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Voltammetric Study of a Cubic Silsesquioxane Organically Modified with Imidazole and their Subsequent Reaction with Cadmium and Hexacyanoferrate (III)

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A hybrid nanocomposite formed by interaction of a octa (3-chloropropyl)octasilsesquioxane modified with imidazol , and its subsequent reaction with cadmium and hexacyanoferrate (II) (CdHSSI) was incorporated into a graphite paste electrode and the electrochemical studies were conducted with cyclic voltammetry. The cyclic voltammogram of the modified graphite paste electrode with CdHSSI (GPE-CdHSSI), showed one redox couple with formal potential $E^{0'}$=0.14V (*vs* Ag/AgCl, $NaNO_3$, 1.0 mol L^{-1}; v = 20 mV s^{-1}), attributed to the $Fe^{2+}(CN)_6$/ $Fe^{3+}(CN)_6$ process. The redox couple presents an electrocatalytic response for determination of ascorbic acid. The modified electrode gives a linear range from 2.0×10^{-4} mol L^{-1} to 9.0×10^{-4} mol L^{-1} (r=0.998) for the determination of ascorbic acid with detection limit of 1.21×10^{-4} mol L^{-1} with a relative standard deviation of 5% (n=3) and amperometric sensitivity of 6.217 mA/ mol L^{-1} for ascorbic acid.

Keywords: silsesquioxane, imidazole, ascorbic acid, graphite paste electrode, voltammetry

1. INTRODUCTION

Hybrid materials have recently been of great interest because their properties are different from those displayed by their precursors. Among the hybrid materials, the inorganic-organic cubic silsesquioxanes offer many applications, for example, they can have outstanding properties in areas such as adsorbents. Cubic silsesquioxanes (cubes) and the related polyhedral oligomeric silsesquioxanes (POSS) are nano-sized inorganic materials with a silica core and reactive functional groups on the surface. The silsesquioxane [1,2] has an empiric formula $(RSiO_{1.5})_n$, where R may be a hydrogen or some organic group such as alkyl, methyl, aryl, vinyl, phenyl or any organofunctional derivative from these organic groups. Each silicon atom is, on average, connected to 1.5 oxygen atoms and to an R group (hydrocarbon). When n = 4,6,8,10; (n ≥ 4), the resulting compounds are called polyhedral oligomeric silsesquioxanes [3,4] (POSS).

Studies suggest that the behavior of these solids, when used as metal adsorbents, is mainly dependent on the presence of active donor atoms such as O, S and N from the functionalized organic groups [5-7].

The molecules used in the preparation of a silsesquioxane are relatively simple. The most used, for example, are tetraethoxysilane, methyltriethoxysilane and dimethyldietoxysilane [8], and the reaction product is a high molecular mass polymer.

When functionalized, silsesquioxanes can improve their mechanical and thermal properties [1,2,9] and their oxidative resistance [2] without affecting its characteristics. Moreover, they can be used to increase the adsorptive capacity of metal ions in solution [10]. Imidazole, also known as 1,3-diaza-2,4-cyclopentadiene and formally designated as 1,3-diazole, is an organic compound of molecular formula $C_3H_4N_2$ [11]. Moreover, it is a highly polar compound, totally soluble in water and other polar solvents, and exhibits amphoricity, in other words, it can function as an acid as well as a base [11,12]. The physical chemical properties of silsesquioxanes can improve substantially when functionalized, behaving as true hybrid materials.

Imidazole, due to the presence of nitrogen donor atoms can coordinate with a variety of transition metal ions [13,14]. It has also been known for many years that imidazole has a particular affinity for electrophilic silanes [15]. Thus, adsorbents prepared using silicon-based substrates functionalized with imidazole are suitable for the sorption of heavy or toxic metals, for example, cadmium, copper, mercury. The advantages of using these adsorbents modified by covalent attachment of organofunctional groups are their easy preparation, fast adsorption kinetics and good chemical stability [16].

Within this context, particularly our interest in the silsesquioxane chemistry is to prepare multifunctional nanostructured materials that can be used as electrochemical sensors. The objective of this work was test a novel composite freshly prepared as a sensor for biological substances of interest, for instance, ascorbic acid. The increasing use of pharmaceuticals and other natural samples containing vitamin C has necessitated the development of an accurate and specific procedure for its determination. It is known that accurate determination of AA using conventional electrodes is very difficult because of its high overpotential, low selectivity and sensitivity and poor reproducibility due to fouling effect caused by the oxidized products of AA.

2. EXPERIMENTAL

2.1. Reagents and solutions

All reagents solutions and supporting electrolytes were prepared using Milli-Q water. Ascorbic acid were used without further purification and all reagents and solvents were of analytical grade (Merck or Aldrich) and were used as purchased. All solutions and supporting electrolytes were prepared using Milli-Q water. The ascorbic acid solutions were prepared immediately before use and were dearated with purified nitrogen. This procedure was adopted because this species can be oxidized to ascorbate by atmospheric oxygen.

2.2. Electrochemical Measurements

Cyclic voltammograms were performed using the Microquimica (MQP1- PGST) potentiostat. The three electrode systems used in these studies consisted of a modified working electrode (graphite paste electrode) an Ag/AgCl reference electrode, and a platinum wire as the auxiliary electrode. The measurements were carried out at 25°C.

2.3. Synthesis of octa-(3-chloropropyl) silsesquioxane (SS)

For the synthesis of octa-(3-chloropropyl)silsesquioxane (SS) a procedure following as described in the literature [17] after minor modifications.

