J. Mater. Environ. Sci. 4 (6) (2013) 887-892
ISSN : 2028-2508
CODEN: JMESCN

Electrocatalytic Oxidation of Glucose at Gold Nanoparticle-modified PFC electrodes in an Alkaline Solution

Sami Ben Aoun*
Department of Chemistry, Faculty of Science, Taibah University
PO. Box 30002 Al-Madinah Al-Munawarah, KSA

Received 15 April 2013, Revised 16 June 2013, Accepted 16 June 2013

* Corresponding author. E-mail: sbenaoun@taibahu.edu.sa; *Tel +966590900727; Fax. +96648470235*

Abstract

The electrocatalytic oxidation of glucose at Au nanoparticle-modified PFC electrodes has been studied using voltammetry technique in a (5 mM glucose + 0.1 M NaOH) solution. The PFC electrode didn't show any activity in the potential of interest (i.e. −0.8 V to 0.8 V). However, a very interesting positive catalytic effect was observed upon modification of the electrode surface with gold nanoparticles (AuNPS). In fact, the effective glucose oxidation, via a two-electron process, to gluconolactone took place with an oxidation peak potential of ca. −0.38 V vs. Ag|AgCl (Sat. KCl) at the modified PFC electrode. The lactone was further oxidized at higher overpotential with a peak current at ca. 0.35 V vs. Ag|AgCl (Sat. KCl). The electrochemical deposition of gold nanoparticles onto PFC electrodes offered a cost-effective and rather simple way to prepare highly-catalytic catalyst (i.e. AuNPS/PFC) for a promising wide range of applications, fuel cells in particular.

Keywords: Fuel cells, Glucose Oxidation, Nanoparticles and Electrocatalysis.

1. Introduction

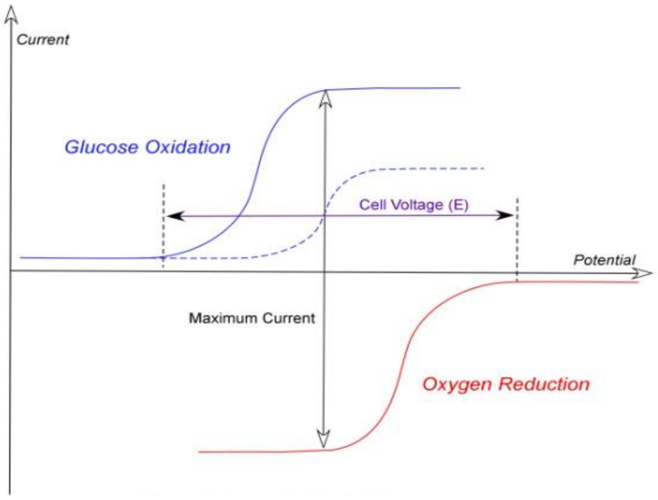
The electrocatalytic oxidation of glucose bas been examined extensively especially on gold substrate [1-12] that has been paid much attention so far due, among others, to an increasing interest in its fuel cells applications. In this respect, underpotential deposited (UPD) metal ad-atoms modified gold electrodes exhibited interesting catalytic activities [1, 2, 10, 11] where, for instance, an effective oxidation of glucose at relatively negative potentials was observed at Ag-UPD Au single crystal electrodes.

On the other hand, the use of nanoparticles of different metal substrates to fabricate highly active electrodes has attracted great interest due to its wide range of electrochemical applications. For instance, Au nanoparticles showed interesting electrocatalytic activity towards many reactions, among which are CO oxidation [13-15], O_2 reduction [16-20] and glucose oxidation [21, 22].

We have a special interest in the fuel cells applications of the elctrocatalytic oxidation of glucose [1, 2, 10, 11, 21, 22]. Our aim is the design and preparation of anode catalysts that would achieve an effective glucose oxidation at reasonable low overpotentials and enable the preparation of a glucose-air fuel cell as schematically presented in scheme 1. The preparation of Au nanoparticles (AuNPS) was reported mainly through chemical reduction of aqueous solution of the chloro-metallate anion [23-25] or the electrochemical deposition on an inert substrate [26-28]. Other methods include metal vapor synthesis, sol-gel, impregnation, deposition-precipitation and dip coating.

