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Imene Chikouche, Charif Dehchar, Ahmed Zouaoui, Sophie Tingry, Fares Rezig, et al.. MODIFICATION OF POLYPYRROLE FILM WITH GOLD MICROPARTICLES FOR GLUCOSE OXIDATION. Surface Review and Letters, 2024, 31 (09), 10.1142/S0218625X24500690 . hal-04782973

HAL Id: hal-04782973

<https://hal.science/hal-04782973v1>

Submitted on 14 Nov 2024

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MODIFICATION OF POLYPYRROLE FILM WITH GOLD MICROPARTICLES FOR GLUCOSE OXIDATION

IMENE CHIKOUCHE^{*,†,¶}, CHARIF DEHCHAR^{*,‡}, AHMED ZOUAOU^{*},
SOPHIE TINGRY[§], FARES REZIG^{*} and BOCHRA BOUHCIDA^{*}
**Laboratoire Croissance et Caractérisation de Nouveaux Semi-conducteurs,
Université Ferhat Abbas, Sétif-1, Algérie*

*†Department of Process Engineering, Faculty of Technology,
University of Ferhat Abbas, Setif-1, Algeria*

*‡Department of Process Engineering, Faculty of Technology,
University of 20 August 1955-Skikda, Algeria*

*§Institut Européen des Membranes, IEM UMR 5635,
Université Montpellier, ENSCM, CNRS Montpellier, France*
¶chikouche_imene@yahoo.fr

Received 1 January 2023

Revised 1 December 2023

Accepted 23 December 2023

Published

This work presents the preparation of a gold-polypyrrole (Au-PPy) composite film on a silicon (Si) semiconductor supported by electrodeposition, and the study of its electrocatalytic activity as an anode catalyst for the glucose oxidation reaction in alkaline media. The microstructure of the as-prepared Au-PPy film is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results show that the presence of the polymer film on the Si support improves the conductivity of the latter and enables better distribution of the Au microparticles on the electrode surface, thus helping to increase their catalytic activity for glucose oxidation.

Keywords: Composites; glucose; gold; oxidation; polypyrrole.

1. Introduction

Capable of producing electrical energy from hydrogen and oxygen from the air, fuel cells are valuable tools for the energy transition. Due to their high electrical efficiency, low greenhouse gas emissions and low noise pollution, these systems represent an efficient way to produce energy while respecting the environment.^{1,2} They would ideally be suited for heavy transport applications, such as trains and trucks, but this would require commercial fuel

cell systems to have a lifetime of at least 20,000 h, which is not still the case.^{3,4} Improving this parameter requires a better understanding of the defects that can appear in the main elements of a fuel cell core, which are often made of fragile materials that are complicated to shape. These include its cost and low durability due to high operating temperature. In addition, the use of hydrogen as a fuel poses storage problems and therefore further limits the commercialization of fuel cells.^{5,6}

Corresponding author.

The main drawback of fuel cells remains their cost linked to the necessary presence and significant quantity of platinum (Pt), a rare and expensive catalyst.^{2,7} To overcome these limitations, it is essential to reduce the amount of Pt in catalysts, or even to replace them entirely with other new materials that are less expensive and offer satisfactory performance. From this point of view, significant progress has been made in recent years in the field of electrode materials in order to improve the effective conductivities as well as the specific surface and/or to reduce the operating temperatures.⁸⁻¹⁰ Modified electrodes, made from conductive organic polymers and noble metals, can meet the dual concerns of electrochemical and mechanical performance to catalyze reactions converting chemical energy into electrical energy.¹¹⁻¹³

This study suggests a facile preparation of an electrode material based on gold (Au) microparticles dispersed on a polypyrrole (PPy) matrix, with the long-term aim of applying this catalyst as an anode for a direct glucose fuel cell. The physicochemical characterization and electrochemical behavior of the electrode for glucose oxidation are studied and discussed.