800 ml of methanol, 27 ml of hydrochloric acid (HCl) and 43 mL of 3-chloropropyliltriethoxysilane were added into a round bottom flask of 1000 mL. The system was kept under constant stirring at room temperature for 6 weeks. The solid phase was separated by filtration in a sintered plate funnel, yielding a white solid, octa-(3-chloropropyl)silsesquioxane (SS), which was then oven dried at 120 ºC for 4 hours. Figure 1 illustrates a representative scheme of this synthesis.

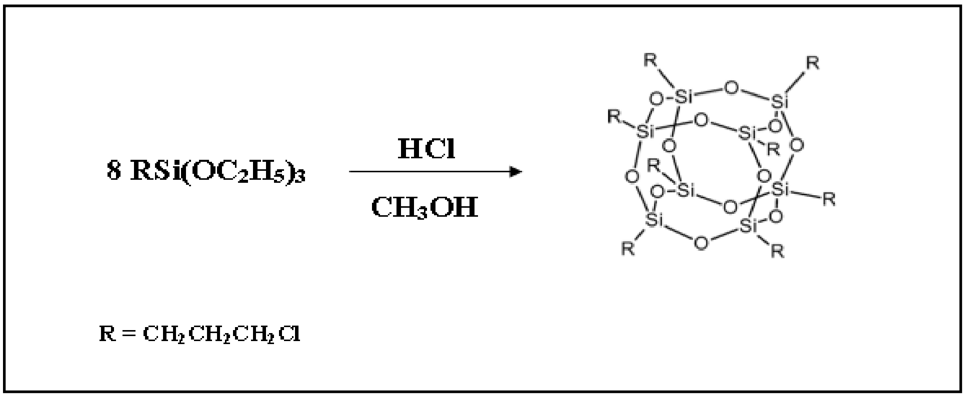

Figure 1. Schematic representation of the preparation of octa-(3-chloropropyl)silsesquioxane [18].

2.4. Functionalization of octa-(3-chloropropyl)silsesquioxane with imidazole

The functionalization of octa-(3-chloropropyl)silsesquioxane (SS) was performed in a 3-neck flask of 500 mL containing 10 g (9.7×10^{-3} mol) of SS, previously dried at 100 °C for 2 hours, 5.923g (8.7×10^{-2} mol) of imidazole and approximately 200 mL of dimethylformamide (DMF). The mixture was refluxed at 160 °C with constant stirring for 96 hours. Then the solid plate was separated in a sintered funnel and washed in a Soxhlet extractor with DMF for 48 hours. The material obtained was oven dried 100°C for 4 hours and described as SSI.

Figure 2 schematically illustrates the organofunctionalization process of SS with imidazole.