Carbon-based catalysts are of special practical interest since they are very cost-effective, offer a more convenient usage and can have quite large surface area. In last decade, a novel carbon material, namely the plastic formed carbon (PFC) was prepared through the mixing of graphite with an organic binder followed by a pyrolysis to a glassy carbon [29]. In the present work, we report the voltammetric studies of the electrocatalytic oxidation of glucose in an alkaline solution (i.e. 0.1 M NaOH) at Au nanoparticle-modified (PFC) electrodes. AuNPS were prepared via the chemical reduction of $AuCl_4^-$ to form Au nanoparticles (ø = 2 nm) followed by “mechanical” deposition onto a plastic formed carbon (PFC) substrate. This material has the advantage to prepare electrodes of large surface area with reasonable rigidity.

By comparison of the voltammetric curves of bare and modified electrodes we could obtain a clear idea about the catalytic activity of the prepared (AuNPS/PFC) electrodes toward the electrocatalytic oxidation of glucose in alkaline media.



Scheme 1. Schematic representation of the parameters of the desired "Glucose-Air" fuel cell.

2. Experimental

2-1. Chemicals and Electrodes:

D-glucose was purchased from Wako Pure Chemical Industries, Ltd. NaOH and H_2SO_4 (ultra pure grade, Kanto Chemical Co., Inc.) were used to prepare the electrolytes. All solutions were prepared using ultra pure water (Milli-Q 18.2 MΩ.cm, Millipore System Inc.). For nanonparticles preparation, tetraoctylammonium bromide (TOAB), ethanol (EtOH) and Toluene (99.5%) from Wako Pure Chemical Industries, Ltd., Japan, along with decane-1-thiol (DT, 96%) and sodium borohydride ($NaBH_4$, 99.995%) purchased from Aldrich Chemical Company, Inc., and $HAuCl_4.3H_2O$ (99.9%) from Sigma-Aldrich Japan, Co.Ltd., were used.

Plastic-formed carbon (PFC) electrodes (Mitsubishi Pencil Co., Japan) were used as working electrodes. Home-made Ag|AgCl|KCl(sat) electrode and Pt-plate served as reference and counter electrodes, respectively.

To avoid any possible contamination, all glassware used were cleaned thoroughly by boiling in three-times diluted nitric acid solution then rinsing and further sonicating in Milli-Q water for 30 min. Additionally, the electrochemical cell was specially designed so that the reference electrode's compartment was separated from the other two by means of a fritted glass wall to avoid any possible leakage of chloride anions into the investigated electrolytic solutions.

Electrochemical measurements were performed in a conventional three-electrode cell using a computer-controlled CV-50 W voltammetric analyzer (Bioanalytical Systems, Inc.). Electrolyte solutions were initially purged with high-purity nitrogen for at least 20 minutes, and during measurements the nitrogen flow was kept uninterrupted to maintain an N_2-saturated experimental condition.

2-2. Nanoparticles preparation:

Gold nanoparticles of 2nm core size were prepared using a two-phase (water-toluene) reduction of $AuCl_4^-$ by ($NaBH_4$) in the presence of decanthiol (DT) as reported elsewhere [24, 30]. $AuCl_4^-$ was transferred from aqueous solution (10 mM) to toluene (80 ml) using TOAB (1.5g) under vigorous stirring for about 15 min. This was visualized as the clearing of the initially yellow-colored aqueous phase and the orange-brown coloring of the toluene phase as $AuCl_4^-$ was transferred into it. The organic phase was then isolated, DT (360 µl) was added and the solution stirred again for about 5 min and the orange-brown color cleared. $NaBH_4$ (0.77g in 25 ml Milli-Q water) was then added very slowly while stirring vigorously, and the solution's color turns to very dark. The organic phase was then stirred for further 3 hours at room temperature then collected and the solvent (toluene) removed on a rotary evaporator. The dark-brown DT-Au nanoparticles were then three-times cleaned with ethanol by centrifugation. Finally, the purified pellet was then dissolved in Hexane (15 ml) for storage.