2. Experimental

Electrochemical experiments were conducted in a conventional three-electrode cell at room temperature ($\sim 22^\circ\text{C}$). Pt wire and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All measured potentials are referred to the SCE. Polymerization of pyrrole (Py) was performed under galvanostatic and potentiostatic control on *n*-doped silicon (Si) wafer using an organic solution of 5 mM Py and 0.1 M tetraethyl ammonium perchlorate (TEAP) of formula $(\text{C}_2\text{H}_5)_4\text{N}(\text{ClO}_4)$ dissolved in acetonitrile (CH_3CN). During preparation of the electrode, the projected surface area of the Si substrate was 0.5 cm^2 . The Au electrodeposition on PPy film was performed using potentiostatic technique in an aqueous solution of 3 mM tetrachloroauric acid ($\text{HAuCl}_4\text{-H}_2\text{O}$, 99.99%) as the source of metal ions and 1 M KCl as the supporting electrolyte.

3. Results and Discussion

3.1. Deposition of PPy film

Figure 1 shows the voltammogram of electrochemical polymerization of Py (5 mM) in the presence of TEAP (0.1 M) at *n*-Si substrate.

Upon scanning the potentials between -1 V and 1.2 V , we observed that both oxidation and reduction currents increased with the number of cycles, indicating the appearance and subsequent growth of a new conductive phase on the electrode surface, corresponding to the polymer (PPy). Visually, this new phase appears as a homogenous black thin layer on the Si substrate.

3.1.1. Study of the electroactivity of the obtained PPy film

The electroactivity and electrostability of the resulting PPy film were checked by cyclic voltammetry in the potential range from -1 V to 0.6 V vs SCE (Fig. 2) in a monomer-free aqueous solution (KCl, 0.1 M).

In Fig. 2(a), the appearance of large anodic and cathodic waves is characteristic of the electroactivity of the PPy film deposited on Si.

During the oxidation of PPy film (*p*-doping process), electronic transfer occurs at the electrode/polymer interface. That is to say, the positive charge carried by the chains formed is neutralized by the

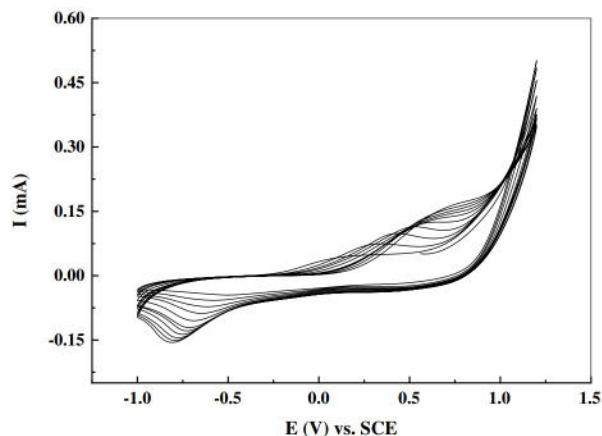


Fig. 1. Cyclic voltammogram reflecting 10 successive cycles of electrochemical response of Si in 0.1 M TEAP/ CH_3CN containing 5 mM Py, scan rate 100 mV/s .

