Int. J. Electrochem. Sci., 6 **(2011)** 4667 - 4675

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Synthesis of Au Nanoparticles/Polyaniline Composites by Electroreduction for Glucose Oxidation

M. Guerra-Balcázar[1], *R.Ortega*[1], *F. Castaneda*[1+], *L.G. Arriaga*[1], *J. Ledesma-Garcia*[2,*]

[1] Centro de Investigación y Desarrollo Tecnológico en Electroquímica S.C., Sanfandila, C.P. 76703, Querétaro, México.
[2] División de Investigación y Posgrado, Facultad de Ingeniería, Universidad Autónoma de Querétaro, C.P. 76010, Querétaro, México.
[+]E-mail: fcastaneda@cideteq.mx

[*]E-mail: janet.ledesma@uaq.mx

Received: 10 April 2011 / *Accepted:* 2 September 2011 / *Published:* 1 October 2011

Au nanoparticles on polyaniline films (Au/Pani) were prepared by electrochemical reduction of Au (III)/Pani complexes previously anchored on glassy carbon electrodes and characterized by scanning electron microscopy, X-ray diffraction and electrochemical techniques. SEM results showed the presence of Au particles with average particle size around13 nm. The composites were used for the glucose electro-oxidation and evaluated in basic media by cyclic voltammetry, where the onset potential showed a negative shift ca. 80 mV compared with polycrystalline Au.

Keywords: Au nanoparticles, Au electroreduction, polyaniline films, glucose oxidation.

1. INTRODUCTION

Glucose oxidation reaction represents an attractive research field due to their applications as fuel, medical applications and food industries [1-3]. Glucose electro-oxidation has been examined extensively by using of great variety of electrode materials as noble metals, modified electrodes with ad-atoms or metallic alloys. [4-6]. However, it is well known that the glucose oxidation on these electrode materials leads to the formation of intermediates, which can be strongly adsorbed on the electrode surface. This effect results in blocking of active sites on the electrocatalyst surface, inhibiting the subsequent glucose oxidation [7]. Au is attractive electrode material for the glucose oxidation in alkaline media and more recently Au nanoparticles have been used for the glucose oxidation [8-9]. Au nanostructured exhibits high eletrocatalytic activity toward this reaction; however the result mainly depends of the nanoparticles distribution [10].

Several efficient methods have been reported for the synthesis of Au nanoparticles in emulsion phase [11-12]. However, exists an inherent difficult to support the Au material on conductor substrates with good dispersion, avoiding their agglomeration. It is not easy to achieve nanostructures with these characteristics and they are obtained as Au thin films commonly [13]. In this context, polyaniline (Pani) has high affinity for metallic ions, specifically for the $AuCl_4^-$ ion, where takes place the spontaneous reduction of $AuCl_4^-$/Pani complex [14]. For this reason, this polymer represents a potential alternative as template of Au nanoparticles. In previous reports, Au/Pani composites have been prepared *in situ* by aniline polymerization in the presence of $HAuCl_4$ as oxidant [15-16]. Baba and coworkers have carried out the synthesis of Au nanoparticles by suspension on Pani substrates [17].

In this paper, we describe an electrochemical method for preparing Au nanoparticles supported on Pani composites [18]. The composites were prepared by the electro-reduction of $AuCl_4^-$/Pani complex on glassy carbon electrodes (GCEs). After that, the glucose oxidation was evaluated using the modified electrode by cyclic voltammetry (CV) in basic media and compared with polycrystalline Au electrode. The onset potential for glucose oxidation on Au/Pani composites showed a negative shift ca. 80 mV compared with polycrystalline Au.

2. EXPERIMENTAL

2.1. Reagents and Materials

Aniline and D-Glucose (Aldrich) were used without further purification. Au nanoparticles were prepared from $HAuCl_4 \cdot 3H_2O$ (Aldrich 99.999%). The electrolytic solutions for electrochemical experiments consisted of 0.5M H_2SO_4 (J. T. Baker) and 0.1M NaOH (J.T. Baker). All aqueous solutions were prepared using deionized water DI ($\rho \geq 18$ MΩ cm). Research-grade N_2 was purchased from Infra (99.999% pure).

