

A novel C/Ag/SiO₂ Sonogel-Carbon electrode Preparation, characterization, application and statistical validation as amperometric sensors for catechol determination

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Abstract— The monitoring of the catechol level is clinically important. In this work a novel C/Ag/SiO₂ Sonogel-Carbon electrode was used for the sensitive voltametric determination of catecholamine. A complete characterization of the electrodes has been performed using scanning electron microscopy, Raman spectroscopy, cyclic voltammetry, and impedance spectroscopy. The novel electrode has shown an increase in the effective area of up to 70%, oxidation peaks and an excellent electrocatalytic activity. The electrochemical response characteristics were investigated by cyclic and differential pulse voltammetry, the limit of detection is estimated to be in the sub micromolar regime.

statistical analysis of measurements performed in water samples has led to good apparent recovery.

Keywords— The statistical analysis, C/Ag/SiO₂ Sonogel-Carbon electrode. Amperometric sensor. Catechol.

I. INTRODUCTION

The application of sensors for clinical measurement are well recognised in the last ten years. In this work a C/Ag/SiO₂ Sonogel-Carbon electrode is used for the sensitive pulse voltammetry determination of catechol. The proper choice of the sensing material, in view of the specific application, is fundamental since it can impart to the device definite physicochemical properties and analytical peculiarities. The main advantages sought by adopting a specific electrode

material are the lowering of the potentials at which charge transfer processes occur, the enhancement of the relevant current and the prevention of the passivation of the surface. The results of this paper have shown an analytical performance and an efficient catalytic activity of the electrode for the electro-oxidation of catechol. The advantage of functional materials as an immobilization matrix for sensors is due to high surface to volume ratio, the presence of reactive groups on the surface, and fast electron transfer kinetics [1]. In recent years, nanostructured materials gained a very important role in the development of amperometric sensors [2]. The high superficial area/volume ratio and the polyhedral shape induce a quite high number of defects to be present at the electrode surface, imparting to the material high reactivity toward species in solution, suitable for the realization of electrocatalytic processes [3]. The result of our proposed modified electrode as compared to other electrochemical methods reported in the literature [4,8] exhibit that our electrochemical sensor Seems to be very promising and they can be considered for quantification of catechol.

Modified materials	Detection	
	limit (μM)	Ref
N-doped carbon nanotubes	0.02	[4] Q. Gou et al., 2016
Reduced graphene oxide	0.18	[5] H. Zhang et al., 2015
Glassy carbon electrode modified with graphene	0.01	[6] H. Du et al., 2011
Activated carbon	0.05	[7] H. Hammani et al., 2019
KOH-activated graphene sheets carbon film	0.1	[8] L. Huang et al., 2016
C/Ag/SiO ₂ Sonogel-Carbon	0.01	This work

II. EXPERIMENTAL

A. Reagents and materials

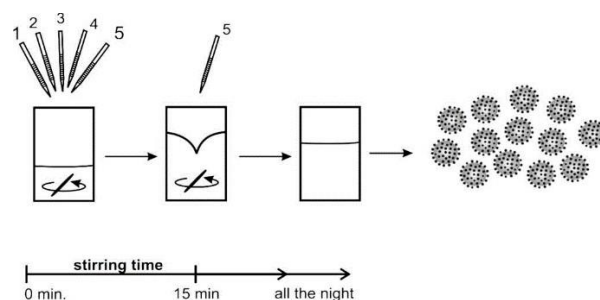
Catechol reagent grade $\geq 98\%$ (HPLC) is purchased from Sigma Aldrich (USA). KH₂PO₄, K₂HPO₄ for phosphate buffer and graphite powder (<20 microns) were purchased from Fluka. Paraffin oil was purchased from a pharmacy. All other chemicals were of reagent grade and used directly without further purification. Plastic capillary tubes, i.d. 2mm, were used as the bodies for the composite electrodes. Solutions were prepared using deionized double-distilled water with a measured resistance higher than 15 $\mu\text{S cm}^{-1}$.