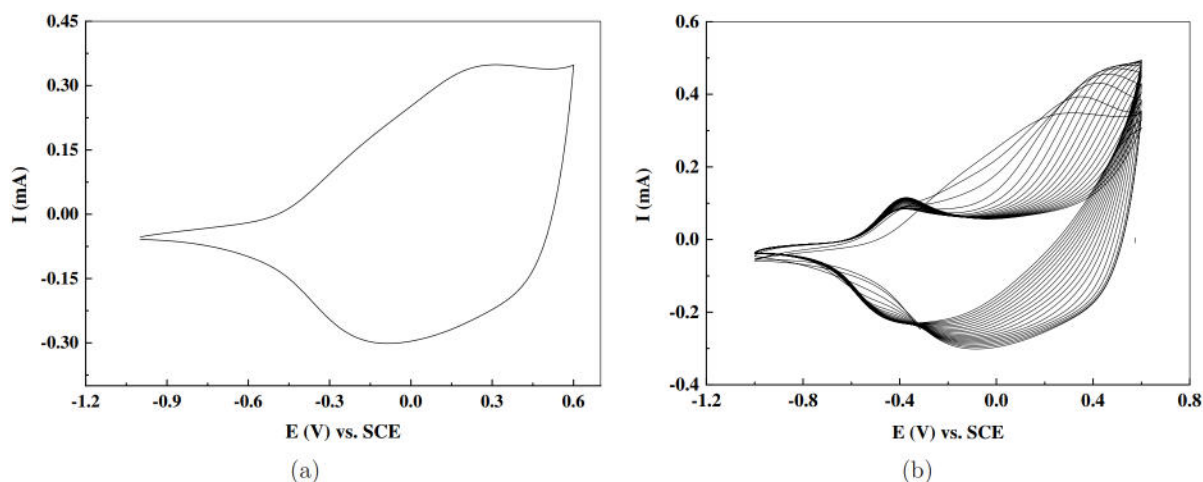


Fig. 2. Cyclic voltammetry curves of PPy deposited on Si electrode in 0.1 M KCl solution free of Py: (a) first cycle and (b) 20 successive cycles, scan rate 50 mV/s.

insertion of anions. During the reduction wave, the film dedoping process occurs.¹⁴

Note also that the PPy film remains stable when subjected to continuous cycling (20 cycles) (Fig. 2(b)). There is no noticeable change in the position of the curves after 7 cycles and the electro-stability is achieved after 12 cycles.

3.1.2. Electrodeposition of PPy film

The galvanostatic deposition method was used to produce a continuous oxidation of the monomer until a homogeneous, coherent PPy layer was formed. This method consists on imposing a constant current of 0.5 mA (chosen from Fig. 1) between the working electrode and counter electrode; it shows the different stages leading to the formation of PPy deposit.

In Fig. 3, three zones are observed: First, a rapid increase in potential up to a maximum value, E_{\max} (indicated by an arrow) for the first 20 s. This corresponds to the growth of a new phase due to the increase in the number of nucleus formed on the surface of the electrode. Then, the potential gradually decreases over time, and finally a stable state is observed indicating a diffusion-limited process.

Figures 4(a) and 4(b) are the atomic force microscopy (AFM) and scanning electron microscopy (SEM) micrographs of the prepared PPy film. The cauliflower-like microstructure, characteristic of

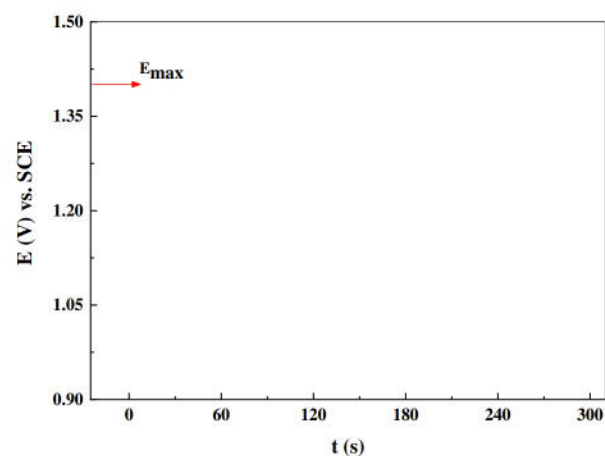


Fig. 3. (Color online) Chronopotentiometry of electropolymerization of Py on *n*-Si substrate at 0.5 mA, electrolyte: 0.1 M TEAP/CH₃CN + 5 mM Py.

PPy, is observed in both images, and the globules are same-sized and cover the entire electrode surface.