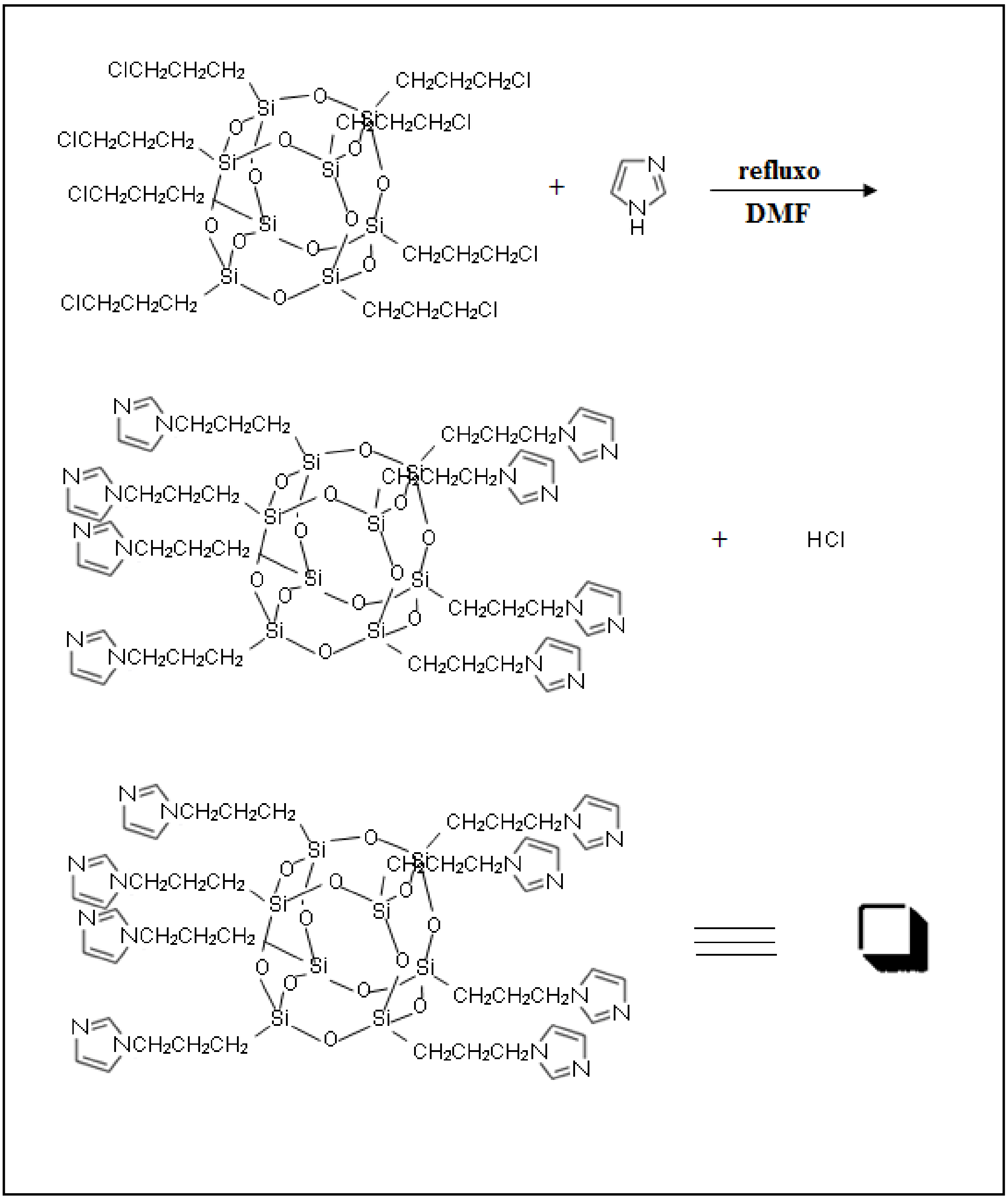

Figure 2. Organofunctionalization of octa-(3-chloropropyl) silsesquioxane (SS) with the modifying agent imidazole.

2.5. Formation of complex CdHSSI

The MHSSI complexes were prepared as follows: 1.0 g of SSI was added to 25 mL of a solution of Cadmium chloride 1.0×10^{-3} mol L^{-1}. The mixture was stirred for 1h at room temperature. The solid phase was then filtered and washed thoroughly with deionized water. The materials resulting from this first phase were oven dried at 70ºC and designated as CdSSI. In the second stage, the CdSSI was added to a solution of 1.0×10^{-3} mol L^{-1} of potassium hexacyanoferrate (III) and the mixture was stirred for 1h at room temperature and then the solid was thoroughly filtered, washed with deionized water and dried at 70ºC. The materials resulting from this stage were described by CdHSSI.

2.6. Preparation of the graphite paste electrode modified with CdHSSI

The graphite paste electrode modified with CdHSSI (GPE- CdHSSI) was prepared by mixing 20 mg of CdHSSI with 90 mg of graphite (Aldrich) and 50 µL of mineral oil. The electrode body was produced from a glass tube of 3 mm i.d. and 14 cm height, containing graphite paste. A copper wire was inserted through the opposite end of the glass tube to establish electrical contact. After homogenizing the mixture, the modified paste was carefully positioned on the tube tip to avoid possible air gaps, which often enhances electrode resistance. The external surface of the electrode was smoothed on soft paper. A new surface can be produced by scraping out the old surface and replacing the graphite paste.

2.7. Procedure

Initially, cyclic voltammograms were recorded for study the sensibility of ascorbic acid, by graphite paste electrode modified with CdHSSI. The supra analite solutions were prepared immediately before use and were deaerated with nitrogen. In most of the experiments, 1.0 mol L^{-1} $NaNO_3$ (pH ~ 6.6) was used as the supporting electrolyte. The catalytic and or sensibility current was estimated by the difference between the electrode current in the presence of analite compounds and that which is established in the blank solution.

3. RESULTS AND DISCUSSION

Figure 3 illustrates the spectra in the infrared region for SSI, potassium hexacyanoferrate (III) and CdHSSI. As stated earlier, the spectrum exhibited by potassium hexacyanoferrate (III) (B) shows significant vibrations at ~2112 and 2030 cm^{-1}, which are related to the vibrations of the $C\equiv N_{(\upsilon C\equiv N)}$ bonding. The spectra exhibited by CdHSSI (C) show typical vibrations of its precursors at ~1100 cm^{-1} attributed to the Si-O-$Si_{(\upsilon Si\text{-}O\text{-}Si)}$ stretching that corresponds to the cage shaped structure of SS and in the region between 1300 and 1530 cm^{-1} attributed to the axial strain of the imidazole ring bonds (A). Furthermore, the spectra exhibited vibrations at ~2100 cm^{-1} related to the estiramento $C\equiv N_{(\upsilon C\equiv N)}$ stretching that is characteristic of the potassium hexacyanoferrate (III) precursor [19].

The spectra in the ultraviolet visible region UV-Vis illustrated in Figures 4 (A) and (B) correspond to CdHSSI and SSI, respectively. The spectra did not allow to clearly observe the typical bands related to the ligand to metal charge transfer process (LMCT) of $[Fe^{III}(CN)_6]^{3-}$.

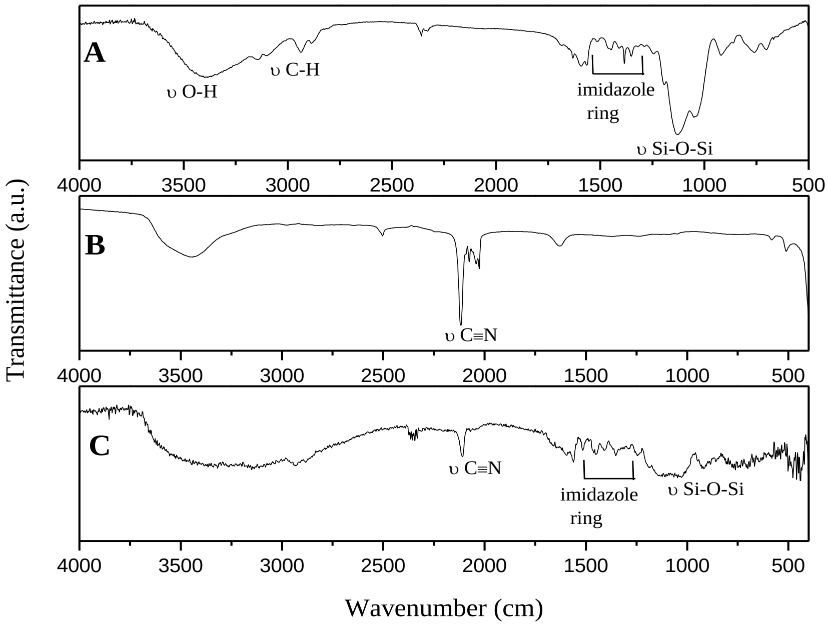

Figure 3. Vibrational spectra in the infrared region: (A) SSI, (B) Potassium hexacyanoferrate (III) and (C) CdHSSI.

