Wang et al., 2015

Volume 1 Issue 1, pp. 139-150

Year of Publication: 2015

DOI- https://dx.doi.org/10.20319/lijshls.2015.s11.139150

This paper can be cited as: Wang, J., Wang, Y., Yu, L., Peng, H., & Zhu, J. (2015). Nano-Fe and Mwcnts Based Non-Enzymatic Sensor for Determination of Glucose in Seruum. LIFE: International Journal of Health and Life-Sciences, 1(1), 139-150.

NANO-FE AND MWCNTS BASED NON-ENZYMATIC SENSOR FOR DETERMINATION OF GLUCOSE IN SERUUM

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Abstract

The enzyme sensors based on glucose oxidase have been widely used for the detection of blood glucose. However, the activity of enzyme can be easily affected by temperature, pH, humidity and toxic chemical. Nanostructured metal-oxides have been extensively explored to develop non-enzymatic glucose sensors. An amperometric electrode based on multiwall carbon nanotubes (MWCNTs) and Fe nanoparticles has been successfully fabricated. The electrode exhibits the linear regression equation is: I = -0.1985 + 1.7499 CG (correlation coefficient is 0.9994). Linear response range: 0.2-20.0 mM, sensitivity: 1.75 a/am, the LOD was evaluated to be 0.03 mM according to IUPAC regulations (S/N = 3). Interference tests illustrated that 0.2 me of ascorbic acid and uric acid didn't have effect on the determination of glucose. In the presence of 0.02 M chloride ion, the current signal of 0.2 mM glucose almost keeps unchanged at the sensor, revealing that this new sensor has high tolerance level to chloride ion. The sensor has been successfully applied to determine glucose in the serum samples and obtained consist results with conventional spectrometry.

Keywords

Non-Enzyme Sensor, Glucose, Multiwall Carbon nanotubes, Nano-Fe Particles

1. Introduction

Diabetes is a group of metabolic diseases affecting about 150 million people worldwide, and is one of the leading causes of death and disability, such as blindness, nerve degeneration and kidney failure (Mercado & Mousse, 1998, Mossy et al., 1994, Privet et al., 2008). The diagnosis and management of diabetic patients require precise monitoring and control of the glucose level in the body. It is necessary to test frequently the physiological glucose level in order to confirm treatment efficiency, prevent long-term complications and avoid a diabetic emergency, such as hypoglycemia (low blood sugar, <3 mM). Currently, diabetics must frequently check their blood glucose levels by “finger-pricking” and adjust their insulin dosage to keep the glucose level as close to “normal” as possible.

The enzyme sensors based on glucose oxidase have been widely used for the detection of blood glucose. However, the activity of enzyme can be easily affected by temperature, pH, humidity and toxic chemical. Nanostructured metal-oxides have been extensively explored to develop non-enzymatic glucose sensors with high sensitivity, fast response times, and stability

for the determination of glucose by electrochemical oxidation, such as Cu nanoparticles (NPs) or Cue NPs (Dong et al., 2015; Jiang & Zhang, 2010; Jiang et al., 2010; Kang et al., 2015; Wang & Zhang, 2011; Yang et al., 2010; Zhang et al., 2013), Knox and metal oxide (Ding et al., 2012; Yuan et al., 2013; Zhu, & Huang, 2012), Ni, NiO or Ni (OH)2 NPs (Li et al., 2011; Liu et al., 2009; Lu et al., 2009; Nile et al., 2011; Safaris et al., 2009; Zhang et al., 2010), Mesoporous Pt (Park et al., 2003), Pup (Cui et al., 2007; Guo et al., 2011; Wang et al., 2008), Put (M= Ru, Pd and Au) NPs (Xiao et al., 2009), grapheme-Au (Zhu et al., 2014), Au@Pdcorre-shell hennas' (Chen et al., 2010), Porous Au (Li et al., 2007), N2-doped Ag (Lout et al., 2014), MnO2 and Me compounds (Chen et al., 2008; Yang et al., 2015), Co3O4/PbO2 (Chen et al., 2014), Bimetallic Macon (M = Cu, Fe, Ni, and Mann) NPs (Li et al., 2015) and so on. In this work, Nano-Fe and MWCNTs were fabricated a non-enzymatic glucose sensor with excellent performances. The sensor has been applied to determination of glucose in serum.