Electrochemical experiments were performed with cyclic voltammetry (CV) using an Autolab PGSTAT302 Potentiostat/Galvanostat. GCEs were used as working electrodes where Pani films were immobilized (3 mm in diameter). A standard three-electrode glass cell equipped with Hg/Hg_2SO_4 (0.5 M H_2SO_4) or Hg/HgO (1 M KOH) as reference electrode and Pt wire as counter electrode was employed. For comparison Au polycristalline (Au poli) bar electrode was employed. Potentials in the text are referred to Normal Hydrogen Electrode (NHE). GCEs were polished with alumina (0.05μm) and rinsed with plenty DI water. After that, the electrodes were sonicated for 10 minutes. Finally, they were cleaned with ethanol (analytical grade from J.T. Baker) and DI water.

2.2. Preparation of Au/Pani Composites

Pani films were prepared on GCE by cycling potential at 50 mVs^{-1} between 0 and 1 V vs. NHE in 0.1 M aniline + 0.5 M H_2SO_4 aqueous solution according to already published procedures [19]. Afterward, Pani-modified GCEs were immersed in 0.5 mM $HAuCl_4 \cdot 3H_2O$ aqueous solution for different times. Lapsed time, the electrodes were rinsed with DI water to eliminate the non-complexed Au ions. The electroreduction in the previously formed complex between Au ions and Pani film was carried out in 0.5 M H_2SO_4 aqueous solution by applying of 0.055 mVpotential during 20 s. The potential pulse for reduction was chosen from a cyclic voltammogram of Pani/Au ions on GCE in acid media.

2.3. Physicochemical Characterization of Au/Pani Composites

Composite obtained was characterized by X-ray diffraction (XRD) patterns from films of Au/Pani deposited onto glassy carbon substrate in an X-pert MPD Phillips Diffractometer using Cu Kα radiation operating at 40 kV and 20 mA. The peak profile of the reflection in the face-centered cubic structure was obtained by using the Marquardt algorithm. The mathematical treatment permits the average crystallite size to be estimated [11]. The morphology of Au/Pani composites was investigated using a JEOL, JSM 5800-LV scanning electron microscope (SEM) operated at 5 kV.

2.4. Glucose oxidation on Au/Pani Composites

Glucose electro-oxidation was evaluated in 0.01 M Glucose + 0.1 M NaOH aqueous solution by CV on Au/Pani-modified GCE at room temperature. For comparison, polycrystalline Au electrode was used.

3. RESULTS AND DISCUSSION

3.1. Preparation and Electrochemical Characterization of Au/Pani Composites

Figure 1 shows the voltammetric profile obtained during the aniline polymerization in acid media on clean GCE. Aniline electro-polymerization starts at 0.75 V in the first cycle. Successive cycles indicate the growth of polyaniline film as evidenced by the increase in the redox currents as can be seen in the Figure. When the polyaniline film is formed, it is possible to observe several processes. The first redox process, located at 0.25 V and 0.08 V in the positive and negative scan respectively, corresponds to electron transfer from/to the electrodeposited polyaniline film. In order to compensate the charge of polyaniline film, anion transport from/to the electrolyte solution, i.e., anion doping and de-doping, should occurs [17, 20-21]. The following redox process, at 0.5 V, is due to polymer decomposition. Finally, the last process located at more positive potential (approximately at 0.8 V) is related with two steps: the first is the electron transfer that can be attributed to the oxidation of the Pani film and the second, is due to the monomer oxidation [22-23].

The presence of metallic Au on the Pani-modified GCE was confirmed by CV in aqueous 0.5 M H_2SO_4. The typical voltammetric profile of metallic Au in acid media is observed in Figure 2, where the Au oxides formation and reduction regions are identified [24]. Figure 2a presents the electrochemical response of an Au/Pani modified-GCE prepared by spontaneous reduction (chemical reduction). On the other hand, Figure 2b shows the modified surface with Au/Pani after that the application of 0.055 mV potentiostatic pulse during 20 s.

