

Determination of N-Acetylcysteine by Cyclic Voltammetry Using Modified Carbon Paste Electrode with Copper Nitroprusside Adsorbed on the 3–Aminopropylsilica.

Acelino Cardoso de Sá¹, Leonardo L. Paim², Urquiza de Oliveira Bicalho,
Devaney Ribeiro do Carmo^{1,*}

¹ Faculdade de Engenharia de Ilha Solteira UNESP - Univ Estadual Paulista, Departamento de Física e Química, Av. Brasil Centro, 56 CEP 15385-000, Ilha Solteira, SP, Brazil. fax: 55 (18)3742-4868

² Instituto de Química de Araraquara UNESP - Univ Estadual Paulista, Rua Francisco Degni s/n, CEP 14801-970, Araraquara, SP, Brazil.

*E-mail: docarmo@dfq.feis.unesp.br

Received: 4 July 2011 / Accepted: 12 August 2011 / Published: 1 September 2011

Copper nitroprusside was formed on aminopropylsilica silica gel (3-AS) surface (SiCuNP) previously prepared following two steps. These materials were thoroughly characterized by Infrared (FTIR) and cyclic voltammetry. The above techniques confirmed the successful formation of the copper nitroprusside on the silica surface. The cyclic voltammogram of CuNPSD were found to exhibit two redox couples with $(E^{0'})_1 = 0.34$ V; $(E^{0'})_2 = 0.76$ V vs. Ag/AgCl, KCl_(sat) (KCl = 1.0 mol L⁻¹; $v = 20$ mV s⁻¹) attributed to the redox processes Cu^(I)/Cu^(II) and Fe^(II)(CN)₅NO/Fe^(III)(CN)₅NO respectively. The second redox process $(E^{0'})_2$ presented by the graphite paste electrode with SiCuNP shows electrocatalytic activity for the oxidation of N-acetylcysteine. The linear range for the determination of N-acetylcysteine was found between 9.9×10^{-5} and 8.9×10^{-4} mol L⁻¹ showing a detection limit of 4.18×10^{-5} mol L⁻¹ and an amperometric sensitivity of 3.02×10^{-2} A / mol⁻¹ L.

Keywords: 3–aminopropylsilica Copper; Nitroprusside; Spectroscopy Cyclic Voltammetry; Carbon Paste Electrode, N-acetylcysteine

1. INTRODUCTION

In electrochemistry, it is shown that chemically modified electrodes (CMEs) have several advantages over conventional electrodes thus contributing in the development of many electroanalytical applications [1-3]. The properties of CMEs are known to depend on the formation and characteristics of the modifier on the electrode surface. One of the main advantages of CME is their ability to catalyze the oxidation of some species which exhibit high potential in non-modified

electrodes, thereby increasing their sensitivity and selectivity [4-6].

A wide variety of organic and inorganic compounds are used for the preparation of modified electrodes, among them worth mentioning the cyanoferrates as hexacyanoferrates and pentacyanonitrosylferrates. The pentacyanonitrosylferrate (PCNF), represented by the structure $[\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}]^{-2}$, is a member of the polycyanide metal complexing reagents has received much attention in the preparation of CMEs in recent years, it has reversible electron transfer and has been cleverly immobilized on the surface of electrodes [7, 8]. Complex of metals PCNF has been used for electrocatalytic oxidation of compounds such as: L-cysteine [7]; N-acetylcysteine [9]; thiosulfate [10]; hydrazine [11]; ascorbic acid [12] and dopamine [13].

Razmi and Habibi [7] used the sol-gel technique to construct a SnPCNF modified composite carbon ceramic electrode (CCE). CCE was built primarily through the sol-gel process from a mixture of graphite powder and metallic Sn in the presence of methyltrimethoxysilane (MTMOS) and drying time of 24 h. The SnPCNF was formed on the surface of modified composite carbon ceramic electrode (CCE) by cyclic voltammetry (CV) in the range of potential between 0.3 and 1.3 V with scan rate of 50 mV s^{-1} for 1 h and electrocatalytic properties of the film have been tested with L-cysteine where it presented a linear range between 2 and 50 mM and a detection limit of $0.62 \times 10^{-6} \text{ mol L}^{-1}$.

Suarez et al. [14] incorporate copper (II) hexacyanoferrate (III) (CuHCF) into a carbon paste electrode (CPE) and the electrochemical studies were performed by sweep linear voltammetry (SLV). The modified CPE with CuHCF gives a linear range between 1.2×10^{-4} to $8.3 \times 10^{-4} \text{ mol L}^{-1}$ for the determination of N-acetylcysteine with a detection limit of $6.3 \times 10^{-5} \text{ mol L}^{-1}$.

Do Carmo et al. [9] prepared modified CPE where iron nitroprusside (FePCNF) used as modifier and the electrochemical studies were performed by cyclic voltammetry. The modified CPE showed electrocatalytic activity toward the N-acetylcysteine where it presented a linear range between 9.6×10^{-4} and $1.4 \times 10^{-2} \text{ mol L}^{-1}$ with detection limit of $1.5 \times 10^{-4} \text{ mol L}^{-1}$.