2. Experimental

2.1 Reagents and Animals

MWCNTs (GMWCNT2, 10–20 nm diameter, 10–20 μm length, purity > 99.9%) were purchased from Shanghai Jakarta Chemical engineering Sci & Tech Co. Ltd. (Shanghai, China) and Nano-Fe (50 nm average diameter, purity 99.99%) was purchased from Beijing Deke Daojin Science & Technology Co. Ltd (Beijing, China). They were used without further purification. Other reagents were of at least analytical-reagent grade. All solutions were prepared using doubly distilled water. Standard stock solution of glucose (20 am) were prepared in a pH 8.0 PBS and stored at 4°C for 1 month. Working standard solutions were prepared daily by diluting the stock solutions with pH 8.0 PBS.

2.2 Electrode Preparation

Fe nanoparticles and MWCNTs with the ratios of WFe/WFe+CNTsof 0.30, 0.25, 0.20, 0.15 and 0.10 were mixed and grinded in a mortar to obtain a homogeneous mixture. The Fe-MWCNTs electrode was prepared by mixing the mixture and silicone oil in a ratio of 3:2 (w/w) in a mortar and grind until a uniform paste was obtained. A portion of the resulting paste was packed firmly into the cavity (3.0 mm diameter and 2 mm depth) of a polytetrafluoroethylene (PTFE) tube. The electric contact was established via a copper wire with the aid of Wood's alloy.

The electrode surface was gently smoothed by rubbing on a piece of weighing paper just prior to use. This procedure was also used to regenerate the surface of the electrode proposed.

2.3 Measurement

Electrochemical experiments were performed on a CHI 832A workstation (CH et al.,) at room temperature. A conventional three electrode system was employed, including a homemade Fe–MWCNTs electrode (3.0-mm-diameter) as a working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counterelectrode. Fe nanoparticles and MWCNTs with different ratios of 0.30, 0.25, 0.20, 0.15, 0.10, 0.0 (WFe/WFe+CNT) were mixed and grinded in a mortar to obtain a homogeneous mixture The Fe-MWCNTs electrode was prepared by mixing the mixture and silicone oil in a ratio of 3:2 (w/w) in a mortar and grind until a uniform paste was obtained. A portion of the resulting paste was packed firmly into the cavity (3.0 mm diameter and 2 mm depth) of a polytetrafluoroethylene (PTFE) tube. The electric contact was established via a copper wire. The electrode surface was gently smoothed by rubbing on a piece of weighing paper just prior to use. This procedure was also used to regenerate the surface of the electrode proposed. Optimal ratio will be obtained through linear sweep voltammetry.

A serious standard solution containing 7.0 mM glucose with different pH values from 7.0 to 10.5 were prepared. The sensor with optimal ratio of WFe/WFe+CNTs was tested in above solution at 0.6 V work potential. Optimal pH of the solution will be found. The sensor was tested in 0.1 M PBS solution (pH 8.0) containing 7.0 mM glucose at a scan rate of 10, 60, 150, 260, 440 and 580 mV/s, respectively to verify what model of electrochemical reaction occur on the electrode.

The sensor was tested in 0.1 M PBS solution (pH 8.0) containing 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 1.0, 12.0, 1.4, 16.0, 1.8 and 20.0 mM glucose at 0.6 V working potential to obtain calibration curve.

The stability, reproducibility and long-term stability of the Fe–MWCNTs electrode were studied in PBS (pH8.0) solution.

100 serum samples from local hospital were tested by the sensor and conventional spectrometry and results obtained were compared.

3. Results and Discussion

3.1 The Ratio between Fe Nanoparticles and Mwcnt

The dependence of response current on the ratio between Fe and MWCNTs is shown in Figure 1. The response current increased with increasing of Fe nanoparticles proportion until the ratio reaches 0.25, because of the improvement of the electrode conductivity. When the ratio was 0.30, the response current became smaller. It could be Fe ratio was too high to adhere on the electrode. Therefore, 0.25 of ratio was used in the following experiments.