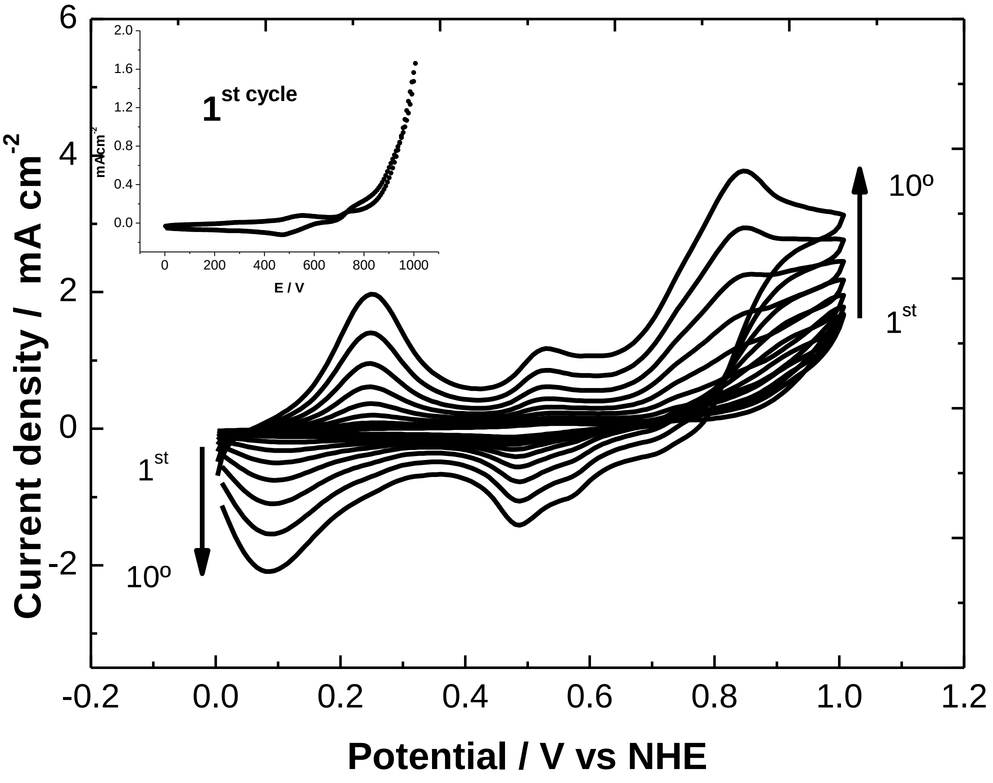

Figure 1. Polymerization of 0.1 M aniline on GCE in N_2-purged 0.5 M H_2SO_4 solution. Scan rate 50 mV s^{-1}. Inset, first cycle of polymerization reaction.