The modified CPE is inexpensive kind of electrode and possess many advantages such as low background current, wide range of potential application, easy fabrication, and rapid surface renewal [15, 16]. Silica and modified silica has a high specific surface area and porosity, and good thermal stability and these properties are responsible for the great interest in applying these silicas as mediators or ligands in CPEs [16]. Recently, the use of silica in modified electrodes is divided into analysis with preconcentration using the technique of anodic stripping [17, 18], or use as a substrate for incorporation of redox mediators [19, 20].

Jaafariasl et al. [17] developed a silica gel-modified carbon paste electrode (Si-CPE) to use as selective and sensitive electrochemical sensor employing a differential pulse adsorptive stripping voltammetric and hydrodynamic amperometric determination of insulin. Using hydrodynamic amperometry, under optimum conditions, calibration plot for insulin was linear in the range of 90–1400 pM and the sensitivity and detection limit of the proposed amperometric method were found to be 107.3 pA/pM and 36 pM, respectively.

Do Carmo et al. [19] modified silica gel surface with the third generation (G-3) polypropylenimine hexadecaamine dendrimer (DAB-Am-16) and in a two-step synthesis, the modified silica allowed forming the copper hexacyanoferrate binuclear complex. The modified silica containing copper hexacyanoferrate (CuHCFSD) was tested for a voltammetric determination of nitrite using a

modified CPE. The CPE modified with CuHCFSD was selective to nitrite and biological substances such as cysteine, N-acetylcysteine and citric acid do not interfere in the redox process.

In order to further explore the properties of modified silica as a modifying agent of CPE, the scope of this paper was report the formation and characterization of the copper nitroprusside adsorbed on the 3-aminopropylsilica (SiCuNP), and the direct application in determination of N-acetylcysteine by cyclic voltammetry using modified CPE. N-acetylcysteine is a derivative of the amino acid cysteine and thus has an important role in the living system. It is a mucolytic drug used in the treatment of respiratory diseases, and its sulfhydryl groups (SH) reacts with the disulfide groups present in the mucoproteins fragmenting them into smaller units thereby reducing the viscosity of mucus [21].

2. EXPERIMENTAL

2.1. Reagents

All reagents were of analytical grade (Merck) and water was deionized using the Milli-Q Gradient system of Millipore. The N-acetylcysteine solutions were prepared and standardized just prior to use.

2.2 Fourier transform infrared measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5DXB FTIR 300 spectrometer (Nicolet Instruments, Madison, WI). Pellets were prepared with 150 mg of KBr and 1% (w/w) of solid samples, a minimum of 64 scans was collected for each sample at a resolution of $\pm 4 \text{ cm}^{-1}$.

2.3. Electrochemical measurements

Cyclic voltammetry measurements were made using a microchemistry potentiostat of model MQPG1. The electrochemical system used was composed of three electrodes: the auxiliary platinum electrode, the reference Ag/AgCl, $\text{KCl}_{(\text{sat})}$ electrode and working graphite paste electrode. The working electrode consisted of a 15 cm long glass tube with an inner diameter of 0.30 cm and external diameter of 0.5 cm, and the internal cavity connected via a copper wire to establish the electrical contact.

The cyclic voltammetry technique was employed to study the electrochemical behavior. The catalytic current was estimated from the difference between the current measured in the presence and in the absence of N-acetylcysteine. The solutions were bled with nitrogen for 10 min before the measurements.

Cyclic voltammograms were recorded for the study of electrocatalysis of N-acetylcysteine. N-acetylcysteine solutions were prepared immediately before use and solutions purged with nitrogen before each measurement. In most experiments, a 1.0 mol L^{-1} KCl (pH 7.0) support electrolyte was

employed. The catalytic current was estimated from the difference between the current measured in the presence of N-acetylcysteine and that obtained in its absence. The solutions were bled with nitrogen for 10 min before measurements. Cyclic voltammograms were recorded in 1.0 mol L^{-1} (pH 7.0) KCl solutions at a scanning rate of 20 mV s^{-1} .

2.4 Formation of Binuclear Complex with Silica

1.0 g of 3-aminopropylsilica was immersed in 25 mL of a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ cupric ion (copper chloride) solution. This mixture was stirred for 30 minutes at room temperature and, the solid phase was filtered and washed with deionized water thus forming the SiCu. After thorough washing, the SiCu was added to a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ solution of the sodium nitroprusside compound, $\text{Na}[\text{Fe}(\text{CN})_5\text{NO}]$. The resulting material was washed with enough deionized water and the compound obtained labeled as SiCuNP.

2.5. Preparation of the graphite paste electrode modified with SiCuNP

The graphite paste modified with SiCuNP was prepared starting from a mixture containing 20% (w/ w) (20 mg SiCuNP with 80 mg graphite powder (Aldrich) and 30 μL of mineral oil). The graphite paste with SiCuNP was include in a cavity with 2 mm inner diameter, connected with a copper wire.

3. RESULTS AND DISCUSSIONS

3.1 FTIR of SiCuNP

The vibrational spectra of silica and 3-aminopropyl silica gel are illustrated in Figure 1.