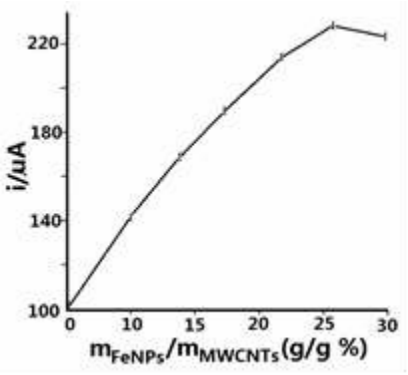

Figure 1: *Dependence of the response current on the ratio between Fe nanoparticles and MWCNT*

3.2 The Influence of pH Value

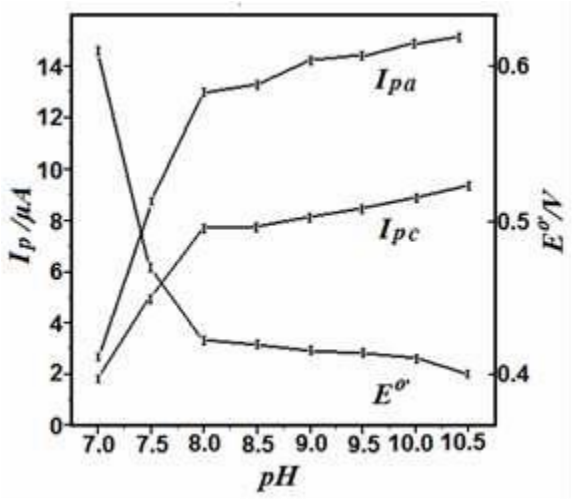

Figure 2: *Influence of pH value on the peak current Ip and peak formal potential Eo of Fe-MWCNT electrode. Scan rate: 100 mV/s.*

To investigate the influence of pH value on the voltammetric behavior of glucose on Fe–MWCNTs electrode was examined in a pH range from 7.0 to 10.5, and the results are shown in Figure 2. As shown, with the increase of pH value of the solution, both anodic peak current, Ipa and cathode peak current, Icy were enhanced and the peak formal potential E0 of the redox couple negatively shifted, suggesting that OH- participated in the redox process of the modified electrode. These were attributed to synergy effects of nano-Fe and MWCNTs.

3.3 The Mechanism of Glucose Oxidation

The mechanism of Glucose oxidation is

- $Fe + 2\ OH^- \rightarrow Fe(OH)_2 + 2\ e^-$ (1)
- $Fe(OH)_2 + OH^- \rightarrow FeO(OH) + H_2O + e^-$ (2)
- $FeO(OH) + Glucose \rightarrow Fe(OH)_2 + H_2O + Glucolactone$ (3)

3.4 Performances

The cyclic voltammograms of glucose on Fe-MWCNTs electrode at different scan rates are shown in Figure. 3 Scan potential is from 0 to 0.7 V. The oxidation and redox peaks of Fe2+/Fe3+ appear at 0.6 and 0.4 V, respectively. The dependence of the peak height on the scan rate is also shown in inset. The linear relationship between the peak height and the square root of the scan rate indicates the electrochemical reaction is a diffusion control type.

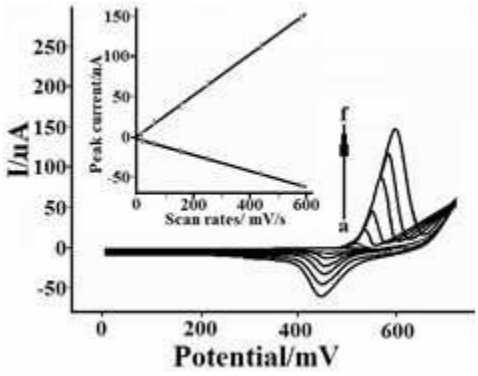

Figure 3: *Cyclic Voltammograms of the Fe–MWCNTs Electrodes in 0.1 M PBS Solution*

（pH 8.0）containing 7.0 mM glucose at a scan rate of a. 10, b. 60, c. 150, d. 260, e. 440, f. 580 mV/s, respectively. Inset: The dependence of the peak height on the scan rate Figure 4 represents the chronoamperogram of the sensor obtained in 0.1 M PBS solution (pH 8.0) at 0.6 V by successively adding aliquots of glucose. The sensor proposed displayed a fast amperometric response time of less than 4 s (95% peak value). The calibration curve is also shown as the inset. The linear regression equation is: I = -0.1985 + 1.7499 CG (correlation coefficient is 0.9994). (Linear response range: 0.2-20.0 mM, sensitivity: 1.75 μA mM−1), the LOD was evaluated to be 0.03 mM according to IUPAC regulations (S/N = 3). Interference tests illustrated that 0.2 mM of ascorbic acid and uric acid didn't have effect on the determination of glucose. In the presence of 0.02 M chloride ion, the current signal of 0.2 mM glucose almost keeps unchanged at the sensor, revealing that this new sensor has high tolerance level to chloride ion.