B. Instrumentation

The cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance (EI) were applied to study the behaviour of C/Ag/SiO₂ Sonogel-Carbon electrode. They were all performed with a Voltalab@40, type PGZ301 from Radiometer (France). A conventional three-electrode cell (20 mL) was used at room temperature ($25 \pm 1^\circ\text{C}$), the counter electrode was a platinum wire and an SCE, 3M KCl electrode was used as the reference, the C/Ag/SiO₂ electrodes were used as working electrode. The scanning electron microscope (SEM) image was obtained using a HITACHI X-650 SEM instrument. The statistical validation was carried out by the MATLAB statistical software.

C. Preparation of the C/Ag/SiO₂ Sonogel-Carbon electrode

To prepare the C/Ag/SiO₂, the following procedure was used: 0.1g of silver nanoparticles silica Ag/SiO₂ (Scheme 1) is dispersed in 0.5 M acetic acid solution, then 1g of Carbon graphite powder was dispersed in the solution until obtaining a unique phase, and then the mixture was heated at 120°C to evaporate the acetic acid and water. In the next step, the carbon powder modified with Ag/SiO₂, is dried and was mixed thoroughly in a mortar with 40% of paraffin oil until obtaining a homogenous paste. Thus, the plastic capillaries were filled, leaving a little extra mixture sticking out of the tube to facilitate the subsequent polishing. For establishing electrical contact, a copper wire was inserted into the capillary. Before usage the electrodes were polished with emery paper No1500, and were electrochemically cleaned by cyclic voltammetry until obtaining a stable cyclic voltammograms between -0,80 and 1,50 V in 0,005 mol.L-1 KCl.



Scheme 1. Procedure for depositing silver nanoparticles on silica spheres:

1. TEOS, 2. ethanol, 3. ammonia, 4. water, and 5. Ag NPs.

III. RESULTS AND DISCUSSION

A. Surface and Electrochemical characterization of modified electrodes

Scanning microscopy (SEM) was used to explore the difference in structure between films of carbon paste alone, and those of carbon paste in the presence of SiO₂ (C / SiO₂), and mixed compound of SiO₂ and Ag (C / SiO₂ / Ag).

Analysis of the surface of the carbon-only paste electrode shows a granular structure of carbon. However, the incorporation of SiO₂ into the carbon paste shows a more structured surface (cauliflower-shaped) with the appearance of bright white particles. An even better organized morphology, when silver is added (C / Ag / SiO₂ electrode), is noted, corresponding to the C paste modified by silica-silver nanoparticles. In this case, the film generated shows a better organization and an oriented structure as well as an increase in the specific surface (Figure 1). The presence of SiO₂ and Ag in the carbon paste therefore seems to have a favorable effect on the structure of the materials prepared.

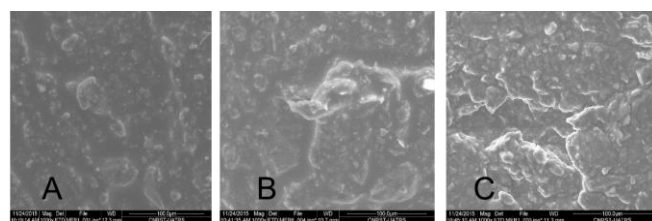


Figure 1. (A) SEM images obtained for C electrode. (B) SEM images obtained for C/SiO₂ modified electrode. (C) SEM images obtained for C/Ag/SiO₂ modified electrode

To characterize the interface features of the modified electrode surface we have used the EIS method. The Figure 2 shows that the charge transfer resistance of C/Ag/SiO₂ electrode is much smaller than that of C/SiO₂ electrode and the C electrode, suggesting that it is easier to transfer electrons at C/Ag/SiO₂, and this indicates that the incorporation of silver nanoparticles on silica spheres promote the electron transfer synergistically and accelerates the diffusion of ferricyanide towards the modified electrode surface.

The active surface area of the modified electrode was estimated according to the slope of the i_p versus $v^{1/2}$ plot, based on the Randles-Sevcik equation [9,10]:

$$L_p = 2.69 \times 10^5 n^{3/2} A_{\text{eff}} D^{1/2} C v^{1/2}$$

Where A_{eff} is the effective surface area, n is the number of electrons transferred, D ($= 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) is the diffusion coefficient of potassium ferricyanide (Gooding et al., 1998), and C are the concentration of potassium ferricyanide. The effective electrode area for $C/Ag/SiO_2$ modified electrode is approximately 0.058 cm^2 whereas 0.037 cm^2 for C/SiO_2 and 0.032 cm^2 for C electrode.