Before each experiment, Au nanoparticle-modified PFC (AuNPS/PFC) electrodes were prepared by casting 50 µl of the above prepared solution onto the pre-cleaned electrode surface (i.e. carefully polished then sonicated in Milli-Q for at least 20 min). Upon air drying at room temperature, the electrode was heated to 300 °C for 2 hours to remove the DT encapsulate. The so-prepared AuNPS/PFC electrode was then sonicated in

Milli-Q water prior to being mounted on the electrochemical cell between an o-ring and a glass disc using a metal clip. The geometrical electrode area (ca. 0.28 cm^2) was defined by the circumference of the o-ring and forms the bottom of the cell. All potentials are reported with respect to Ag|AgCl|KCl(sat) electrode and current densities are calculated based on the apparent geometric area. All experiments were carried out at room temperature.

3. Results and discussion

The data obtained at a bare, unmodified (PFC) electrode in a (5mM glucose + 0.1 M NaOH) solution showed that this surface is completely inactive for glucose oxidation in the potential range of interest and only oxidation and reduction peaks of the electrode surface itself are observed (cf. inset of figure 1). This kind of behavior is indeed expected for carbon-based electrodes [21, 22, 31].

Upon modification of the PFC electrode surface by deposition of AuNPS, as described in the experimental section, the as-prepared AuNPS/PFC electrode showed an extraordinary, completely different catalytic activity towards glucose oxidation in the same experimental conditions as displayed in figure 1.

Two distinct oxidation peaks were observed at around ca. −0.38 V and ca. 0.35 V that are due to the direct electrochemical oxidation of glucose to gluconolactone, its two-electron oxidation product, and the further oxidation of the latter at more positive potentials, respectively [1-3, 5, 32, 33]. The electrocatalytic oxidation of glucose in the present work condition is believed to proceed via the scheme outlined in scheme 2 [1].

This data is in a good agreement with a previously published work of our group with a more positive catalytic effect obtained in the current one, however. The reason for that would most probably be related to the careful preparation of the modified electrodes in the current study, especially the pre-treatment of the electrodes before electrochemical measurement as well as the electrochemical cell thorough cleaning. This is in line with the behavior at Au single crystal electrodes were electrocatalytic activity of both bare and modified electrodes depended clearly on the electrode surface quality (annealing) as well as the electrochemical cell preparations (cleaning and reagents)[1, 2, 10, 11]. In a previous work we demonstrated the impact of the electrochemical pre-treatment of carbon-based substrate electrodes on the obtained catalytic activities [21, 22].

Additionally, this observed catalytic activity is interestingly comparable to that obtained at Ag-UPD modified single crystal Au(111) and Au(100) electrodes [1, 2, 10] while it is very much cost-effective which is one major concern in the field of fuel cells applications.