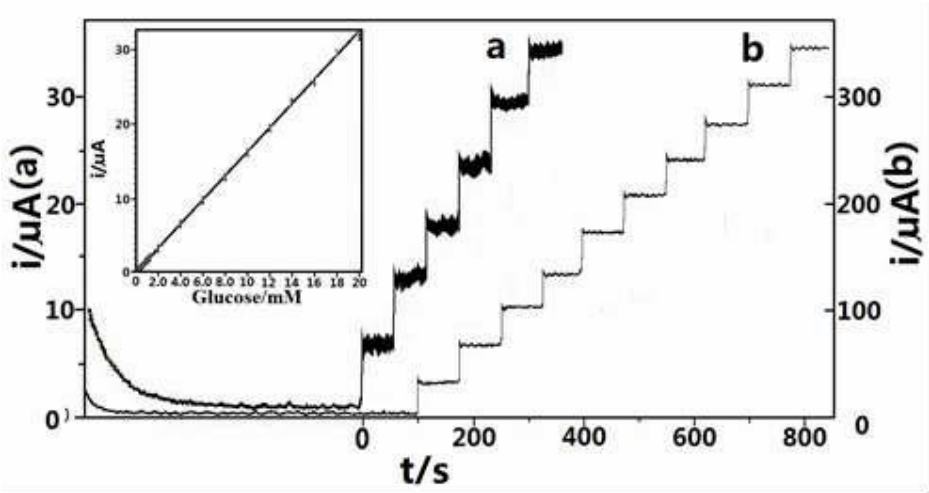

Figure 4: *Amperometric responses of Fe–MWCNTs electrode in 0.1 M PBS solution*

(pH8.0) by successive addition of 0.2 (a) and 2.0 (b) mM glucose. Applied potential: 0.6 V. Inset: calibration curve. The response currents has a linear relationship with the concentration of glucose in a range from 0.2 to 20.0 mM. The linear regression equation is: i = -0.1936 + 1.7503 CG (correlation coefficient is 0.9992.)

The stability and reproducibility of the Fe–MWCNTs electrode were studied in PBS (pH8.0) solution. A set of 11 replicate measurements for 2.0 mM glucose yielded a relative standard deviation (RSD) of 3.5%. Five Fe–MWCNTs electrodes were fabricated, and the RSD for the individual determination of 2.0 mM glucose was 3.8%. The long-term stability of the modified electrode was tested after being stored in dry conditions at room temperature for 60

days, and no significant change in current responses was observed. Thus, the Fe–MWCNTs electrode exhibited acceptable stability and reproducibility.

Table1: *Recovery of Glucose in the Sensor Assay*

Spiked (mM)	Detected (mM) (n=5)	Recovery (%)
0.10	0.09	90
0.50	0.52	104
1.00	0.95	95
5.00	5.04	108
10.00	9.9	99
15.0	15.3	102

Recovery of glucose detected in serum samples were listed in Table 1. Recovery was from 90 – 108%. Therefore, this new electrochemical method using the sensor is feasible and accurate for the detection of glucose. The results confirm that the sensor reaches the needs of glucose determination in the serum samples.

3.5 Application

In order to testify the performance of this sensor in real sample analysis, the blood sugar values were analyzed by the conventional spectrometry method and the sensor proposed method. Each sample solution undergoes three-parallel detections. Figure 5 shows the relationship between the results obtained by the proposed sensor and the conventional method for 100 water samples. It is found that the glucose value detected by spectrometry method (indicated as CT) has good correlation with that by the sensor (denoted as CS). The linear regression equation is CT = 1.207 Cs + 1.006, and the correlation coefficient is 0.988, indicating that the two methods agreed very well.

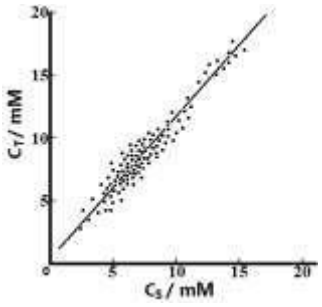

Figure 5: *Relationship between blood sugar values obtained by the sensor proposed (CS) and the conventional spectrometry method (CT). The linear regression equation is CT = 1.207*

Cs + 1.006, and the correlation coefficient is 0.988

4. Conclusion

A novalnonenzymatic glucose sensor modified with multiwall carbon nanotubes (MWCNTs) and Fe nanoparticles has been fabricated. The sensor proposed shows good electrochemical performance due to the synergetic electro catalysis effects of MWNTs and Fe nanoparticles. The sensor has been successfully applied to determine glucose in the serum samples and obtained consist results with conventional spectrometry. The highlights of this research work are that the no enzymatic sensor can used in 8.0 of pH value and 0.6 V working potential as well as easy renew for the electrode.