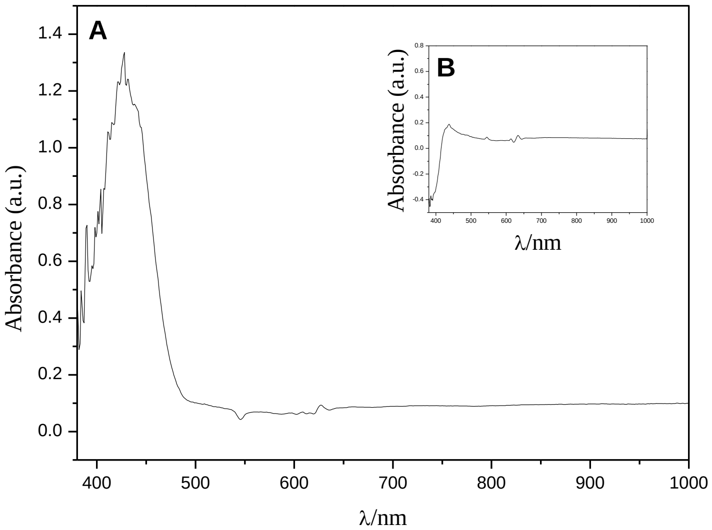

Figure 4. Spectroscopy in the ultraviolet visible region (UV-Vis) by diffuse reflectance of (A) CdHSSI and (B) SSI.

CdSSI and CdHSSI were also characterized using cyclic voltammetry technique as illustrated in Figures 5 (A) and (B), respectively. The cyclic voltammogram of CdSSI did not exhibit any peak and therefore no studies were performed for this system, however the cyclic voltammogram of CdHSSI exhibited only one redox pair with E^{θ}=0,14V, attributed to the $Fe^{2+}(CN)_6$/ $Fe^{3+}(CN)_6$ process.

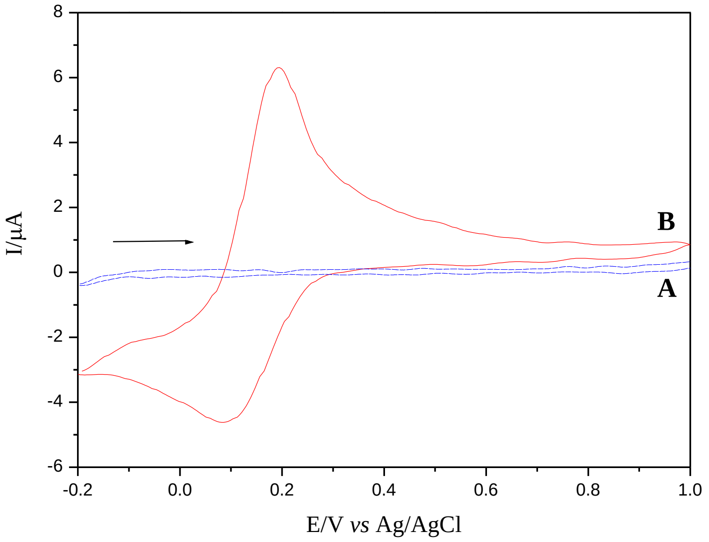

Figure 5. Cyclic voltammograms of (A) CdSSI and of (B) CdHSSI ($NaNO_3$ 1.0 mol L^{-1}, v=20 mVs^{-1}, 50%w/w).

Figure 6 illustrates the study of the influence of cations and anions from the supporting electrolyte on the voltammetric behavior of CdHSSI. Different supporting electrolytes were tested, such as KCl, NaCl, LiCl, NH_4Cl, KNO_3 and $NaNO_3$ (1.0 mol L^{-1} and v=20 mVs^{-1}) and it was observed that the nature of the cations did not affect $E^{\theta'}$ and the current intensities, however, although the nature of the anions did not affect $E^{\theta'}$, it affected the current intensities.

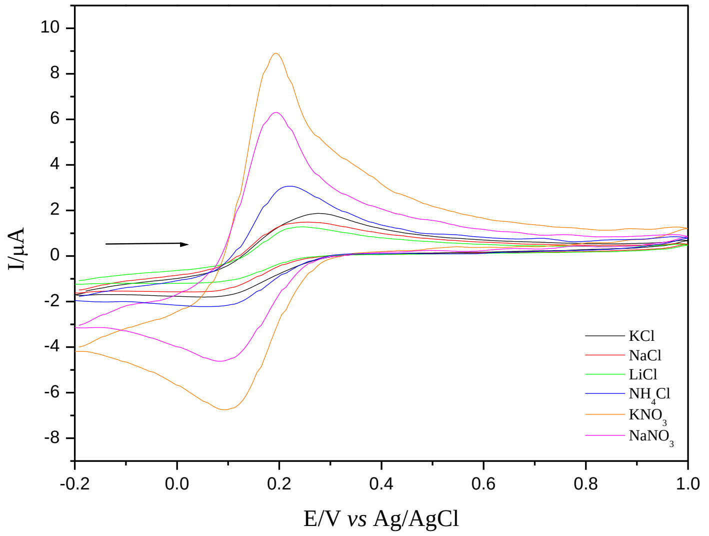

Figure 6. Cyclic voltammograms of the graphite paste modified with CdHSSI in different electrolytes (*v* = 20mVs^{-1}, 1.0 mol L^{-1}, 50% w/w).