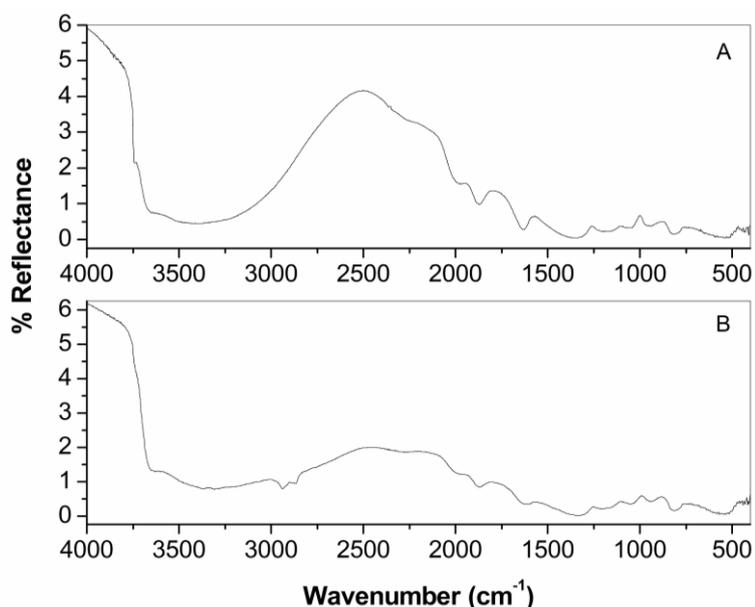


Figure 1. The vibrational spectra of silica and 3-aminopropyl silica gel.

The spectrum of silica gel illustrated by Figure 1A shows a band near 3750 cm^{-1} which was attributed to stretching of the surface silanol groups [22]. In the region between 3700 and 3200 cm^{-1} , we observed a broad band corresponding to symmetric stretching vibrations of Si-OH group. The absorption related to the combination of the silica skeleton occur in the region between 2000 - 1870 cm^{-1} . Also there was a band in 1630 and another in 3350 cm^{-1} , corresponding to angular deformation of water molecule [23]. To the region below 1300 cm^{-1} vibrations of asymmetric chain Si-O-Si was observed [23]. A better view of these absorptions above the 3-aminopropyl silica gel is depicted in Figure 2.

Much absorption expected for the 3-aminopropyl silica gel, such as $\delta(\text{NH}_2)$ 1596 cm^{-1} and $\nu(\text{NH})$ at 3342 cm^{-1} and other weak absorptions intensities were not able to be identified. Unfortunately the infrared spectrum of pure silica gel, has limitations for the characterization of organofunctional groups chemically bound due same factors such as: physical affinity for water, low amount of organic material on the surface and also the strong absorption of the matrix (silica gel), which obscures the absorptions of the functional group in some regions of the spectrum, for example, However we identified the presence of two bands at 2878 and 2944 cm^{-1} assigned to both $\nu(\text{CH})$, as can be seen in Figure 2.

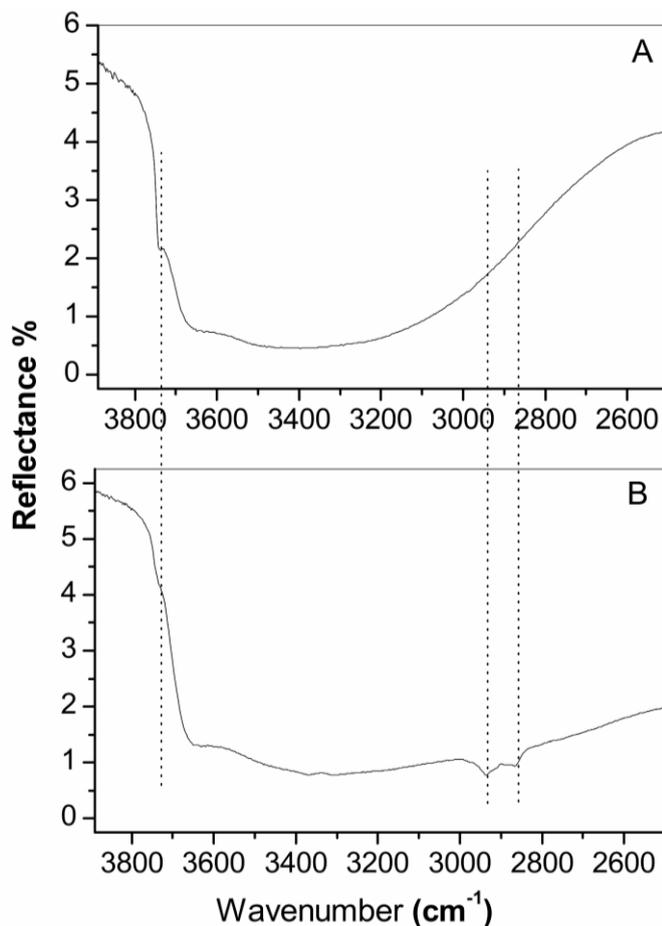


Figure 2. The vibrational spectra of silica and 3-aminopropyl silica gel (zoom).