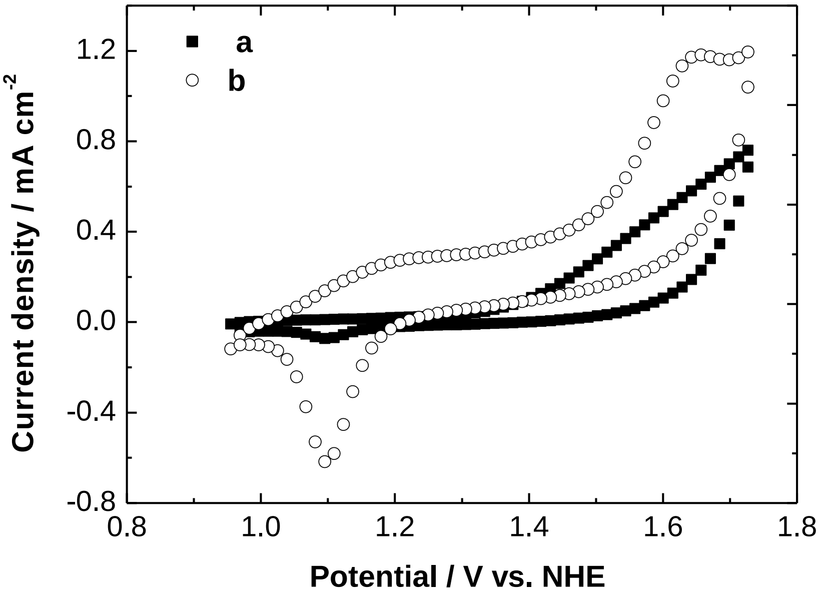

Figure 2. Voltammetric profiles of Au/Pani on GCEs in N_2-purged 0.5M H_2SO_4: (a) before and (b) after potentiostatic pulse. Scan rate 50 mV s^{-1}.

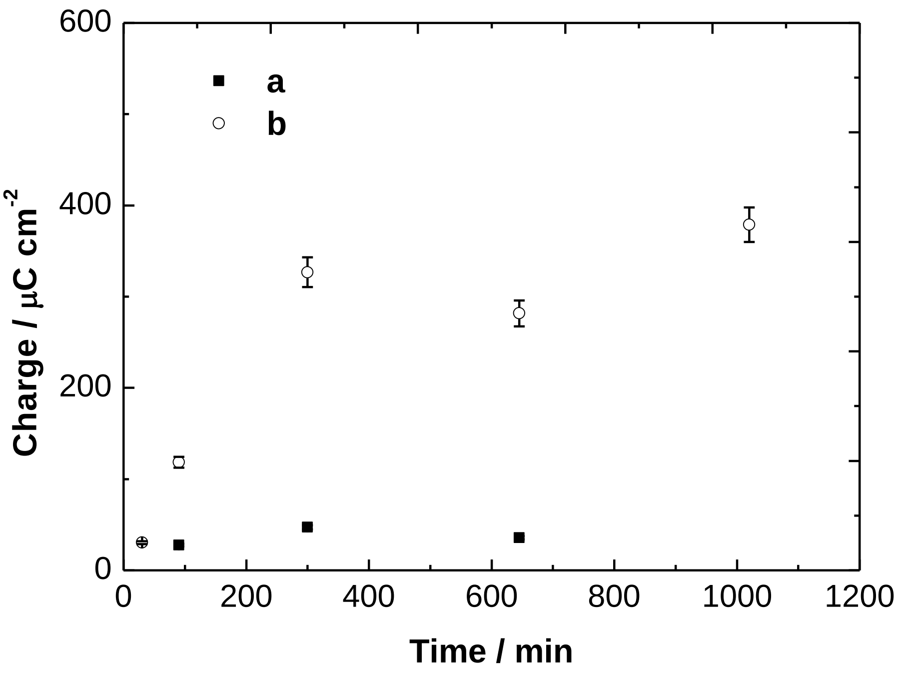

Figure 3. Comparison of charges related with Au oxide reduction peak (a) spontaneous reduction and (b) electrochemical reduction at different immersion times.

In order to optimize the Au nanoparticles quantity on Pani film, several immersion times of the Pani-modified GCEs in 0.5 mM $HAuCl_4 \cdot 3H_2O$ aqueous solution were tested following the same procedure described in section 2.2. Afterward, the charge attributed to Au oxides reduction peak after subtraction of double-layer was estimated as a function of immersion time. Figure 3 compares the calculated charges before and after of the application of the potentiostatic pulse. It is important to note that even without the pulse application, is evident the presence of metallic Au in the polyaniline film (Figure 3a). However, the Au amount incremented considerably by electroreduction effect (Figure 3b).

According to results in Figure 3a and 3b, the Au reduction on polyaniline film takes place by two steps: first corresponds to spontaneous chemical reduction of Au ions and the following is due to electrochemical reduction of adsorbed auric ions by the action of potential pulse. Previous reports emphasize the ability of polyaniline for the first process [14].