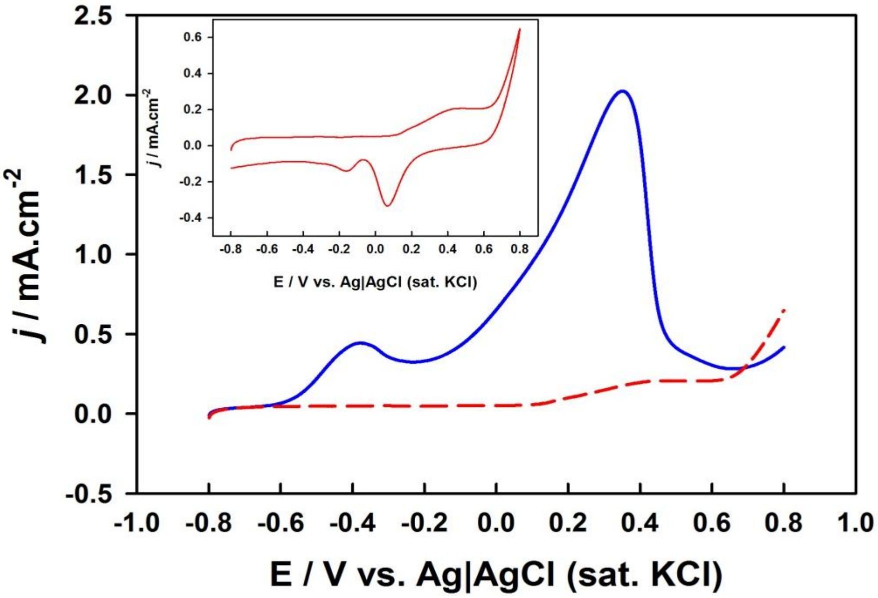
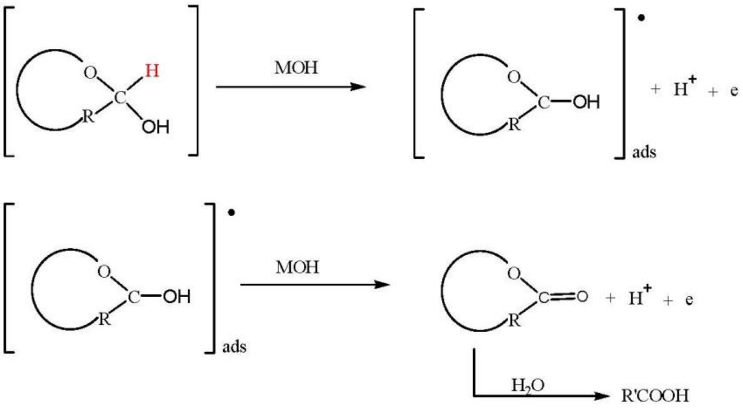


Figure 1. Voltammetric curves of glucose oxidation in a (5 mM glucose + 0.1 M NaOH) solution at bare (dashed line) and AuNPS-PFC electrodes. Scan rate: 50 mV s^{-1}. The inset shows the cyclic voltammogram at bare PFC electrode in the same conditions.

It is noteworthy that the oxidation peak current density (j_p) of glucose electrocatalytic oxidation in the present work conditions is linearly proportional to the scan rate (v) confirming the adsorption electrochemical process of the studied glucose oxidation at the prepared catalyst in the present work conditions as well-documented in literature for similar catalysts [12, 25, 31, 32, 34] and in accordance with scheme 2. Moreover, the as-prepared (AuNPS/PFC) catalyst is much easier to design and handle compared with previously reported Au single crystal-based electrodes [1, 2, 10, 11]. In fact, the latter require a very careful pr-treatment, for instance annealing and quenching, in addition to the high cost demanded for the preparation of a larger-scale surface area when it comes to the design of fuel cells prototype. This is very obviously not the case of the investigated (AuNPS/PFC) catalyst in the present work.



Scheme 2. Oxidation mechanism of glucose at gold electrodes (M = Au) at potentials more negative than 0 V vs. Ag|AgCl. MOH denotes the active site on the electrode surface.

The durability of the prepared catalyst was checked by constant potential (ca. −0.3V) electrolysis in the same work solution (5 mM glucose + 0.1 M NaOH) and results are reported in figure 2 displaying the variation of the ratio (j/j_0) with time. Where j and j_0 are the current densities at a given time t (min) and that at the beginning of the electrolysis (t = 0 min), respectively.