The absorption spectrum in the infrared region of 3-aminopropyl silica gel adsorbed copper (SiCu) and 3-aminopropyl silica gel adsorbed with copper nitroprusside (SiCuNP), are illustrated in Figure 3. A broad strong band at 3448 cm^{-1} characteristic of the symmetric stretching vibration of the ν_s OH group was observed [23]. Around 2936 cm^{-1} an asymmetrical stretching that is characteristic of methylene groups CH was verified [23].

Also there was absorption at 1630 cm^{-1} and another at 1100 cm^{-1} , corresponding to angular deformation of the OH groups water and asymmetric stretching vibrations Si-O-Si respectively. The absorptions observed in regions less than 1100 cm^{-1} assigned to the skeleton of silica, such as the absorption at 480 cm^{-1} which is related to the bond O-Si-O [23].

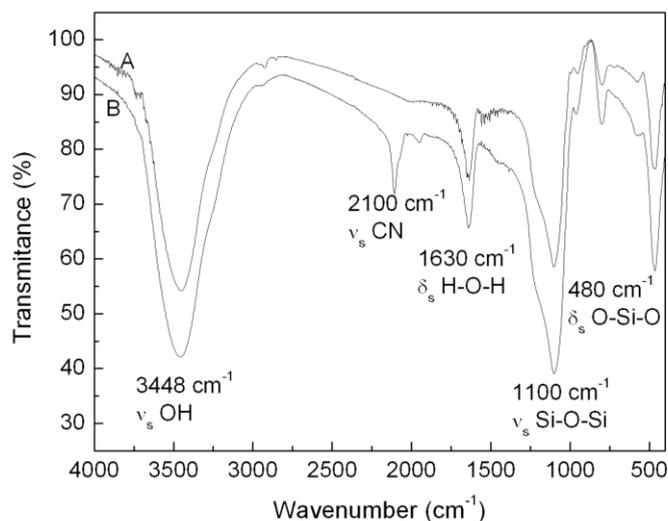


Figure 3. The vibrational spectra of SiCu and SiCuNP.

In the FTIR of SiCu and SiCuNP, are illustrated. Figure 3 (B) showed a peak at 2108 cm^{-1} characteristic stretch ν_s (CN) seen in pentacyanoferrate. The fact that this frequency to be shifted relative one found in copper Nitroprusside (where the values of ν_s (CN) are around 2196 cm^{-1} to 2208 cm^{-1}) suggests a possible matrix effect of 3 - aminopropyl silica gel. We also observed a small band around 1949 cm^{-1} characteristic stretch ν_s (NO) [24].

The quantity of Iron and Copper in SiCuNP was estimated by atomic absorption spectroscopy using a Perkin Elmer 300 spectrometer. The obtained Fe, Cu contents in the solid were found to be respectively 0.17 and 0.11 mmol metal /g of silica.

3.2 Electrochemical Characterization of SiCuNP

The cyclic voltammogram of the SiCuNP modified electrode was found to exhibit two redox couples, I and II, as illustrated in Figure 4. The first redox couple presents no well defined process with formal potential $(E^{\theta'})_1 = 0.34\text{ V}$ (peak 1) attributed to the process $\text{Cu}^{(\text{I})}/\text{Cu}^{(\text{II})}$. The second redox

couple (peak II) exhibit a formal potential with $(E^{\theta'})_2 = 0.76 \text{ V vs Ag/AgCl}$ ($\text{KCl} = 1.0 \text{ mol L}^{-1}$; $\nu = 20 \text{ mV s}^{-1}$) attributed to $\text{Fe}^{\text{III}}(\text{CN})_5\text{NO}/\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}$ of the binuclear complex formed.

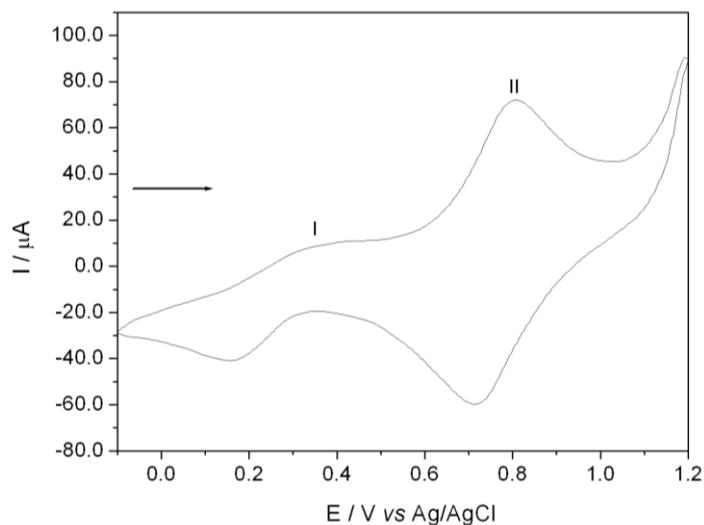


Figure 4. Cyclic voltammogram of SiCuNP ($1.0 \text{ mol L}^{-1} \text{ KCl}$; $\text{pH } 7.0$; $\nu = 20 \text{ mV s}^{-1}$).