3.2. Electrodeposition of Au on PPy film

The electrochemical deposition of Au particles on PPy film was carried out potentiostatically. The deposition potential was chosen from the voltammogram recorded on the PPy/Si electrode in an acid solution of 0.5 M H₂SO₄ containing 3 mM HAuCl₄-H₂O and 0.1 M KCl (Fig. 5). This voltammogram shows, during the cathodic sweep from 1.6 V to -0.3 V, a well-defined cathodic peak centred at

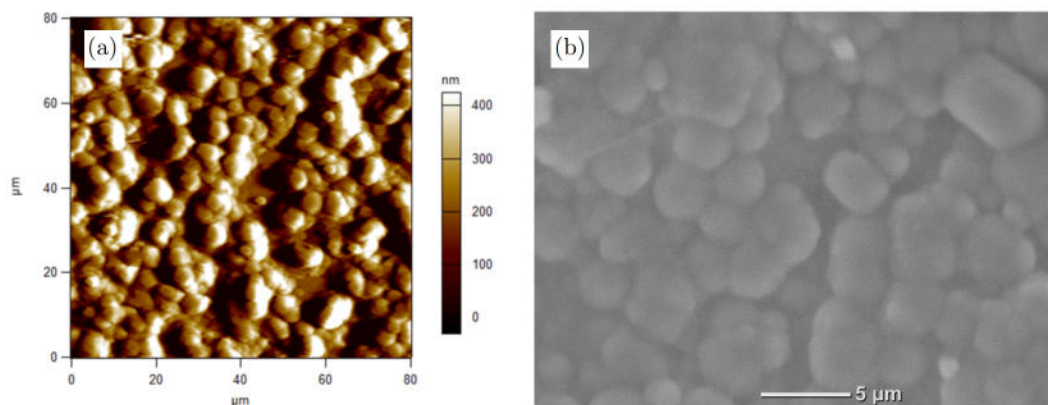


Fig. 4. (Color online) (a) 2D AFM and (b) SEM images of PPy electrodeposited on Si at 0.5 mA.

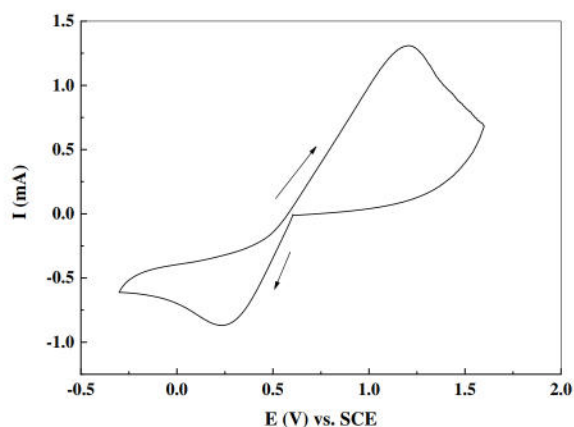
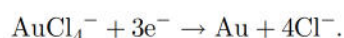


Fig. 5. Cyclic voltammetry curve recorded on PPy/Si in 0.5 M H_2SO_4 containing 3 mM $\text{HAuCl}_4\text{-H}_2\text{O}$ and 0.1 M KCl, scan rate 50 mV/s.

0.25 V, corresponding to the reduction of Au on the electrode surface following the equation:



The anodic peak observed during the backward scan corresponds to the oxidation reaction of the Au particles deposited on the PPy/Si electrode, indicating a reversible process. In light of this result, the potential of 0.2 V vs SCE was chosen to prepare the Au-PPy/Si electrodes; the corresponding current transient curve is shown in Fig. 6.