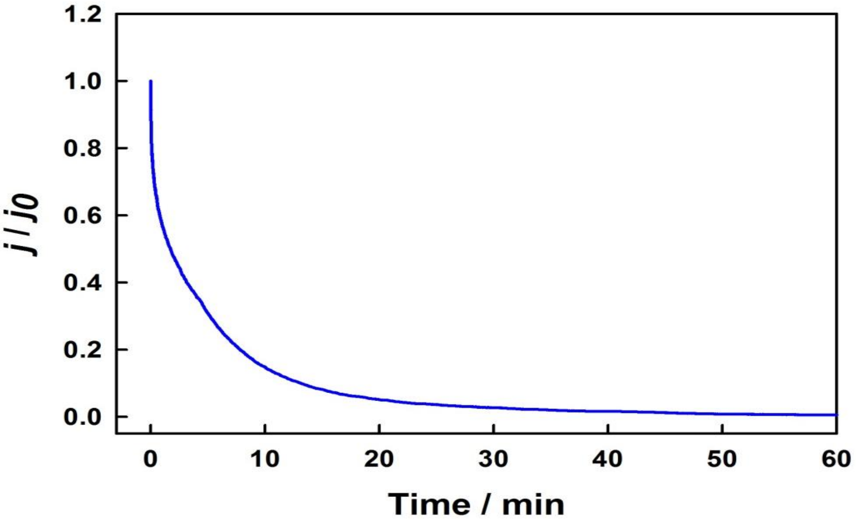


Figure2. Time-variation of the anodic current density during the constant potential electrolysis (E = −0.3 V) of glucose oxidation in a (5 mM glucose + 0.1 M NaOH) solution AuNPS-PFC electrodes.

As can be depicted from figure 2, despite its decrease with increasing electrolysis time, there is always a positive anodic current flow even after one hour of continuous electrolysis. This makes the prepared AuNPS-PFC catalyst a potential candidate for fuel cells application. An improved anodic current would be more preferable, though.

4. Conclusion

Glucose electrocatalytic oxidation has been investigated at Au nanoparticle-modified plastic formed carbon electrodes. The prepared AuNPS-PFC catalyst showed a very interesting catalytic activity that was nicely comparable to the reported data for one of the best bimetallic electrodes for glucose electrocatalytic oxidation (i.e. Ag-UPD modified single crystal Au electrodes).

The voltammetric investigations of the catalytic activity of AuNPS/PFC electrode revealed that the oxidation current flow commenced at ca. −0.6 V and reached the peak potential of the effective two-electron oxidation of glucose to gluconolactone at ca. −0.38 V. Sweeping the potential to higher range confirmed the further effective oxidation of the initially produced lactone with an oxidation peak potential appearing at ca. 0.35 V vs. Ag|AgCl|KCl(sat).

This new approach enabled the preparation of a very much cheaper yet highly-active catalyst paving the way to an interesting step forward, towards to design of glucose-based fuel cells.

A more “tunable” catalytic activity at similar catalysts is currently under investigation and will be the subject of an upcoming communication.

Acknowledgment - S. Ben Aoun acknowledges the partial financial support to this work from the Deanship of Scientific Research, Taibah Univeristy (Project No. 658/432).