It was found that in the presence of electrolytes containing the nitrate anion (NO_3^-) the current intensities were higher than those obtained in the presence of electrolytes containing chloride (Cl^-). Moreover, these studies indicate that there was no formation of a crystal lattice for CdHSSI. The ratio Ipa/Ipc was of ~1.1 to 1.6 and ΔEp between 100 and 210 mV, for the various supporting electrolytes, which also suggests that the process $Fe^{2+}(CN)_6/Fe^{3+}(CN)_6$ is quasi reversible.

Table 1 lists the main electrochemical parameters obtained from the cyclic voltammograms of the graphite paste modified with CdHSSI in different electrolytes.

Table 1. Electrochemical parameters of the graphite paste modified with CdHSSI in different electrolytes (v = 20mVs^{-1}, 1.0 mol L^{-1}, 50% w/w).

Electrolyte	|Ipa/Ipc|	$E^{\theta'}$ (V)	ΔEp (V)
KCl	1.24	0.18	0.21
NaCl	1.10	0.15	0.20
LiCl	1.30	0.14	0.21
NH_4Cl	1.58	0.15	0.14
KNO_3	1.49	0.14	0.10
$NaNO_3$	1.63	0.14	0.10

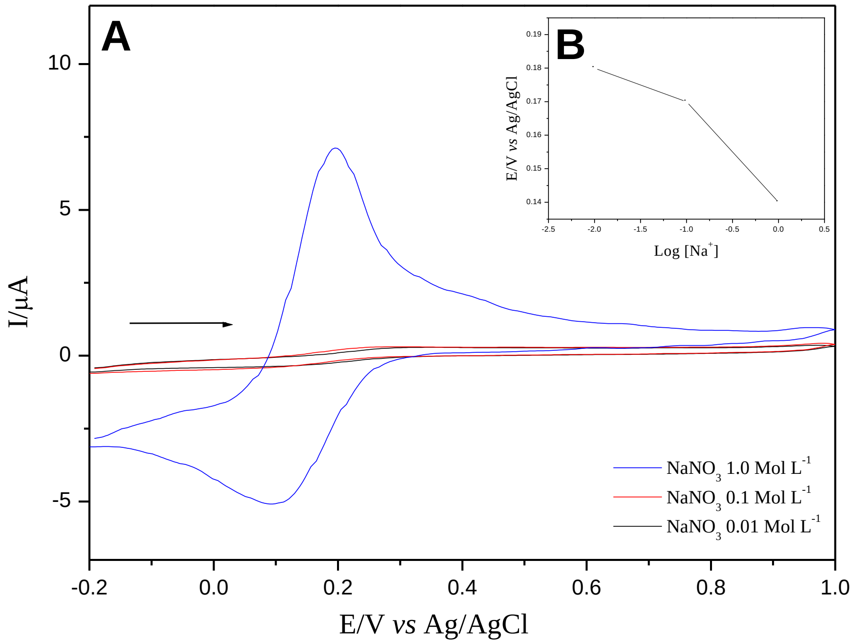

Figure 7. (A) Cyclic voltammograms of the graphite paste modified with CdHSSI at different concentrations of $NaNO_3$ (v= 20mVs^{-1}, 50% w/w). (B) Average potential ($E^{\theta'}$) of the graphite paste modified with CdHSSI depending on the log concentration of $NaNO_3$ (v = 20mVs^{-1}, 50% w/w).

It was observed that the voltammetric performance of CdHSSI is also similar in all electrolytes tested and therefore it is suggested that there was an electrostatic interaction between imidazole and hexacyanoferrate ion ($Fe(CN)_6^{3-}$) where the transition metal, in this case cadmium, acts as a Lewis acid [20].

For future studies, $NaNO_3$ was chosen as the supporting electrolyte for exhibiting a better voltammetric performance.

Figure 7 illustrates the cyclic voltammograms recorded at different concentrations of $NaNO_3$ (0.01 mol L^{-1} to 1.0 mol L^{-1}).

Figure 7 (A) shows that there is a change in performance and an increase in the current intensity with increasing concentration of the supporting electrolyte. It was found that the relationship between the average potential and the logarithm (log) of the Na^+ concentration did not show a linear relationship, as illustrated by Figure 7 (B), however, the dependence of the redox process with respect to Na^+ concentration is evident. With increase of bulky cations concentrations the charge propagation is increased to active iron center of CdHSSI. It must be noted that, when electrode is transfered throught 0.1 moL L^{-1} electrolyte solution to 1.0 mol L^{-1} the voltammogram is restored.

After this study, the concentration of the supporting electrolyte chosen to continue the ensuing studies was 1.0 mol L^{-1} due to the better voltammetric performance.

Figure 8 illustrates the cyclic voltammograms obtained at different hydrogen ion concentrations (pH 2.0 to 8.0) obtained for CdHSSI. It was found that with the pH increase there is a decrease in the current intensity, ranging anodic current values between 5.84 and 3.89 μA and $E^{\theta'}$ remained between 0.15 and 0.16 V. Figure 9 illustrates the anodic current intensity dependence at different pH values for CdHSSI.