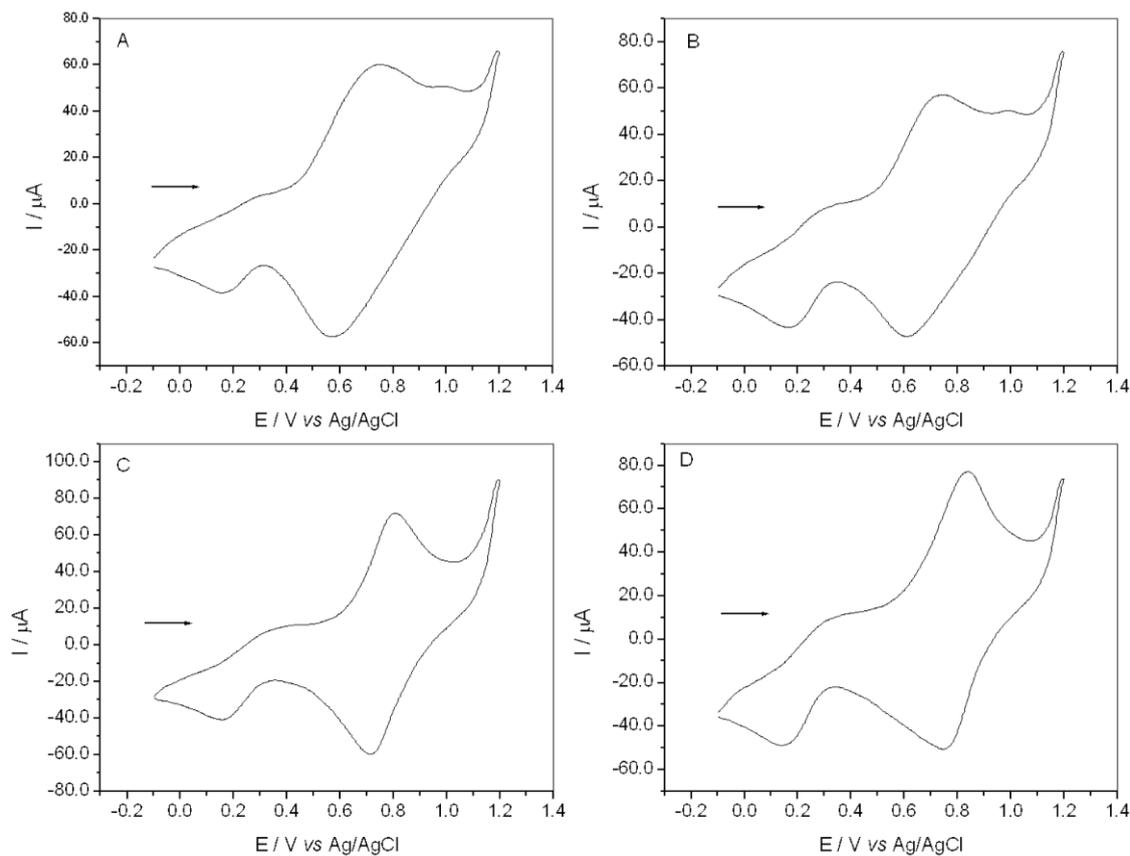


Figure 5. Influence of the nature of cations in the graphite electrode modified with SiCuNP: A – LiCl ; B – NaCl ; C – KCl ; D – NH_4Cl (1.0 mol L^{-1} ; $\nu = 20 \text{ mV s}^{-1}$).

The process of oxidation and reduction of the modified compounds on the surface of takes place initially by the equilibrium of the cation present in the support electrolyte with the electrode surface containing the material. For different electrolytes tested, the nature of cations was observed to affect the E^0 as well as the intensities of current. As illustrated in Figure 5, in studies performed with different cations, both the current intensity and the average potential of redox couples of the two processes (E^0)₁ and a (E^0)₂ were influenced by the nature of the cation, with these potentials shifted to more anodic regions according to the sequence: $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.

Table 1 lists the main electrochemical parameters of the compounds mentioned above and their hydration radii. Compounds such as Prussian blue and similar compounds exhibit structures which present zeolitic cavity, i.e., channels which allow the insertion of small molecules and ions and therefore behave as zeolites [25]. Because they have smaller hydration radii, the cations K^+ and NH_4^+ are more easily lodge in the pores of the zeolite structure. Due to a higher affinity of these cations, it was possible to observe, as shown in the voltammograms of Figure 5, a better electrochemical response of electrode graphite paste modified with SiCuNP in the presence of electrolyte containing the cations K^+ and NH_4^+ . The cation K^+ has a better voltammetric performance in relation to the cation NH_4^+ although almost the same hydrated radius. This can be explained by the fact that the cation NH_4^+ presents a low ion mobility compared to K^+ [25]. Cyclic voltammograms of the carbon paste electrode modified with SiCuNP recorded in presence of different anions indicated that the two redox processes are not strongly influenced by the nature of the anion (Cl^- , NO_3^- , SO_4^-) (results not shown).

Table 1. Main voltammetric parameter of SiCuNP in the presence of different support electrolytes.