It can be seen that the current begins with an intense cathodic value, which corresponds to the charge of the double layer, then it decreases and reaches its maximum value to finally stabilize in accordance with Cottrell's law.¹⁵

The SEM micrographs of the obtained Au-PPy sample (Fig. 7(a)) show two distinct phases attributed

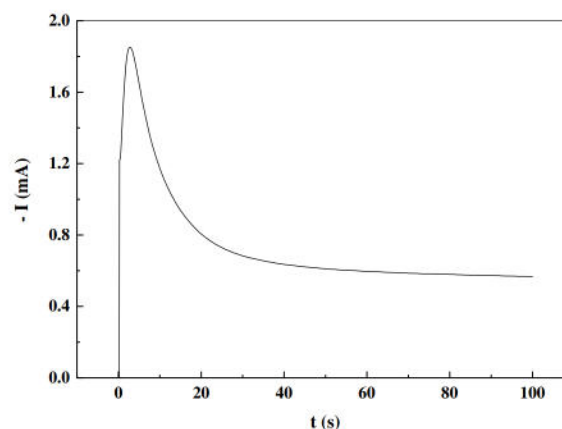


Fig. 6. Current-time transient for Au electrodeposition on PPy/Si electrode at $E = 0.2$ V vs SCE.

to the continuous PPy film with a cauliflower-like microstructure and the Au microparticles homogeneously dispersed on the polymer surface. As can be seen in the enlargement SEM image in Fig. 7(b), the Au particles are spherical shaped with rough surface and a diameter close to $0.5 \mu\text{m}$. The presence of Au particles on the PPy surface is confirmed by the EDX spectrum in Fig. 7(c).

3.3. Oxidation of glucose on Au-PPy/Si

3.3.1. Cyclic voltammetry in the presence of glucose

Figure 8 shows the electrochemical behavior of the Au-PPy/Si electrode in 0.1 M KOH electrolyte in the presence and absence of glucose. The voltammograms were recorded over a potential range from -0.6 V to 1.0 V and a scan rate of 20 mV/s.

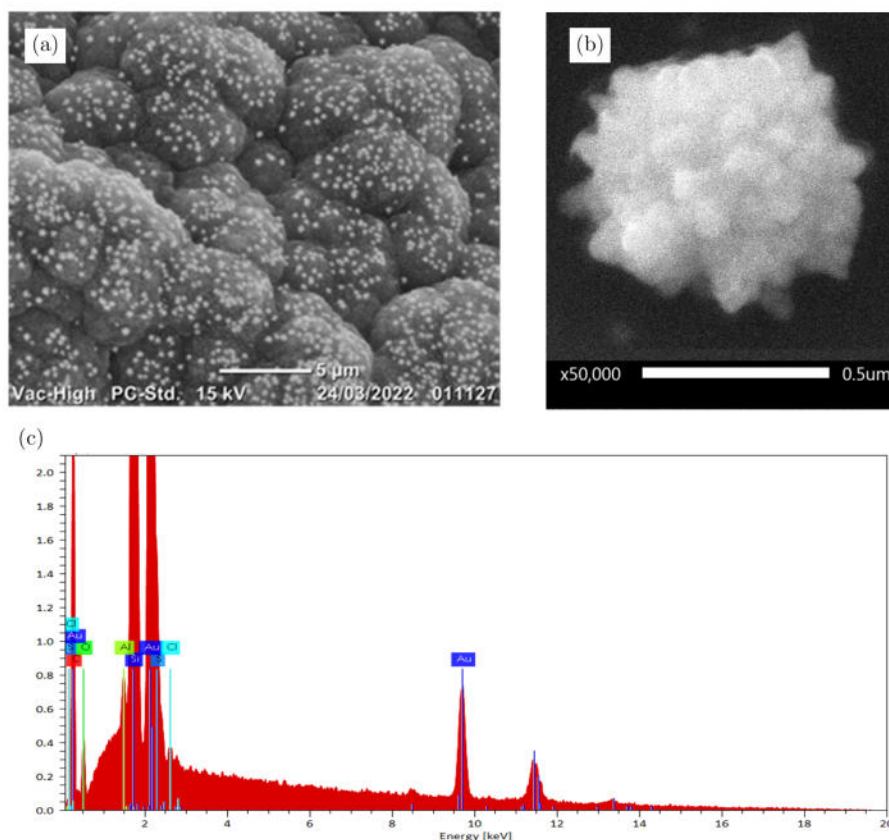


Fig. 7. (Color online) (a) SEM micrograph of Au-PPy sample, (b) corresponding enlargement SEM image and (c) EDX spectrum of Au-PPy sample.