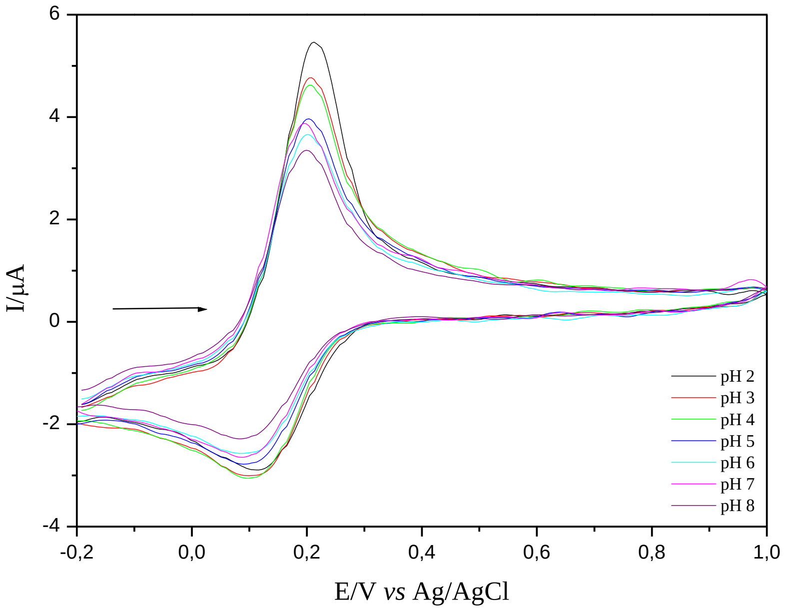

Figure 8. Cyclic voltammograms of the graphite paste modified with CdHSSI at different pH values (2.0 to 8.0); ($NaNO_3$ 1.0 mol L^{-1}, v = 20mV s^{-1}, 50% w/w).

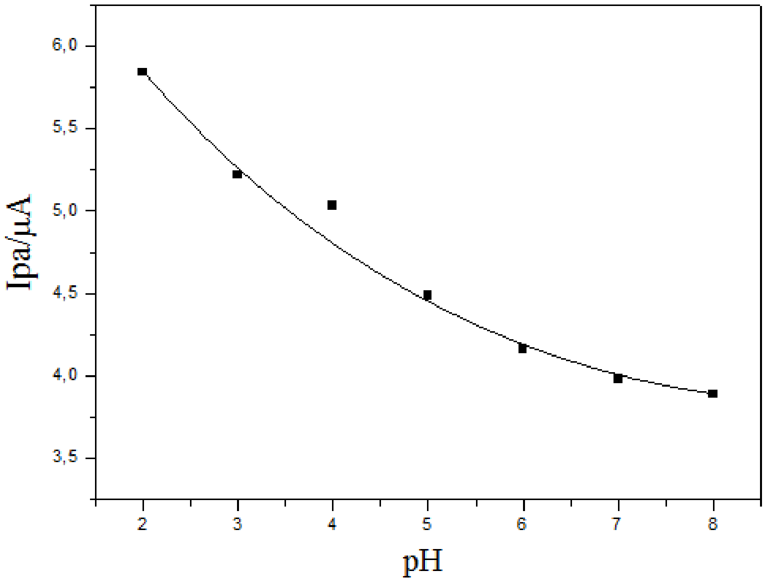

Figure 9. Current intensity dependence of the graphite paste modified with CdHSSI at different pH values (2.0 to 8) ($NaNO_3$ 1.0 mol L^{-1}, v = 20mV s^{-1}, 50% w/w).

With increasing pH values, there is a slower penetration (charge propagation) of H^+. The reason for the depletation in rate of charge transfer and decrease in intensity peak currents, is not clear, but can be due a cupric hydroxide formed on the material surface [21].

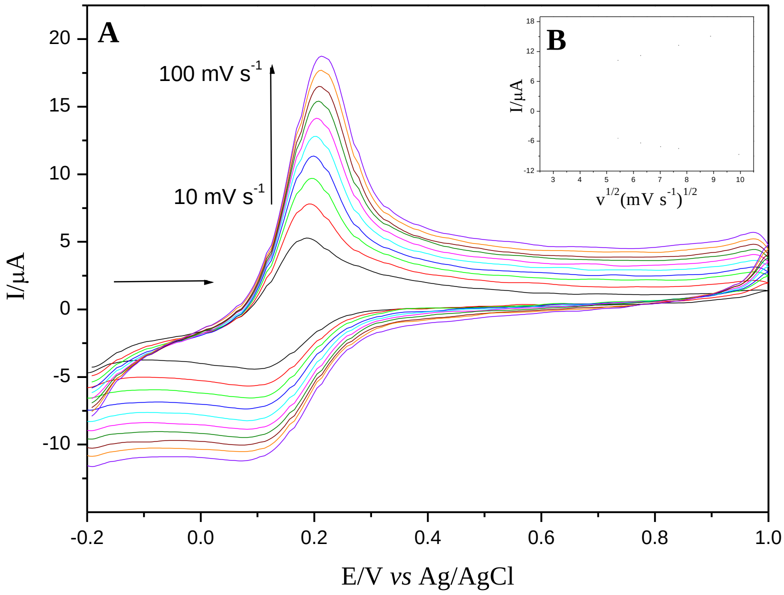

Figure 10. (A) Cyclic voltammograms of the graphite paste modified with CdHSSI at different scan rates ($NaNO_3$ 1.0 mol L^{-1}, pH 7.0, 50% w/w) and (B) dependence on current intensity of the anodic and cathodic peaks with the square root of the scan rate.

Despite a decrease in the current intensity there was no performance change in CdHSSI, therefore the pH value chosen for the ensuing studies was 7.0, for being close to the biological pH.

Figure 10 (A) illustrates the cyclic voltammograms of CdHSSI at different scan rates (10 to 100 mV s^{-1}). It was observed that by increasing the scan rate there is an increase in the current intensity and $E^{\theta'}$ kept values between 0.14 and 0.15 V. Figure 10 (B) illustrates the linear dependence between the current intensity of the anodic/cathodic peak and the square root of the scan rate, characterizing a diffusion controlled process [22]. In concordance of the table 2, the peak separation potential (ΔE_p) is greater than 59/n mV (n = 1) as expected for a system which shows quasi reversible behavior for the Fe (II)/Fe(III) redox system [22].