Cation	$[I_{pc}/I_{pa}]$	ΔE_p^* (V)	$(E^0)_2$ (V)	Diameter of the hydrated cation (nm)
Li^+	1.17	0.18	0.66	0.470
Na^+	0.74	0.13	0.68	0.360
K^+	0.63	0.08	0.76	0.240
NH_4^+	0.70	0.09	0.79	0.245

* $\Delta E_p = E_{pa} - E_{pc}$; E_{pa} (anodic peak potential); E_{pc} (cathodic peak potential)

Figure 6 presents the cyclic voltammograms for different concentrations of KCl support electrolyte of 1.0×10^{-2} to 2.0 mol L^{-1} . Peak I was found to show a potential shift to more positive values with increasing electrolytes concentration. On increasing the concentration of KCl, the influence of K^+ ion in the redox process is easily observed with the potential shifts attributed to the change in the activity of these ions [26]. For the graphite paste electrode modified with SiCuNP, the slope of this line was found to be 66 mV per decade concentration of potassium ions thus indicating an almost Nernstian process [26]. Similarly to the electrode modified with $\text{Fe}^{(II)}\text{NP}$, the almost nernstian response observed for the concentration of potassium indicates the participation of this ion in the redox

process. The dependence of the potential ($E^{0'}$) with electrolyte concentration can be explained by the equilibrium existing between the cation and CuNP [26].

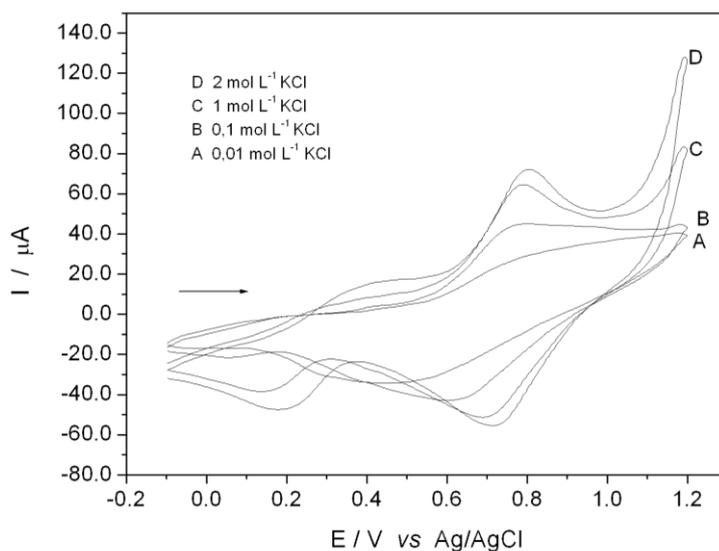


Figure 6. Cyclic voltammograms for different concentrations of KCl support electrolyte (1.0×10^{-2} to 2.0 mol L^{-1}).

Figure 7 shows the cyclic voltammogram at different pH values (2-8). With the increase in hydrogen ion concentration, a large increase in current intensity was observed in the redox process I (peak I) previously attributed to the redox couple $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$.

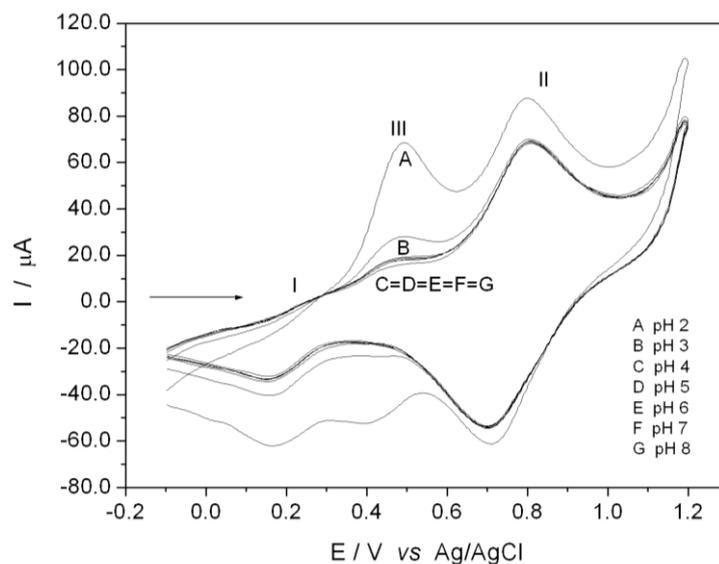


Figure 7. Cyclic voltammogram at different pH values: a) 2.0; b) 3.0; c) 4.0; d) 5.0; e) 6.0; f) 7.0; g) 8.0 ($\nu = 20 \text{ mV s}^{-1}$; $\text{KCl } 1.0 \text{ mol L}^{-1}$).

Meanwhile, for the second process (peak II), the average potential $(E^{0'})_2=0.76\text{V}$ was found to remain virtually unchanged. Therefore, from $\text{pH}<4$, the redox process I became more distinct, which can be explained by the presence of high concentrations of H^+ ions which governs the electroactivity of one or more forms of intermediate species [26].

Figure 8 illustrates the cyclic voltammogram of SiCuNP at different scanning rates (10-100 mV s^{-1}). With increasing scanning rate, a linear dependence was observed to occur between the intensity of the anodic/cathodic peak current and the square root of scanning rate for peak I, thus characterizing a diffusion process [27].