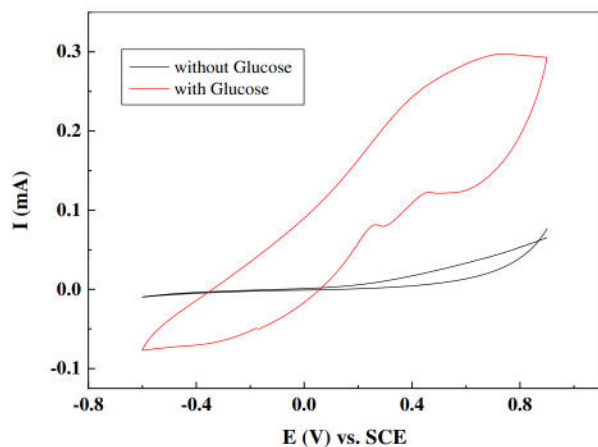
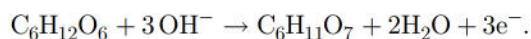


Fig. 8. (Color online) Cyclic voltammograms recorded on Au-PPy/Si electrode in the absence and presence of glucose (0.1 M), scan rate 20 mV/s.

In the absence of glucose, no obvious current is recorded in the range of the studied potential, indicating that no redox process occurs, and that the electrode is stable in KOH electrolyte. However,

in the presence of glucose into the electrolyte, an intense anodic peak centred at 0.65 V vs CSE is observed during the direct scan. This peak is characteristic of the glucose oxidation on the electrode surface leading to the formation of gluconic acid according to the following equation:



3.3.2. Effect of the presence of Au particles

Figure 9 compares the glucose oxidation responses on Au-PPy/Si and PPy/Si electrodes in 0.1 M KOH electrolyte. We clearly see that the PPy/Si electrode shows low redox currents, indicating that pristine PPy film has no activity to oxidize glucose, whereas a large anodic peak on the Au-PPy/Si electrode is observed, corresponding to glucose oxidation. This result suggests that Au microparticles are responsible for the electroactivity of the electrode for glucose oxidation, owing to their high electrical conductivity,

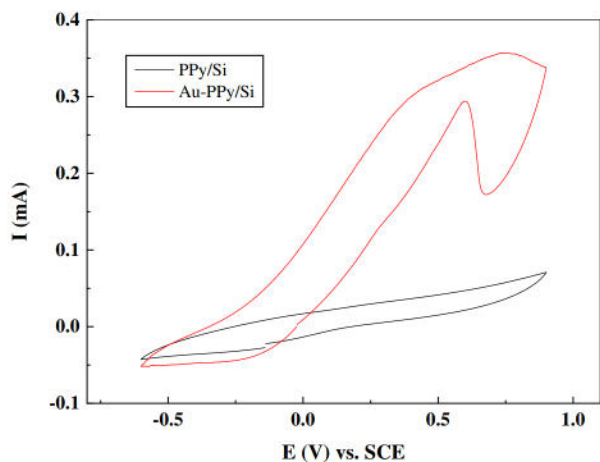


Fig. 9. (Color online) Cyclic voltammograms of glucose oxidation on PPy/Si and Au-PPy/Si electrodes. Electrolyte: 0.1 M KOH + 0.1 M glucose, scan rate 50 mV/s.

intrinsic catalytic properties and high active surface due to their good distribution on the polymer film.