References

1. Ben Aoun S., Dursun, Z., Koga, T., Bang, G.S., Sotomura, T., Taniguchi, I., Effect of metal ad-layers on Au(111) electrodes on electrocatalytic oxidation of glucose in an alkaline solution; *J. Electroanal. Chem.*, 567 (2004) 175-183.
2. Ben Aoun S., Bang, G.S., Koga, T., Nonaka, Y., Sotomura, T., Taniguchi, I., Electrocatalytic oxidation of sugars on silver-UPD single crystal gold electrodes in alkaline solutions; *Electrochem. Commun.*, 5 (2003) 317-320.
3. Larew L.A., Johnson, D.C., Concentration dependence of the mechanism of glucose oxidation at gold electrodes in alkaline media; *Journal of Electroanalytical* 262 (1989) 167-182.
4. Vassilyev Y.B., Khazova, O.A., Nikolaeva, N.N., Kinetics and mechanism of glucose electrooxidation on different electrode-catalysts: Part II. Effect of the nature of the electrode and the electrooxidation mechanism; *J. Electroanal. Chem.*, 196 (1985) 127-144.
5. Adzic R.R., Hsiao, M.W., Yeager, E.B., Electrochemical oxidation of glucose on single crystal gold surfaces; *J. Electroanal. Chem.*, 260 (1989) 475-485.
6. De Mele M.L.F., Videla, H.A., Arvia, A.J., The influence of glucose and electrolyte composition on the voltammetric response and open-circuit potential decay of bright polycrystalline gold electrodes; *Bioelectrochem. Bioenerg.*, 16 (1986) 213-233.
7. Luna A.M.C., de Mele, M.F.L., Arvia, A.J., The electro-oxidation of glucose on microcolumnar gold electrodes in different neutral solutions; *J. Electroanal. Chem.*, 323 (1992) 149-162.
8. Hsiao M.W., Adzic, R.R., Yeager, E.B., The effects of adsorbed anions on the oxidation of D-glucose on gold single crystal electrodes; *Electrochim. Acta*, 37 (1992) 357-363.
9. Hsiao M.W., Adžić, R.R., Yeager, E.B., Electrochemical Oxidation of Glucose on Single Crystal and Polycrystalline Gold Surfaces in Phosphate Buffer; *J. Electrochem. Soc.*, 143 (1996) 759-767.
10. Taniguchi I., Nonaka, Y., Dursun, Z., Ben Aoun, S., Jin, C., Bang, G.S., Koga, T., Sotomura, T., Electrocatalytic oxidation of sugars at Ag ad-layer modified Au(100) electrodes in alkaline solutions; *Electrochemistry*, 72 (2004) 427-429.
11. Dursun Z., Ben Aoun, S., Taniguchi, I., Electrocatalytic oxidation of D-glucose using a Cd ad-atom-modified Au(111) electrode in alkaline solution; *Turk. J. Chem.*, 32 (2008) 423-430.
12. Liang W., Zhuobin, Y., Direct Electrochemistry of Glucose Oxidase at a Gold Electrode Modified with Single-Wall Carbon Nanotubes; *Sensors*, 3 (2003) 544-554.
13. Haruta M., Size- and support-dependency in the catalysis of gold; *Catal. Today*, 36 (1997) 153-166.
14. Grunwaldt J.-D., Kiener, C., Wögerbauer, C., Baiker, A., Preparation of Supported Gold Catalysts for Low-Temperature CO Oxidation via “Size-Controlled” Gold Colloids; *J. Catal.*, 181 (1999) 223-232.
15. Boccuzzi F., Chiorino, A., Manzoli, M., Au/TiO2 nanostructured catalyst: effects of gold particle sizes on CO oxidation at 90 K; *Mater. Sci. Eng., C*, 15 (2001) 215-217.
16. El- Deab M.S., Ohsaka, T., An extraordinary electrocatalytic reduction of oxygen on gold nanoparticles-electrodeposited gold electrodes; *Electrochem. Commun.*, 4 (2002) 288-292.
17. El-Deab M.S., Sotomura, T., Ohsaka, T., Oxygen reduction at electrochemically deposited crystallographically oriented Au(1 0 0)-like gold nanoparticles; *Electrochem. Commun.*, 7 (2005) 29-34.
18. El-Deab M.S., Okajima, T., Ohsaka, T., Electrochemical Reduction of Oxygen on Gold Nanoparticle-Electrodeposited Glassy Carbon Electrodes; *J. Electrochem. Soc.*, 150 (2003) A851-A857.