Table 2. Electrochemical parameters of the graphite paste modified with CdHSSI in different scan rates ($NaNO_3$, 1.0 mol L^{-1}, 50% w/w).

Scan Rates (mV s^{-1})	|Ipa/Ipc|	$E^{\theta'}$ (V)	ΔEp (V)
10	1.24	0.15	0.09
20	1.46	0.14	0.10
30	1.55	0.15	0.09
40	1.62	0.15	0.11
50	1.60	0.15	0.11
60	1.66	0.15	0.10
70	1.67	0.15	0.12
80	1.72	0.15	0.12
90	1.76	0.16	0.11
100	1.78	0.16	0.13

Figure 11 illustrates the electrocatalytic oxidation of ascorbic acid at the graphite paste electrode modified with CdHSSI, where it was observed that the graphite paste electrode (A) did not show any redox pair in the potential range between -0.2 and 1.0V in the absence of ascorbic acid, however, it showed an oxidation peak at 0.32 in the presence of ascorbic acid (B). The graphite paste electrode modified with CdHSSI, (C) in the absence of ascorbic acid, exhibited a redox pair with $E^{\theta'}$= 0.14V and in the presence of ascorbic acid (D) there was an increase in the anodic peak current intensity, followed by a decrease of the cathodic peak current, and a decrease of 50mV in the oxidation potential of ascorbic acid, demonstrating an electrocatalytic effect.

The current intensity of the anodic increases due to the electrocatalytic oxidation of ascorbic acid. Fe(III) produced during the anodic scan, chemically oxidizes the ascorbic acid, whereas Fe(III) is reduced to Fe(II), which will again be electrochemically oxidized to Fe(III). Ascorbic acid is easily oxidized to dehydroascorbic acid, which undergoes further chemical reaction to form the *gem*-diol.

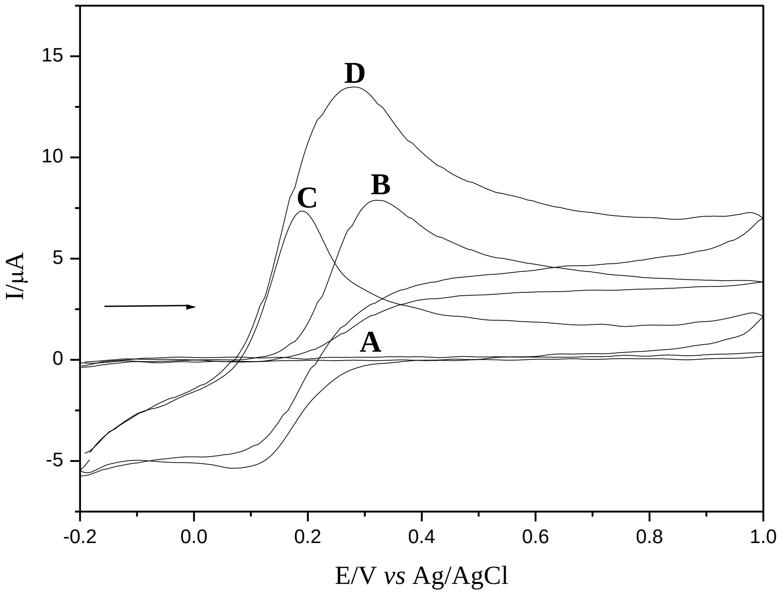

Figure 11. Cyclic voltammograms of: (A) graphite paste electrode, (B) graphite paste electrode in 9.0×10^{-4} mol L^{-1} ascorbic acid, (C) graphite paste electrode modified with CdHSSI and (D) graphite paste modified with CdHSSI in 9.0×10^{-4} mol L^{-1} of ascorbic acid ($NaNO_3$ 1.0 molL^{-1}; pH 7.0, v = 20mVs^{-1}).

To this system , the electrocatalytic process can also be represented according to the equations 1and 2:

$$2\ K_2Cd^{II}[Fe^{II}(CN)_6] \rightleftharpoons 2\ KCd^{II}[Fe^{III}(CN)_6] + 2K^+ + 2e^- \qquad \text{(Eq. 1)}$$

$$2\ KCd^{II}[Fe^{III}(CN)_6] + K^+ + AA^- \rightleftharpoons 2\ K_2Cd^{II}[Fe^{II}(CN)_6] + DAA^- + 2H^+ \qquad \text{(Eq. 2)}$$

where AA^- and DAA^- correspond to the dissociated forms of ascorbic acid and of dehydroascorbic acid, respectively. For this attribution an electro inactivity nature of silicate cage was considered [23]

Figure 12 shows the voltammetric behavior of CdHSSI after the additions of different portions of ascorbic acid. The analytic curve of the anodic current as a function of ascorbic acid concentration of CdHSSI is illustrated in Figure 13, in which the modified graphite paste electrode showed a linear response in the concentration range of 2.0×10^{-4} mol L^{-1} to 9.0×10^{-4} mol L^{-1} with a corresponding equation Y(µA) = 5.843 + 6.217×10^{3} [ascorbic acid] and a correlation coefficient R=0.988. The detection limit was of 1.21×10^{-4} mol L^{-1} with a relative standard deviation of ±5% (n=3) and amperometric sensitivity of 6.217 mA/ mol L^{-1}.