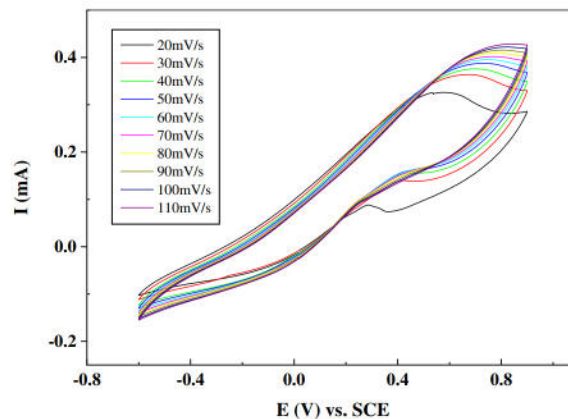
We also note the presence of a well-defined anodic peak during the reverse scan centred at 0.6 V vs SCE. According to the literature,¹³ this peak is attributable to the oxidation of intermediates, such as CO or other by-products produced by incomplete glucose oxidation. The ratio of the forward to reverse peak current indicates the good activity of the electrode for glucose oxidation reaction.

3.3.3. Scan rate effect

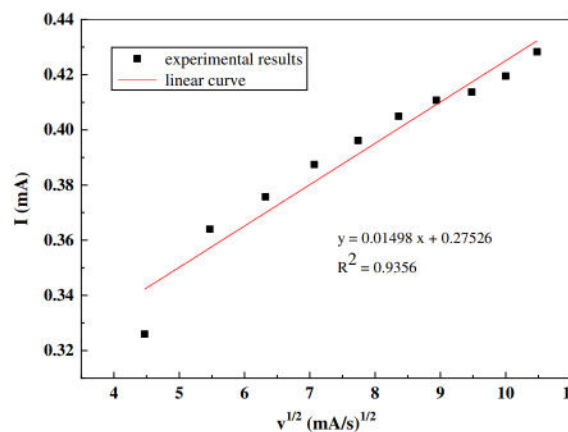
Figure 10(a) shows the cyclic voltammetry curves for glucose oxidation recorded on the Au-PPy/Si electrode at different scan rates. It can be seen that as the scan rate increases, the intensity of the glucose oxidation peak increases, with a slight positive shift in peak potential. Besides, as shown in Fig. 10(b), the oxidation peak current varies linearly with the square root of scan rate indicating a typical diffusion-controlled process.

3.3.4. Effect of Au particles electrodeposition time

The influence of the electrodeposition time of Au particles on the reactivity of Au-PPy/Si modified electrode towards the glucose oxidation was investigated. Figure 11 compares the responses of three



(a)



(b)

Fig. 10. (Color online) (a) Cyclic voltammograms recorded on the Au-PPy/Si electrode at different scan rates (v) in 0.1 M KOH, containing 0.1 M glucose. (b) Plot of the oxidation peak current as a function of the square root of the scan rate.

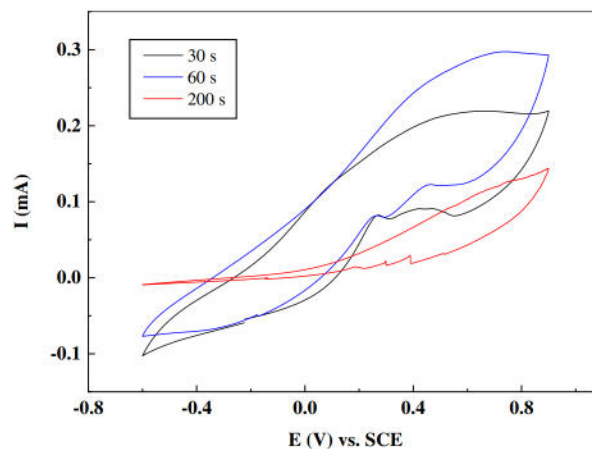


Fig. 11. (Color online) Cyclic voltammograms of glucose oxidation on Au-PPy/Si electrodes prepared at different times of Au particles electrodeposition. Electrolyte: 0.1 M KOH + 0.1 M glucose, scan rate 50 mV/s.

Table 1. Glucose oxidation potential on different electrode materials.