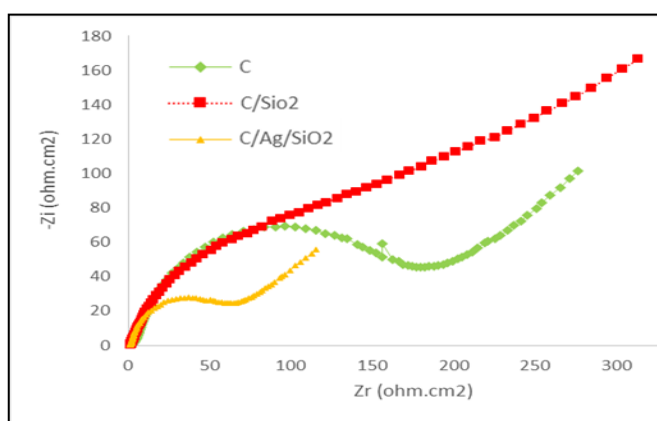


Figure 2. Nyquist plots of EIS in 10^{-2} M potassium ferricyanide prepared in 0.05 M KCl for $C/Ag/SiO_2$ electrode and C/SiO_2 electrode and Carbon electrode, Amplitude: 5 mV ; frequency range: $100 \text{ kHz} - 10 \text{ mHz}$; potential: 0 V .

B. Electrochemical Behaviour of catechol at the Modified Electrode Use an unique style for units.

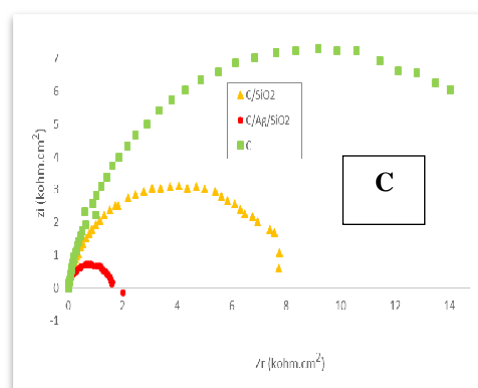
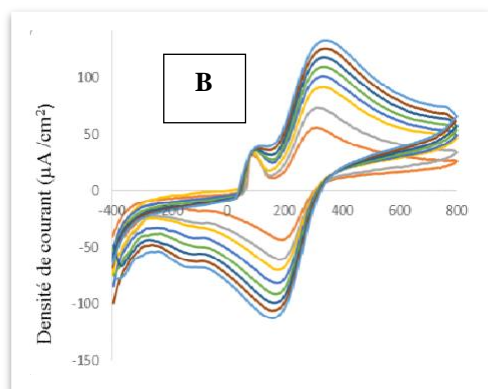
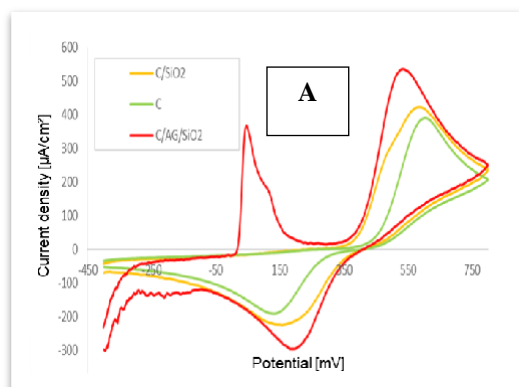


Figure 3. (A) cyclic voltammetry of 10^{-5} M of catechol at $C/Ag/SiO_2$ electrode and C/SiO_2 electrode and Carbon electrode in PBS (0.05 M), $\text{pH} = 2$, $T = 25^\circ \text{ C}$. (B) Cyclic voltammograms obtained at different scan rates from the $C/Ag/SiO_2$ modified electrode in a PBS at $\text{pH} 2$ containing $2 \mu\text{M}$ of catechol. Scan rates: $40, 60, 80, 100, 120, 140, 160$ and 180 mV/s , (C) Nyquist plots of 10^{-5} M of catechol at $C/Ag/SiO_2$ electrode and C/SiO_2 electrode and Carbon electrode in PBS (0.05 M), $\text{pH} = 2$, $T = 25^\circ \text{ C}$.