5. Acknowledgements

The project is supported by National Natural Science Foundation of China (60976004) and Shanghai Municipal Commission for Science and Technology (11JC1403800).

References

Chen, J., Zhang, W.D., Ye, J.S. (2008). No enzymatic electrochemical glucose sensor based on MnO2/MWNTs nanocomposite. Electrochem. Commun, 10, 1268–1271.

ChenT., Li X.W., QiuC.C., Zhu W.C., Ma H.Y., Chen S.H., Meng O. (2014). Electrochemical sensing of glucose by carbon cloth-supported Co3O4/PbO2 core-shell nanorod arrays, Biosensors and Bioelectronics, 53 (15), 200–206

Chen X.L., Pan H.B., Liu H.F., Du M. (2010). No enzymatic glucose sensor based on flowershapedAu@Pd core–shell nanoparticles–ionic liquids composite film modified glassy carbon electrodes, ElectrochimicaActa56, 636–643

Cui, H.F., Ye, J.S., Zhang, W.D., Li, C.M., Luong, J.H.T., Sheu, F.S. (2007). Selective and sensitive electro-chemical detection of glucose in neutral solution using platinum-lead alloy nanoparticle/carbon nanotube nanocomposites. Anal. Chim. Acta, 594, 175–183.

Ding R.M., Liu J.P., Jiang J., Zhu J.H., Huang X.T.(2012). Mixed Ni–Cu-oxide nanowire array on conductive substrate and its application as enzyme-free glucose sensor, Anal. Methods, 4,4003-4008

Ding Y., Wang Y., Zhang L.C., Zhang H., Lei Y.(2012). Preparation, characterization and application of novel conductive NiO–CdOnanofibers with dislocation feature, J. Mater. Chem., 22, 980-986

Dong J.P.,Tian T.L., Ren L.X, Zhang Y, Xu J.Q., Cheng X.W. (2015). CuO nanoparticles incorporated in hierarchical MFI zeolite as highlyactiveelectrocatalyst for non-enzymatic glucose sensing, Colloids and Surfaces B: Biointerfaces 125, 206–212

Guo M.Q., Wang R., Xu X.H. (2011). Electro synthesis of pinecone-shaped Pt–Pub nanostructures based on the application in glucose detection, Materials Science and Engineering C 31, 1700–1705

Jiang, L.C., Zhang, W.D. (2010). A highly sensitive no enzymatic glucose sensor based on Cu Onanoparticles-modified carbon annotate electrode. Biosens. Bioelectron. 25, 1402–1407.

Kang, X.H., Mai, Z.B., Zou, X.Y., CAI, P.X., Mo, J.Y. (2007). A sensitive nonenzymatic glucose sensor in alkaline media with a copper nanocluster/multiwall carbon annotate-modified glassy carbon electrode. Anal. Biochem 363, 143–150.

Li, M., Liu, L.B., Xiong, Y.P., Liu, X.T., Nsabimana, A., Bo, X.J., Guo, L.P. (2015). Bimetallic MCo (M = Cu, Fe, Ni, and Mn) nanoparticles doped-carbon nanofibers synthesized by electrospinning for no enzymatic glucose detection. Sensors and Actuators B207, 614-622

Li,X., Hu A.Z.,Jiang J., Ding .M., Liu J.P., Huang X.T. (2011). Preparation of nickel oxide and carbon nanosheet array and its application in glucose sensing, Journal of Solid State Chemistry, 184 (10), 2738–2743,

Li, Y., Song, Y.Y., Yang, C., Xia, X.H. (2007). Hydrogen bubble dynamic template synthesis of porous gold for no enzymatic electrochemical detection of glucose. Electrochem. Commun 9, 981–988.

Liu, Y., Teng, H., Hou, H.Q., You, T.Y. (2009). Nonenzymatic glucose sensor based on renewableelectrospun Ni nanoparticle-loaded carbon nanofiber paste electrode. Biosens Bioelectron. 24, 3329–3334.

Lu, L.M., Zhang, L., Qu, F.L., Lu, H.X., Zhang, X.B., Wu, Z.S., Huan, S.Y., Wang, Q.A., Shen,

G.L., Yu, R.Q. (2009). A nano-Ni based ultrasensitive no enzymatic electrochemical sensor for glucose: Enhancing sensitivity through a nanowire array strategy. Biosens. Bioelectron. 25, 218–223.