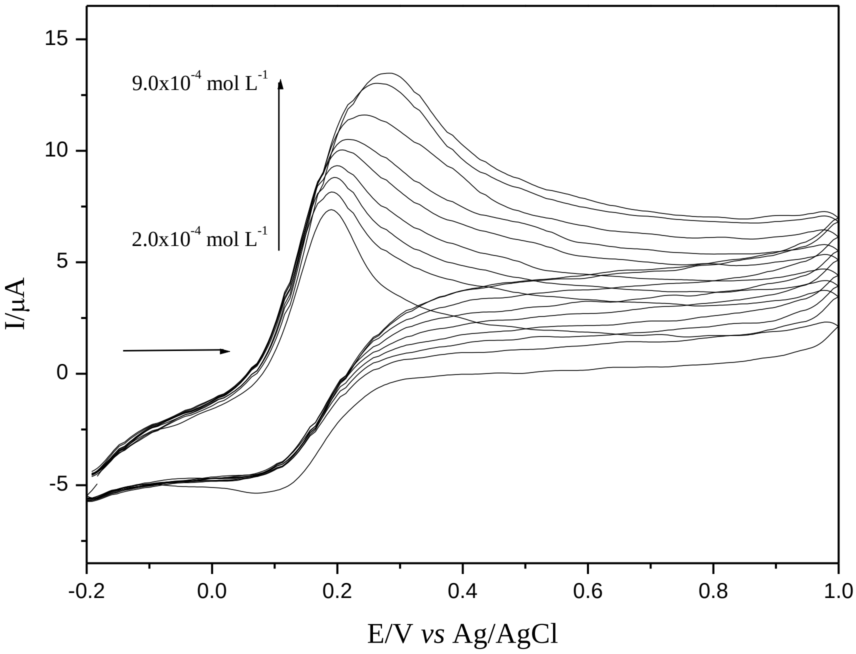

Figure 12. Cyclic voltammograms obtained for the graphite paste electrode modified with CdHSSI in the presence of different ascorbic acid concentrations (2.0×10^{-4} to 9.0×10^{-4} mol L^{-1}); ($NaNO_3$ 1.0 mol L^{-1}, pH 7.0 , v = 20 mV s^{-1}).

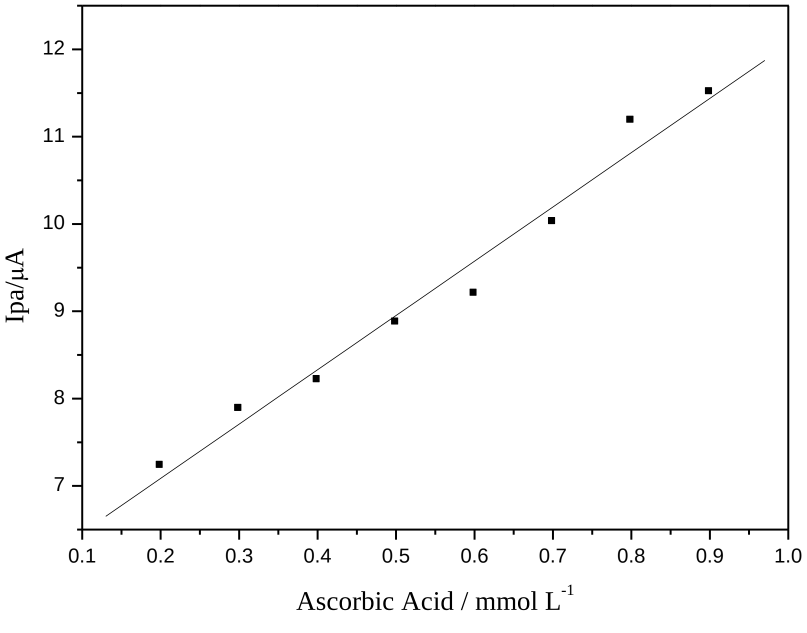

Figure 13. analytic curve of the anodic peak current as a function of ascorbic acid concentration using the graphite paste electrode modified with CdHSSI. ($NaNO_3$ 1.0 mol L^{-1}, pH 7.0, v = 20 mV s^{-1}).

The linear dependence of the calibration curve in Figure 13 suggest that the response of modified electrode is appropriated for quantitative ascorbic acid determination even in the millimolar concentration range. Such a wide concentration range of analytical useful response was also reported for ascorbic acid determination by chemically modified electrodes using voltammetric technique [24, 25].

The reproducibility is satisfactory for the investigated concentration range (RSD 5.0%) for ascorbic acid.

4. CONCLUSIONS

A hybrid nanocomposite formed by interaction of a octa (3-chloropropyl)octasilsesquioxane and imidazol, after cadmium adsorption and subsequent reaction of hexacyanoferrate (CdHSSI) was incorporated into a graphite paste electrode and the electrochemical studies were conducted with cyclic voltammetry. The cyclic voltammogram of the modified graphite paste electrode with CdHSSI (GPE- CdHSSI), showed one redox couple with formal potential E^{θ}=0.14V, attributed to the $Fe^{2+}(CN)_6$/ $Fe^{3+}(CN)_6$ process (E^{θ}) =V (*vs* Ag/AgCl; $NaNO_3$ 1.0 mol L^{-1}; v = 20 mV s^{-1}). The redox couple presents an electrocatalytic response for selective determination of ascorbic acid . The modified electrode gives a linear range from 2.0×10^{-4} mol L^{-1} to 9.0×10^{-4} mol L^{-1} (r = 0.998) for the determination of ascorbic acid with detection limit of 1.21×10^{-4} mol L^{-1} with a relative standard deviation of 5% (n=3) and amperometric sensitivity of 6.217 mA/ mol L^{-1} for ascorbic acid.

This method is very simple convenient, economical and no separation step and elimination of specie strangers is required.

ACKNOWLEDGEMENTS

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