3.2. Physicochemical Characterization of Au/Pani Composites

SEM micrograph and particle size histogram of Au/Pani-modified GCE are shown in Figure 4a and 4b respectively, where is possible to appreciate good dispersion of Au nanoparticles on the Pani surface with 13 nm of average crystal size. Further, two morphologies can be observed: the first one corresponds to polyaniline in fibers form. The second one shows the nanoparticles anchored on polymer. XRD analysis (not shown) of the composite showed the existence of fcc metallic phase with the main peaks correspond to the planes (111), (200), (220), (311) and (222) located at 38◦, 45◦, 65◦, 78◦ and 82◦ respectively [25]. The average crystal size was estimated by XRD pattern in 16.5 nm.

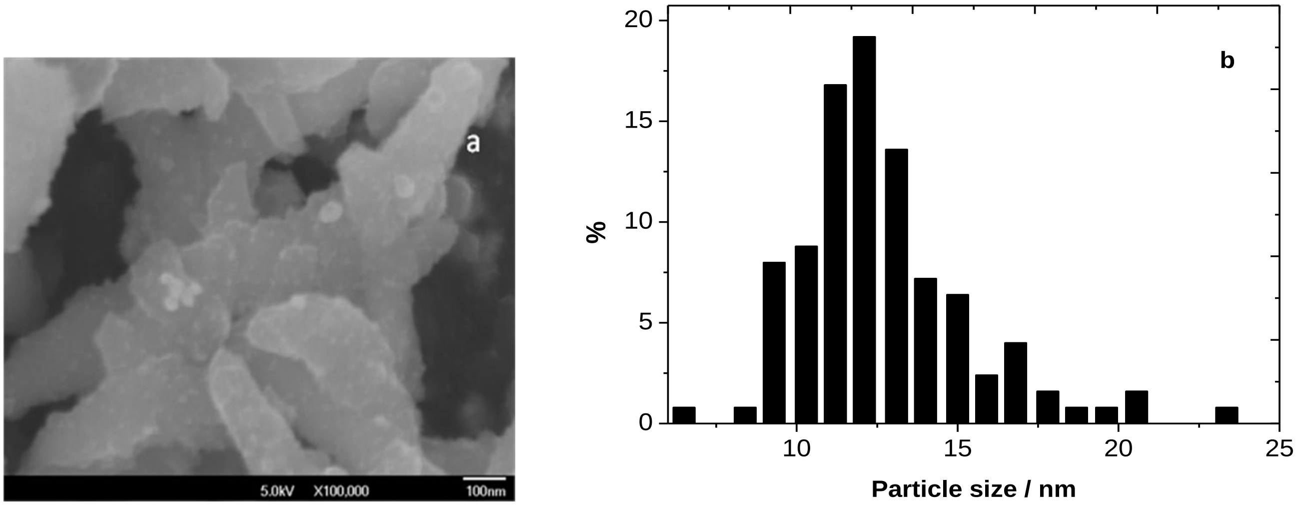

Figure 4. (a) SEM micrograph and (b) particle size distribution.

3.3. Electrochemical Response for Glucose Oxidation

The electrocatalytic properties of Au/Pani for glucose electro-oxidation were investigated in 0.01 M glucose + 0.1 M NaOH aqueous solution by CV. Figure 5 (for clarity only shows the response measured between -0.6 and 0.9 V at 50 mVs^{-1}). For comparison glucose electrooxidation on polycrystalline Au is also presented (Figure 5a).