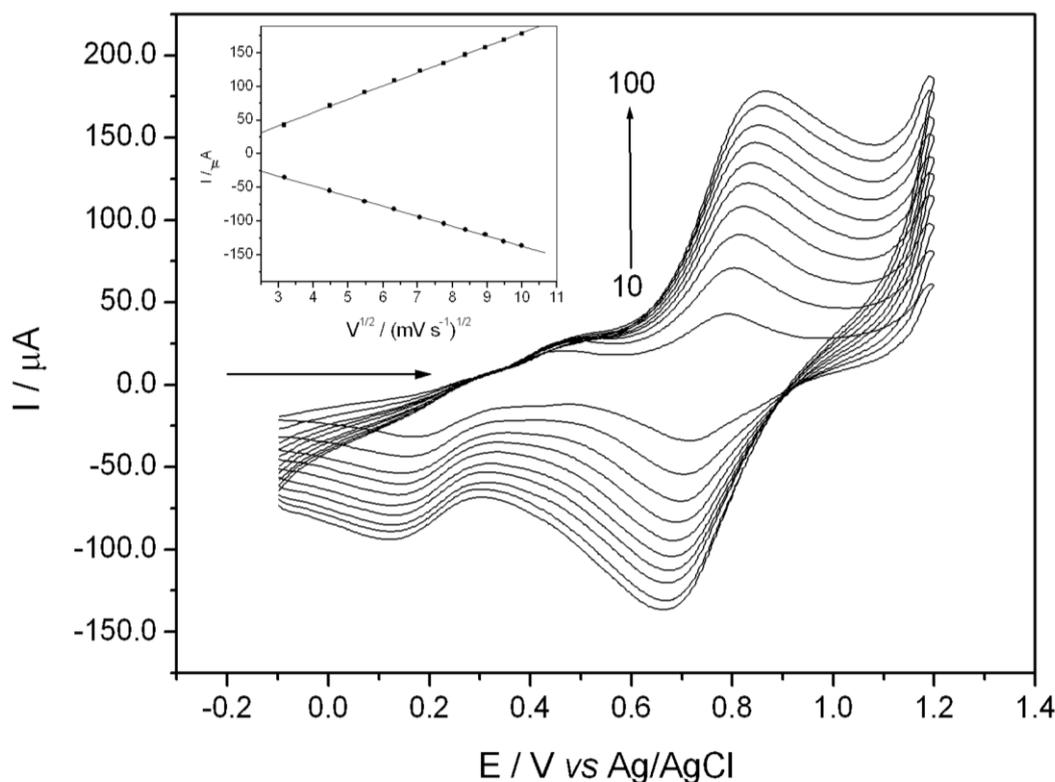


Figure 8. Cyclic voltammogram of SiCuNP at different scanning rates (10-100 mV s^{-1}) insert anodic/cathodic peak current and the square root of scanning rate for peak I.

Given the results above, the KCl (1.0 mol L^{-1} , $\text{pH } 7.0$) was chosen for use in subsequent voltammetric studies.

3.3 Determination of *N*-acetylcysteine

Figure 9 illustrates the behavior of the graphite paste electrode in a 1.0 mol L^{-1} of KCl solution. The voltammogram in the absence (curve a) and presence (curve b) of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ *N*-acetylcysteine assigned to the bare graphite paste electrode showed no electroactivity in the potential range studied (-0.1 to 1.2 V).

The graphite paste electrode modified with SiCuNP in the absence of N-acetylcysteine is shown in curve c. It was observed that in the presence of 2.0×10^{-3} mol L⁻¹ of N-acetylcysteine the current of peak II increases as illustrated in curve d. The intensity of the anodic peak current increases proportionally with increasing concentration of N-acetylcysteine as depicted by Figure 9. This increase in intensity of the anodic peak current is due to the electrocatalytic oxidation of N-acetylcysteine by the electron mediator SiCuNP.

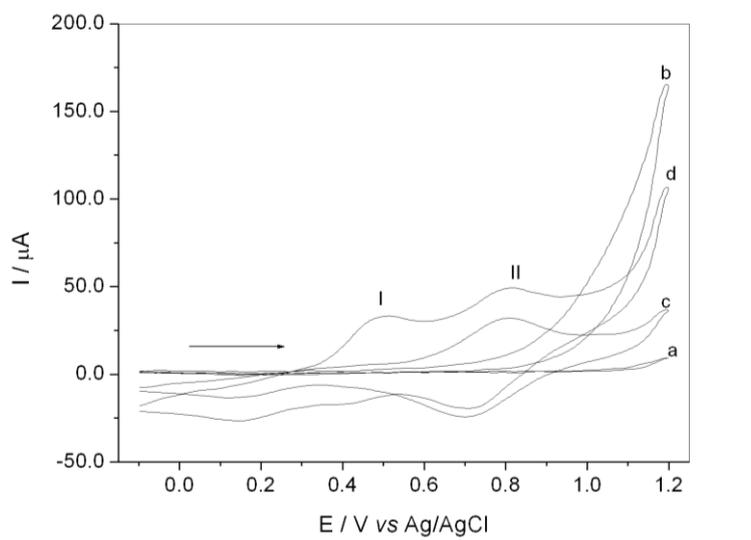
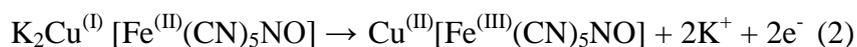


Figure 9. Cyclic voltammogram: a) graphite paste electrode; b) graphite paste electrode in 2.0×10^{-3} mol L⁻¹ N-acetylcysteine; c) modified graphite paste electrode with SiCuNP in ausense of N-acetylcysteine; d) graphite paste electrode modified with SiCuNP after addition of 2.0×10^{-3} mol L⁻¹ N-acetylcysteine (1.0 mol L⁻¹ KCl ; $\nu = 20$ mV s⁻¹).