Electrode material	Solution composition	Oxidation potential (V/SCE)	References
Au-AgNPs/GC	10 mM + 0.3 M KOH	0.2	16
SC/AuNPs	0.1 M NaOH + 0.1 M glucose	0.35	17
GC/AuNPs/GOx	10 mM PBS + 0.8 mM glucose	0.55	18
NiOx/Gr/GCE	0.5 M NaOH + 2.5 mM glucose	0.4	19
NiOx/MnOy/GC or MnOy/NiOx/GC	0.5 M NaOH + 20 mM glucose	0.5	20
PPy/Pt-Pd	0.1 M D-glucose	0.6	21
Au-PPy/Si	1 M KOH + 0.1 M glucose	0.5	This work

Au-PPy/Si electrodes prepared at various times of electrodeposition of 30, 60 and 200 s.

As observed, the high electrode activity, in terms of oxidation peak current, is obtained for a deposition time of 60 s. This means a relatively good electrocatalytic behavior of the electrode with respect to glucose oxidation. Note that with deposition times above 100 s, a net decrease of the electrode activity can be observed. This behavior may be explained by the fact that with a long deposition time, the density of Au microparticles electrodeposited on the PPy film increases significantly and the particles tend to form aggregates, which reduces dramatically the effective surface area of the electrode and thus decreases its activity. So, to obtain the best activity of the electrode, we recommend a deposition time of 60 s.

The electrocatalytic performance of our modified electrode, assessed in terms of glucose oxidation overpotential, was compared with catalysts from the literature, utilizing various materials such as gold-silver nanoparticles (Au-AgNPs), platinum-palladium (Pt-Pd) composites, and metal oxide-based catalysts for glucose oxidation in alkaline media (Table 1). Although experimental conditions may differ, this comparison revealed a satisfactory performance of our electrode.

3.4. Stability of Au-PPy/Si material

Electrode material stability testing is crucial for assessing the durability of electrode performance in fuel cells.²²⁻²⁵ In order to address this issue, chronoamperometry was performed for the Au-PPy/Si electrode in response to glucose oxidation at 0.4 V vs SCE in 0.1 M KOH (Fig. 12). The resulting current

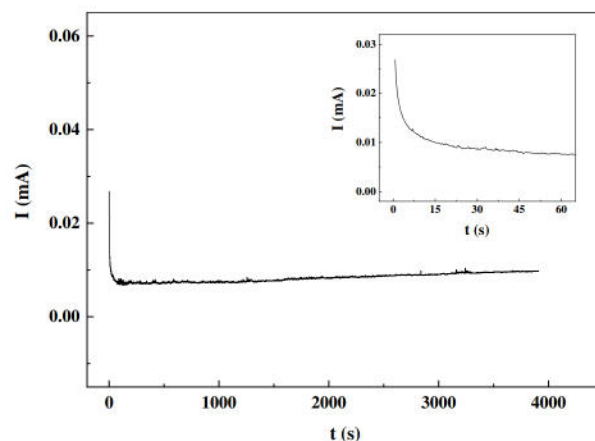


Fig. 12. Stability test of Au-PPy/Si electrode by chronoamperometry at 0.4 V vs SCE in 0.1 M KOH containing 0.5 M of glucose, Inset: current evolution over the first 60 s.

decreases rapidly over the first 60 s (inset in Fig. 12) before reaching a relatively stable state over a test period of 4000 s. This result demonstrates the stability and the efficiency of the Au-PPy/Si material for glucose oxidation.

4. Conclusion

In this work, a modified electrode material based on Au microparticles inserted on a PPy matrix was successfully elaborated and used as an anode for the electro-oxidation of glucose in 0.1 M KOH electrolyte. The preparation method is very easy to handle, and the parameters that can influence the electrode performance are easily assessed. The electrochemical study shows that the modified electrode is efficient for glucose oxidation in basic media, and that the electrode activity depends significantly on Au particles deposition time, with an optimized value of 60 s.

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