The Figure 3.A, shows the electrochemical behaviour of the catechol at $C/Ag/SiO_2$ electrode and C/SiO_2 electrode and Carbon electrode in PBS $\text{pH} 2$ using CV; First, the catechol ($\text{pK}_a = 9.5$) presents an electroactive character that appears with an oxidation peak in the studied potential ranges (Tables.1), also we noticed the appearance of E_{pa} peak corresponding to the oxidation of Ag incorporated in the paste of the modified electrode at 100 (mV)/ECS . The relationship between the oxidation peak current (i_{pa}) and the square root of the scan rate ($v^{1/2}$) (Figure 3.B) is linear with linear correlation coefficients $R = 0.9974$, indicates that the electrochemical process is controlled by diffusion.

The (Figure 3.C), shows the Nyquist plots behaviour of the catechol at $C/Ag/SiO_2$ electrode and C/SiO_2 electrode and Carbon electrode in PBS $\text{pH} 2$, the (Tables.2) presents the charge transfer resistance and the capacitance of the electrical layer at the electrode/solution interface, and the apparent rate of electron transfer at different modified electrodes.

Electrod e	I_{pa} ($\mu\text{A}/\text{cm}^2$)	I_{pc} ($\mu\text{A}/\text{cm}^2$)	I_{pa}/I_{pc}	E_{pa} (mV)/EC S	E_{pc} (mV)/EC S	ΔE_p (mV)/EC S
Carbon electrode	263.513	-136.987	1.92	592	138	454
C/SiO ₂ electrode	254.479	-147.27	1.72	570	178	392
C/Ag/SiO ₂ electrode	373.19	-203.091	1.83	506	200	306

Tables.1 Electrochemical characterization of catechol on three types of electrodes

Electrode	R_{tc} (kohm .cm ²)	C_{dc} (µf/cm ²)	K_{app} (cm /s)
Carbon electrode	17.04	10.45	$1.56.10^{-5}$
C/SiO ₂ electrode	7.239	19.69	$3.68.10^{-5}$
C/Ag/SiO ₂ electrode	1.507	23.65	$1.77.10^{-4}$

Tables.2 the electrical parameters of the three types of electrodes

From the table (Tables.2) we notice that the charge transfer resistance (R_{tc}) decreases for the Ag / SiO₂ carbon paste electrode, a remarkable increase in the capacitance of the electric layer (C_{dc}) and an apparent speed increase of the electron transfer. These results show the efficiency of Ag / SiO₂ carbon modified electrode.

Given the results obtained in Figure 3 and Tables 1 and 2, the presence of SiO₂ and Ag in the carbon paste therefore seems to have a favorable effect on the structure of the materials prepared. The modified electrode should promote the sensitivity and the selectivity of determination of catechol. As a result, C/Ag/SiO₂ can accelerate the electron transfer and decrease the overpotentials of catechol oxidation at different levels of diffusion modes, which is the key factor to adjust the problem of adsorption at the electrode surface and realize the determination of catechol.

3.3. Analytical Calibration Curves of determinations of catechol.

The DPV was used to obtain the calibration curve of catechol at the modified electrode in PBS pH2. The result in Figure 4 shows the linear relationship between the oxidation peak current and catechol concentrations. The peak intensities are increased linearly in the range of 1–120 µM, the equation is $I_{pa} (\mu A) = 0.3 C + 0.5$ with a correlation coefficient of $R^2 = 0.9992$ and the detection limit ($S/N = 3$) estimated to be 0.01 µM in terms of signal to noise ratio of 3:1.