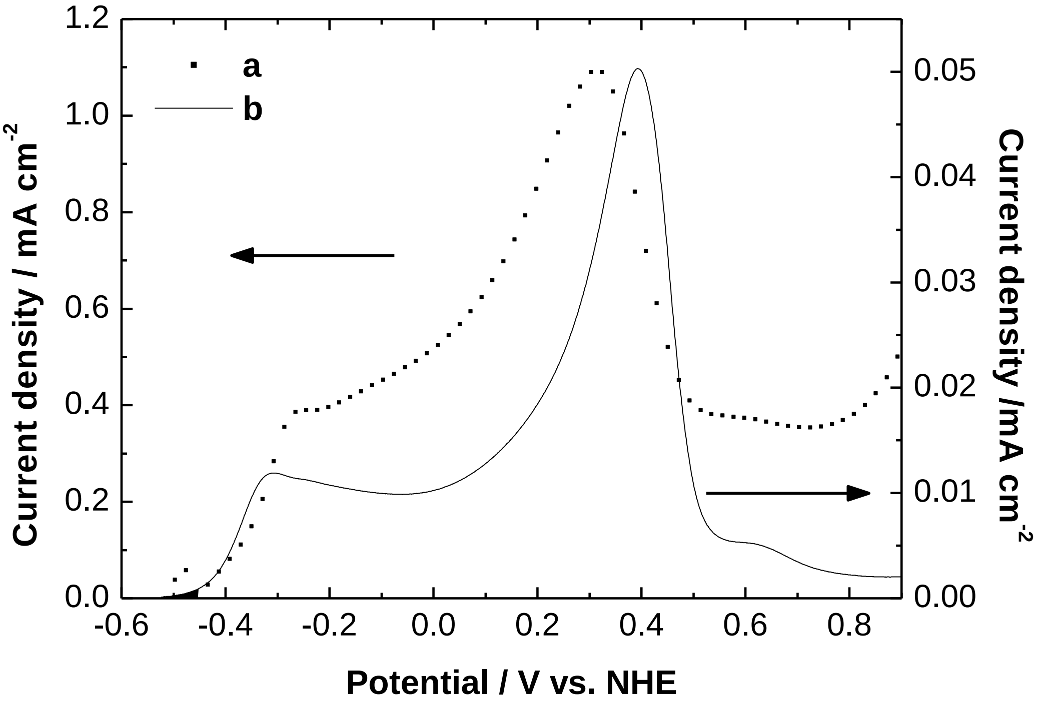

Figure 5. LSV obtained on (a) Au/Pani and (b) polycrystalline Au electrodes in 0.1 M glucose + 0.1M NaOH aqueous solution at 50 mV s^{-1}.The measurements were carried out at room temperature in saturated N_2 environment.

Glucose electro-oxidation peak was observed in the forward scan at -0.280 V. According to previous reports, glucose oxidation occurs at -0.3 V approximately [7]. This process is directly related with the transfer of two electrons to the gluconic acid formation or similar species, which are adsorbed on the electrode surface [7, 9]. The following process located at 0.310 and 0.390 V in Figure 5a and 5b, for polycrystalline Au and Au/Pani respectively, is related with the successive oxidations, where another set of short-chain carboxylic acids as formic or oxalic can be formed [26]. The onset potential for glucose electro-oxidation on Au/Pani showed a negative shift ca. 80 mV compared with polycristalline Au.