19. El-Deab M.S., Ohsaka, T., Hydrodynamic voltammetric studies of the oxygen reduction at gold nanoparticles-electrodeposited gold electrodes; *Electrochim. Acta*, 47 (2002) 4255-4261.
20. Ben Aoun S., Dursun, Z., Sotomura, T., Taniguchi, I., Effect of metal ad-layers on Au(1 1 1) electrodes on electrocatalytic reduction of oxygen in an alkaline solution; *Electrochem. Commun.*, 6 (2004) 747-752.
21. Ben Aoun S., Taniguchi, I., Highly Catalytic Electrode for Glucose Electro-oxidation Based on Au Nanoparticles Electrodeposited onto HOPG Substrate; *Chem. Lett.*, 36 (2007) 898-899.
22. Ben Aoun S., Taniguchi, I., Effective Electrocatalytic Oxidation of Glucose at Platinum Nanoparticle-based Carbon Electrodes; *Chem. Lett.*, 37 (2008) 936-937.
23. Chen W., Cai, W.P., Liang, C.H., Zhang, L.D., Synthesis of gold nanoparticles dispersed within pores of mesoporous silica induced by ultrasonic irradiation and its characterization; *Mater. Res. Bull.*, 36 (2001) 335-342.
24. Brust M., Walker, M., Bethell, D., Schiffrin, D.J., Whyman, R., Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid-Liquid system; *J. Chem. Soc., Chem. Commun.*, (1994) 801-802.
25. Li J., Yu, J., Zhao, F., Zeng, B., Direct electrochemistry of glucose oxidase entrapped in nano gold particles-ionic liquid-N,N-dimethylformamide composite film on glassy carbon electrode and glucose sensing; *Anal. Chim. Acta*, 587 (2007) 33-40.
26. Finot M.O., Braybrook, G.D., McDermott, M.T., Characterization of electrochemically deposited gold nanocrystals on glassy carbon electrodes; *J. Electroanal. Chem.*, 466 (1999) 234-241.
27. Finot M.O., McDermott, M.T., Characterization of n-alkanethiolate monolayers adsorbed to electrochemically deposited gold nanocrystals on glassy carbon electrodes; *J. Electroanal. Chem.*, 488 (2000) 125-132.
28. Guerra-Balcázar M., Torres-González, J., Terol-Villalobos, I., Morales-Hernández, J., Castañeda, F., Glassy carbon electrode-supported au nanoparticles for the glucose electrooxidation: On the role of crystallographic orientation; *Journal of Nanomaterials*, 2012 (2012).
29. Ikarashi Y., LeRoy Blank, C., Suda, Y., Kawakubo, T., Maruyama, Y., Application of a novel, plastic formed carbon as a precolumn packing material for the liquid chromatographic determination of acetylcholine and choline in biological samples; *J. Chromatogr. A*, 718 (1995) 267-272.
30. Hostetler M.J., Wingate, J.E., Zhong, C.-J., Harris, J.E., Vachet, R.W., Clark, M.R., Londono, J.D., Green, S.J., Stokes, J.J., Wignall, G.D., Glish, G.L., Porter, M.D., Evans, N.D., Murray, R.W., Alkanethiolate Gold Cluster Molecules with Core Diameters from 1.5 to 5.2 nm: Core and Monolayer Properties as a Function of Core Size; *Langmuir*, 14 (1998) 17-30.
31. Zhang J., Zhu, X., Dong, H., Zhang, X., Wang, W., Chen, Z., In situ growth cupric oxide nanoparticles on carbon nanofibers for sensitive nonenzymatic sensing of glucose; *Electrochim. Acta*, 105 (2013) 433-438.
32. Feng D., Wang, F., Chen, Z., Electrochemical glucose sensor based on one-step construction of gold nanoparticle–chitosan composite film; *Sensors and Actuators B: Chemical*, 138 (2009) 539-544.
33. Arjona N., Guerra-Balcazar, M., Trejo, G., Ledesma-Garcia, J., Arriaga, L.G., Electrochemical growth of Au architectures on glassy carbon and their evaluation toward glucose oxidation reaction; *New J. Chem.*, 36 (2012) 2555-2561.
34. Cui H.-F., Zhang, K., Zhang, Y.-F., Sun, Y.-L., Wang, J., Zhang, W.-D., Luong, J.H.T., Immobilization of glucose oxidase into a nanoporous TiO2 film layered on metallophthalocyanine modified vertically-aligned carbon nanotubes for efficient direct electron transfer; *Biosens. Bioelectron.*, 46 (2013) 113-118.

(2013) ; http://www.jmaterenvironsci.com