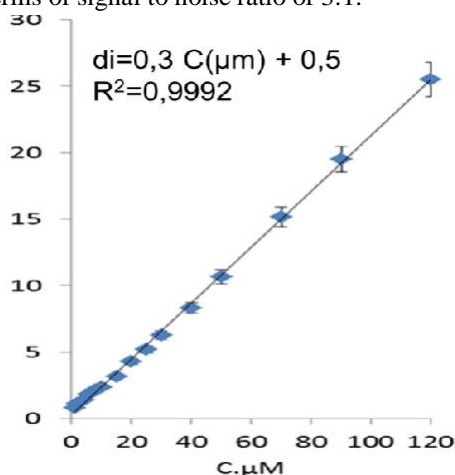


Figure 4. Calibration plots of catechol (from 1 to 120 µmol L⁻¹)

3.4 Determination of catechol at C/Ag/SiO₂ in Urine.

The objective of this study is the simultaneous detection of the catechol in the presence of AA and AU in the urine. In this context, and in order to evaluate the applicability of the proposed method for the determination of the catechol and AA and AU in urine, the measurements were conducted in urine samples diluted 500% (with 0,05M PBS at pH 2) was then added to this mixture a deferred reports of AA, AU and catechol (table 4).

the AA and UA is the principal organic constituents of urine, the phenomenon of interference on the electrochemical response of catechol in the presence of the urinary AA and UA is one of the major problems that hinders electrochemical detection of its substances in biological media, since the unmodified carbon electrode could not separate catechol and AA and UA oxidation peaks. The development of a simple and inexpensive device for the simultaneous determination and separation of the electrochemical responses of these substances remains the challenge of this work.

The Tables.4 shows that the peak currents for catechol increase linearly with increases their respective concentrations, without considerable effects on the other peak currents of AA and UA while varying the concentration of catechol from 10 to 100 µmol L⁻¹.

In addition, a various concentrations of AA from 20 to 100 µmol L⁻¹ in the presence of catechol and UA exhibit excellent responses to AA, AU, and catechol without any obvious intermolecular effects among them, the peak current of AA increased linearly with increased concentration. is also indicated that the peak current of UA increased linearly with increases concentration of UA, without considerable effects on the other peak currents while varying the concentration of UA from 30 to 40 µmol L⁻¹.

These results confirm that the oxidation processes of catechol, AA, UA at C/Ag/SiO₂ electrode are independent from each other, this separation allows a simultaneous determination of AA, UA and catechol in a mixture. The C/Ag/SiO₂ possessed a higher active surface area and can separate catechol and AA and UA oxidation peaks.

Table 3:

Simultaneous determination of catechol, AA and UA in mixtures synthesis samples (\pm SD; the standard deviation for $n=3$).

Sample	Added ($\mu\text{mol/L}$)			Found ($\mu\text{mol/L}$)			Recovery (%)		
	CATHECOL	AU	AA	CATHECOL	AU	AA	CATHECOL	AU	AA
1	10	30	20	9.86 \pm 0.2	31 \pm 1.5	19.6 \pm 0.5	98.0%	103.3%	98.0%
2	30	40	40	28.4 \pm 1.3	41 \pm 2.7	38.3 \pm 1.5	94.7%	102.5%	95.8%
3	70	35	80	68.47 \pm 1.8	33.2 \pm 0.8	78.2 \pm 2.1	97.8%	100.6%	97.8%
4	100	40	100	98.5 \pm 1.7	40.3 \pm 1.3	98.7 \pm 1.2	98.5%	100.8%	98.7%

The feasibility of the C/Ag/SiO₂ sensor is demonstrated for analytical application, the recovery test was performed by the standard addition method (Table 3), with 4 different additions of catechol, AA and UA to the urine diluted samples, the obtained recoveries ranged from 94.7 to 98.5 for catechol; 95.8 to 98.7 for AA and 100.6 to 103.3 for UA. This high recovery and the perfect selectivity exerted by our C/Ag/SiO₂ electrochemical sensor looks very promising for the simultaneous detection of catechol, AA and AU. So, an effective sensor has been obtained for catechol determination in urine sample in this work.

C. Conclusions

The use of electrochemical techniques for the sensitive and selective determination of catechol in urine by differential pulse voltammetry using C/Ag/SiO₂ modified electrode was shows that the C/Ag/SiO₂ modified electrode present a perfect selectivity on the detection of the catechol in presence of AA and UA in 0,05M PBS at pH 2, with a detection limit 0,01 $\mu\text{mol L}^{-1}$ is obtained. This selectivity is maintained when the study is conducted in biological fluids such as in urine diluted 500% with 0,05M PBS at pH 2. Indeed, the results obtained were validated by the statistical validation methods and our electrochemical sensor looks very promising and they can be considered for early quantification of catechol in clinical preparations.

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