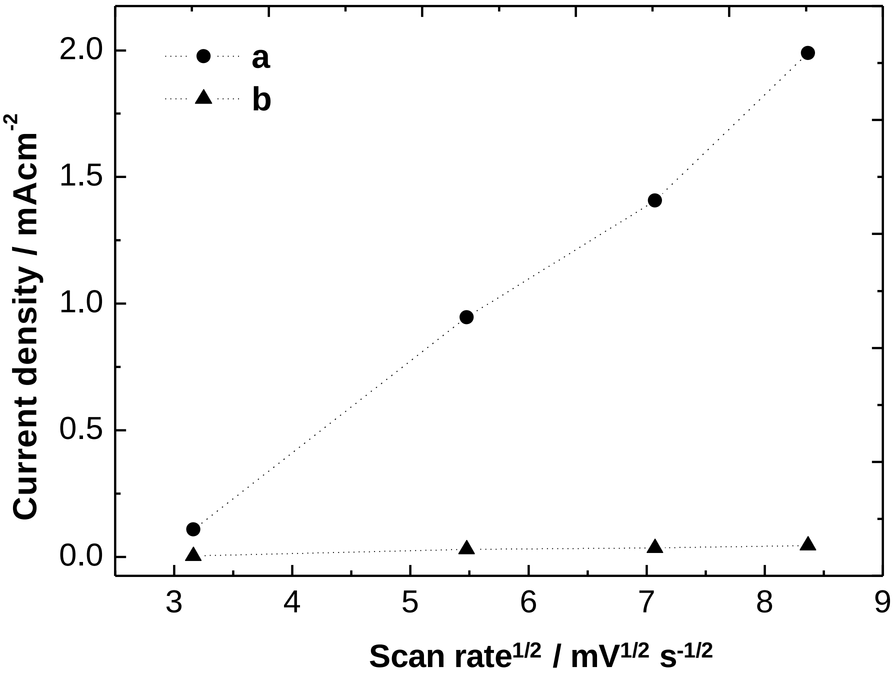

Figure 6. Plot of the anodic current density of 0.1M glucose in 0.1M NaOH *vs* the scan rate, using a) Au/Pani composite and b) polycrystalline Au. LSV experiments were carried out at room temperature in saturated N_2 environment.

In order to explain the process on the electrode surface during the glucose electro-oxidation is necessary to consider the following factors: 1) the presence of OH^- adsorbed on the electrode surface permits the reaction to be proceeded. However the OH^- coating on the surface has direct dependency of applied potential. 2) The surface partially covered by OH^- permits the glucose oxidation to form gluconate. 3) At more positive potential values in the scan, must occur the organic molecule desorption, while the OH^- coating increases on the electrode surface. 4) At this point, organic molecules located in the vicinity of electrode surface (glucose or gluconate) are re-adsorbed on the surface covered with OH^-. Although the number of sites where the molecules can be anchored is much higher (there are more adsorbed OH^-), those are adsorbed in more than one active site or with various functional groups, causing the breaking of the carbon chain to form smaller carboxylic acids [27].

For Au/Pani composite, some factors may accelerate the first desorption of organic molecules, including: particle size, the presence of (311) plane with characteristic of low coordination number, metal support interactions that can modify the electronic properties of metal, the type and number of active sites or greater presence of metallic atoms with low coordination number. It is necessary to consider that the adsorption on active sites located near to support is weaker. Then, the energy required to carry out the process is lower, which could suggest that the Au/Pani based material favors the glucose electro-oxidation compared with polycrystalline Au [28-29].

The effect of scan rate on the behavior of glucose oxidation on Au/Pani composite and polycrystalline electrode was investigated by linear sweep voltammetry (LSV) measurements. In Figure 6 the current density was plotted as function of the scan rate ($v^{1/2}$). The result clearly reveals that the peak current density associated to the glucose electro-oxidation increases linearly with the scan rate. This behavior indicates that the electrocatalytic process under study is controlled by diffusion [30]. Furthermore, the current density value recorded with Au/Pani composite electrode is larger than that obtained by using of polycrystalline electrode. This interesting electrode concept offers a promising approach for the development of electrocatalytic surfaces for fuel cells applications where glucose is used as fuel.

4. CONCLUSIONS

In summary Au/Pani on glassy carbon surfaces were prepared by means of potentiostatic electro-reduction. SEM results showed the presence of Au particles with average diameter around 13 nm. The electrocatalytic properties Au/Pani composite were evaluated for the glucose electro-oxidation by electrochemical techniques. Au/Pani composite exhibit better catalytic properties and more negative anodic potential associated to this reaction than that achieved with polycrystalline Au (80 mV approximately). Au nanoparticles prepared by this method and supported on Pani films show some advantages over particles prepared by conventional methods, such as absence of further support for the nanoparticles, prevention of their aggregation and simple preparation.

ACKNOWLEDGMENTS

M. Guerra-Balcázar thanks to Mexican Council for Science and Technology CONACYT for graduate fellowship.

References

1. M. do S. Maia Quintino, H. Winnischofer, M. Nakamura, K. Araki, H.E. Toma and L. Angnes, *Anal. Chim. Acta*, 539 (2005) 215.
2. J. Wang and M. Musameh, *Anal. Chim Acta*, 539 (2005) 209.
3. C. Jin and I. Taniguchi, *Mater. Lett.*, 61 (2007) 2365.
4. C. Zhao, C. Shao, M Li and K. Jiao, *Talanta* 71 (2007) 1769.
5. F. Matsumoto, M. Harada, N. Koura and S. Uesugi, *Electrochem. Commun.*, 5 (2003) 42.
6. G. Wittstock, A. Strübing, R. Szargan and G. Werner, *J. Electroanal. Chem* 444 (1998) 61.

