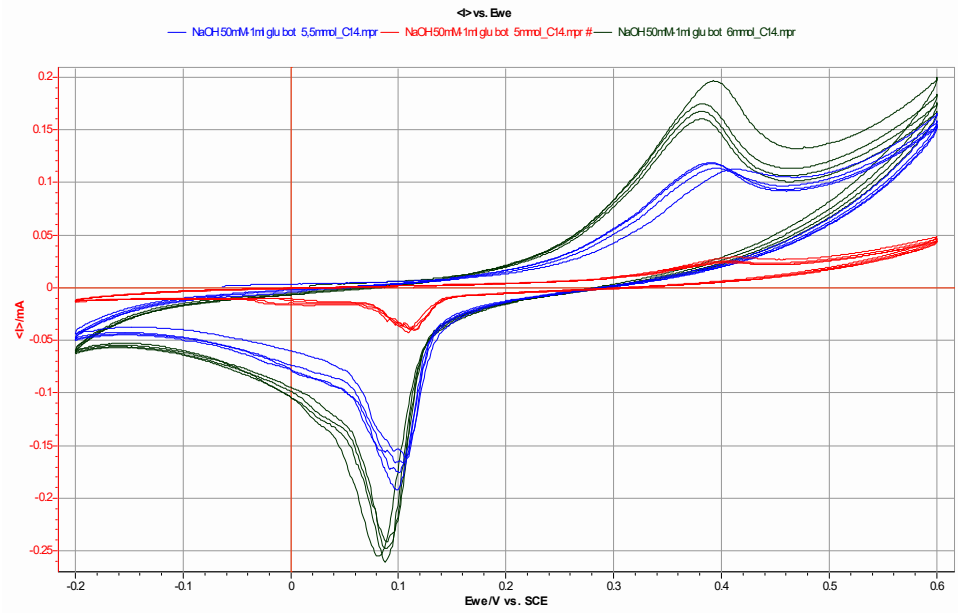

Fig. 5: Cyclic voltammograms of Ag NPs/CuO NFs-IGZO in a glucose solution with various concentrations: 5,0 mM; 5,5 mM; 6,0 mM; in the medium of sodium hydroxide 50 mM

4 CONCLUSIONS

The effects of the main parameters in electrospinning of PVP have been investigated. A nonenzymatic biosensor based on the Ag/CuO nanofibers for glucose oxidation has been fabricated. The nanofibers were prepared by an electrospininning method based on the PVP solution with $Ag(NO_3)$ and $Cu(NO_3)_2$. After carbonization at 450^oC, the Ag/CuO nanofibers were obtained and used as a catalyst for oxidation of glucose. The cyclic voltammogram method was used for studying the catalytic activity of the oxidation of glucose in sodium hydroxide medium. The anodic oxidation peak at 0.40 V indicates the strong catalytic effect of the Ag/CuO NFs-IGZO on direct oxidation of glucose. Thus, Ag/CuO nanofibers would be potential for the development of nonenzymatic glucose sensor.

ACKNOWLEDGEMENT

We would like to thank Dr. Tran Van Man (Department of Chemistry, Ho Chi Minh City University of Science) for his assistance in set up of glucose sensors.

REFERENCES

Ahmad, M., Pan, C., Luo, Z., Zhu, J., 2010. A Single ZnO Nanofiber-Based Highly Sensitive Amperometric Glucose Biosensor. The Journal of Physical Chemistry C. 114: 9308-9313.

Anu Prathap, M.U., Kaur, B., Srivastava, R., 2012. Hydrothermal synthesis of CuO micro-/nanostructures and their applications in the oxidative degradation of methylene blue and non-enzymatic sensing of glucose/H2O2. Journal of Colloid and Interface Science. 370: 144-154.

Ding, Y., Wang, Y., Su, L., Bellagamba, M., Zhang, H., Lei, Y., 2010a. Electrospun Co3O4 nanofibers for sensitive and selective glucose detection. Biosensors and Bioelectronics. 26: 542-548.

Ding, Y., Wang, Y., Su, L., Zhang, H., Lei, Y., 2010b. Preparation and characterization of NiO-Ag nanofibers, NiO nanofibers, and porous Ag: towards the development of a highly sensitive and selective nonenzymatic glucose sensor. Journal of Materials Chemistry. 20: 9918-9926.

Li, X., Yao, J., Liu, F., He, H., Zhou, M., Mao, N., Xiao, P., Zhang, Y., 2013. Nickel/Copper nanoparticles modified TiO2 nanotubes for non-enzymatic glucose biosensors. Sensors and Actuators B: Chemical. 181: 501-508.

Mayorga-Martinez, C.C., Guix, M., Madrid, R.E., Merkoci, A., 2012. Bimetallic nanowires as electrocatalysts for nonenzymatic real-time impedancimetric detection of glucose. Chemical Communications. 48: 1686-1688.

Meng, L., Jin, J., Yang, G., Lu, T., Zhang, H., Cai, C., 2009. Nonenzymatic Electrochemical Detection of Glucose Based on Palladium-Single-Walled Carbon Nanotube Hybrid Nanostructures. Analytical Chemistry. 81: 7271-7280.

Nie, H., Yao, Z., Zhou, X., Yang, Z., Huang, S., 2011. Nonenzymatic electrochemical detection of glucose using well-distributed nickel nanoparticles on straight multi-walled carbon nanotubes. Biosensors and Bioelectronics. 30: 28-34.

Reitz, E., Jia, W., Gentile, M., Wang, Y., Lei, Y., 2008. CuO Nanospheres Based Nonenzymatic Glucose Sensor. Electroanalysis. 20: 2482-2486.

Sahay, R., Sundaramurthy, J., Suresh Kumar, P., Thavasi, V., Mhaisalkar, S.G., Ramakrishna, S., 2012. Synthesis and characterization of CuO nanofibers, and investigation for its suitability as blocking layer in ZnO NPs based dye sensitized solar cell and as photocatalyst in organic dye degradation. Journal of Solid State Chemistry. 186: 261-267.

Singh, A., Poshtiban, S., Evoy, S., 2013. Recent Advances in Bacteriophage Based Biosensors for Food-Borne Pathogen Detection. Sensors. 13: 1763-1786.

Sun, Y., Buck, H., Mallouk, T.E., 2001. Combinatorial discovery of alloy electrocatalysts for amperometric glucose sensors. Analytical chemistry. 73: 1599-1604.

Tang, H., Yan, F., Tai, Q., Chan, H.L.W., 2010. The improvement of glucose bioelectrocatalytic properties of platinum electrodes modified with electrospun TiO2 nanofibers. Biosensors and Bioelectronics. 25: 1646-1651.

Wang, G., Lu, X., Zhai, T., Ling, Y., Wang, H., Tong, Y., Li, Y., 2012. Free-standing nickel oxide nanoflake arrays: synthesis and application for highly sensitive non-enzymatic glucose sensors. Nanoscale. 4: 3123-3127.

Wang, J., 2001. Glucose Biosensors: 40 Years of Advances and Challenges. Electroanalysis. 13: 983-988.

Wang, J., 2008. Electrochemical Glucose Biosensors. Chemical Reviews. 108: 814-825.

Zheng, B., Xie, S., Qian, L., Yuan, H., Xiao, D., Choi, M.M.F., 2011. Gold nanoparticles-coated eggshell membrane with immobilized glucose oxidase for fabrication of glucose biosensor. Sensors and Actuators B: Chemical. 152: 49-55.