Luo, S.P., Chen Yu, Xie A.J. (2014), Nitrogen Doped Graphene Supported Ag Nanoparticles as Electrocatalysts for Oxidation of Glucose, ECS Eectrochem Lett, 3, B20-B22

Mercado, R.C., Moussy, F. (1998). In vitro and in vivo mineralization of nafion membrane used for implantable glucose sensors. Biosens. Bioelectron.,13, 133–145.

Moussy, F., Jakeway, S., Harrison, D.J., Rajotte, R.V. (1994).In vitro and in vivo performance and lifetime of perfluorinatedionomer-coated glucose sensors after high-temperature curing. Anal. Chem. 66, 3882–3888.

Nie, H., Yao, Z., Zhou, X., Yang, Z., Huang, S. (2011). No enzymatic electrochemical detection of glucose using well-distributed nickel nanoparticles on straight multi-walled carbon nanotubes. Biosens. Bioelectron 30, 28–34.

Park, S., Chung, T.D., Kim, H.C. (2003). No enzymatic glucose detection using mesoporous platinum. Anal. Chem., 75, 3046–3049.

Privets, B.J., Shin, J.H., Schoenfisch, M.H.(2008). Electrochemical sensors. Anal. Chem. 80, 4499–4517

Safavi, A., Maleki, N., Farjami, E. (2009). Fabrication of a glucose sensor based on a novel nanocomposite electrode. Biosens. Bioelectron., 24, 1655–1660.

Wang, J., homas, D.F., Chen, A. (2008). Nonenzymatic electrochemical glucose sensor based on nanoporousPtPb networks. Anal. Chem., 80, 997–1004.

Wang J., Zhang W. D. (2011). Fabrication of CuOnanoplatelets for highly sensitive enzyme-free determination of glucose, Electrochimica Acta, 56 (22), 7510–7516

Xiao F., Zhao F.Q., Mei D.P., Mo Z.R., Zeng B.Z. (2009). Nonenzymatic glucose sensor based on ultrasonic-electrodeposition of bimetallic PtM (M= Ru, Pd and Au) nanoparticles on carbon nanotubes–ionic liquid composite film, Biosens. Bioelectron., 24, 3481–3486

Yang, J., Jiang, L.C., Zhang, W.D., Gunasekaran, S. (2010). A highly sensitive non-enzymatic glucose sensor based on a simple two-step electrodeposition of cupric oxide (CuO) nanoparticles onto multi-walled carbon nanotube arrays. Talanta, 82, 25–33.

Yang, J., Zhang, W.D., Gunasekaran, S. (2010). An amperometric non-enzymatic glucose sensor by electrodepositing copper nanocubes onto vertically well-aligned multi-walled carbon nanotube arrays. Biosens. Bioelectron., 26, 279–284.

Yang, S.L., Gang Li, G. Wang, G.F., Junhong Zhao, J.H., Gao, X.H., Qu L.B. (2015). Synthesis of Mn3O4 nanoparticles/nitrogen-doped graphene hybrid composite for nonenzymatic glucose sensor. Sensors and Actuators B221, 172-178

Yuan B.Q., Xu C.Y., Liu L., Zhang Q.Q., Ji S.Q., Pi L.P., Zhang D.J.,Huo Q.S. (2013).

Cu2O/NiOx/graphene oxide modified glassy carbon electrode for the enhanced electrochemical oxidation of reduced glutathione and nonenzyme glucose sensor, ElectrochimicaActa104 78– 83

Zhang J., Ma J.L., Zhang S.B., Wang W.C., Chen Z.D. (2015). A highly sensitive nonenzymatic glucose sensor based on CuO nanoparticles decorated carbon spheres, Sensors and Actuators B211, 385-391.

Zhang J., Zhu X.L., Dong H.F., Zhang X.J., Wang W.C., Chen Z.D. (2013). In situ growth cupric oxide nanoparticles on carbon nanofibers for sensitive nonenzymatic sensing of glucose, ElectrochimicaActa105, 433– 438

Zhang, W.D., Chen, J., Jiang, L.C., Yu, Y.X., Zhang, J.Q. (2010). A highly sensitive nonenzymatic glucose sensor based on NiO-modified multi-walled carbon nanotubes. Microchim. Acta, 168, 259–265.