7. M. Tominaga, M. Nagashima, K. Nishiyama and I. Taniguchi, *Electrochem. Commun*., 9 (2007) 1892.
8. C. Jin and Z. Chen, *Synth. Met*., 157 (2007) 592.
9. M. Tominaga, M. Nagashima, K. Nishiyama and I. Taniguchi, *Electrochem. Commun.* 7 (2005) 189.
10. S. Guo and E. Wang, *Anal. Chim. Acta*, 598 (2007) 181.
11. M.J. Hostetler, J.E. Wingate, C-J Zhong, J.E. Harris, R.W. Vachet, M.R. Clark, J.D. Londono, S.J. Green, J.J. Stokes, G.D. Wignall, G.L. Glish, M.D. Porter, N.D. Evans and R.W. Murray, *Langmuir*, 14 (1998)17.
12. M. Brust, M. Walker, D. Bethell, D.J. Shiffrin and R. Whyman, *J. Chem Soc. Chem Commun.*, 7 (1994) 801.
13. M. Tominaga, T. Shimazoe, M. Nagashima, H. Kusuda, A. Kubo and Y. Kuwahara, *J. Electroanal. Chem.*, 590 (2006) 37.
14. D.W. Hatchett, M. Josowics, J. Donald and R. Baer, *Chem. Mater*., 11 (1999) 2994.
15. Z. Guo, Y. Zhang, A. Xu, M. Wang, L. Huang, K. Xu and N. Gu, *J. Phys. Chem. C*, 112 (2008) 12638.
16. Z. Guo, Y. Zhang, L. Huang , M. Wang, J. Wang, J. Sun and L. Xu, *J. Colloid Interf. Sci*., 309 (2007) 518.
17. A.Baba, S. Tian, F. Stefani, C. Xia, Z. Wang, R.C. Advincula, D. Johannsmann and W. Knoll, *J. Electroanal. Chem*., 562 (2004) 95.
18. J. Ledesma-García, L. G. Arriaga, Thomas W. Chapman, R. Velázquez-Castillo and Luis A. Godinez, *J. Electrochem. Soc.*, 157 (2010) E1.
19. A. Sezai Sarac, Murat Ates and Bilge Kilic, *Int. J. Electrochem. Sci*., 3 (2008) 777.
20. S. Mu, C. Chen and J. Wang, *Synth. Met*., 88 (1997) 249.
21. W.S. Huang, B.D. Humphrey and A.G. MacDiarmid, *J. Chem. Soc. Faraday Trans,*. 1 (1986) 82.
22. Z. Tang, D. Geng and G. Lu, *Thin Solid Films*, 497 (2006) 309.
23. E.M. Genies and C.J. Tsintavis, *J. Electroanal. Chem*., 195 (1985) 109.
24. H. Angerstein-Kozlowska, B.E. Conway, A. Hamelin and L. Soicoviciu, *Electrochim.Acta*, 31 (1986) 1051.
25. B. D. Cullity and S.R. Stock, *Elements of X-ray Difraction*, Prentice Hall, New Jersey (2001).
26. M. Tominaga, T. Shimazoe, M. Nagashima and I. Taniguchi, *J. Electroanal. Chem.*, 615 (2008) 51. L.A. Larew and D.C. Johnson. *J. Electroanal Chem.*, 262 (1989) 167.
27. J. Hernández, J. Solla-Gullón, E. Herrero, A. Aldaz and J.M. Feliu, *Electrochim. Acta*, 52 (2006) 1662.
28. Y. Chen, W. Schuhmann and A.W. Hassel, *Electrochem. Commun*., 11 (2009) 2036.
29. A.J. Bard and L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York (1980).