The equation for the electrochemical oxidation of L-cysteine as described in the literature [28] can be represented as follows:



Therefore, in view of this reaction of L-cysteine, the oxidation of N-acetylcysteine on the surface of the graphite paste electrode modified with SiCuNP can be described by the following reactions:



where NACySH = N- Acetylcysteine and NACySSCy = N-Acetylcystine

Thus, it was determined that by adding aliquots of the N-acetylcysteine, the drug was oxidized on the electrode surface and the drug is oxidized through an electrocatalytic oxidation process. The electrocatalytic oxidation of N-acetylcysteine occurs as follows: Fe^{III} produced during anodic scanning chemically oxidizes the N-acetylcysteine molecule when it is reduced to Fe^{II} , which will again be electrochemically oxidized to Fe^{III} .

The peak potential is not affected by the N-acetylcysteine concentration and the catalytic current is also linear with the square root of scan rate.

The electrochemical behavior of the oxidation of N-acetylcysteine in the electrode modified with CuNP is very similar to that of an electrode modified with a film of Prussian blue, which shows an increase of current in the two oxidation potentials (0.79 and 0.95 V) in the presence of N-acetylcysteine (1.0 mol L^{-1} KCl, pH 3.5 vs. Ag/AgCl) [26].

Figure 10 illustrates an analytical curve for the determination of N-acetylcysteine. The modified electrode was found to show a linear response from 9.9×10^{-5} to $8.9 \times 10^{-4} \text{ mol L}^{-1}$ with a corresponding equation given by: $Y (\mu\text{A}) = 2.54 + 30.194 [\text{N-acetylcysteine}]$ with a correlation coefficient $r = 0.998$. The method shows a detection limit of $4.18 \times 10^{-5} \text{ mol L}^{-1}$ with an amperometric sensitivity of $3.02 \times 10^{-2} \text{ A/ mol}^{-1} \text{ L}$ relative to N-acetylcysteine.

These analytical parameters are similar one studies reported for the electroanalytical determination of N-acetylcysteine by modified electrode in aqueous media, where other modified electrode with similar compounds, such as, FeNP [9], CuHCF [14] and CuNP [31] that showed worse detection limits in around of $1.5 \times 10^{-4} \text{ mol L}^{-1}$, $6.3 \times 10^{-5} \text{ mol L}^{-1}$ and $4.5 \times 10^{-4} \text{ mol L}^{-1}$, respectively.

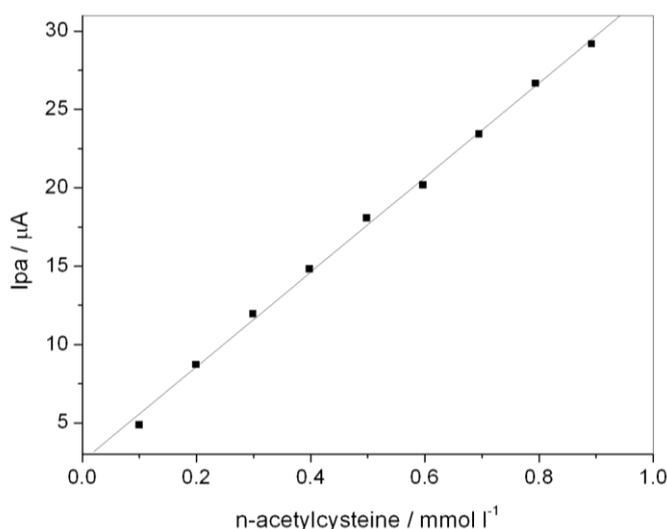


Figure 10. Analytical curve for the determination of N-acetylcysteine.

4. CONCLUSIONS

The two redox process presented by the graphite paste electrode modified with SiCuNP shows electrocatalytic activity for the oxidation of N-acetylcysteine. The linear range for the determination of

N-acetylcysteine was found between 9.9×10^{-5} and 8.9×10^{-4} mol L⁻¹ showing a detection limit of 4.18×10^{-5} mol L⁻¹ and an amperometric sensitivity of 3.02×10^{-2} A/ mol⁻¹ L.

When compared to other electroanalytical methods, the main advantage of the modified electrode SiCuNP is the easy of manufacture and the fact that its surface can be renewed. This feature is important when one wants to effectively implement various measurements in a short time. Another advantage is that it needs no for prior chemical treatment.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (Processes 03/12882-6, 04/09326-7 and 07/07700-7) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

References

1. S. M. Chen, *J. Electroanal. Chem.*, 521 (2002) 29
2. D. R. do Carmo, L. L. Paim, D. R. Silvestrini, U. O. Bicalho, A. C. Sá and N. R. Stradiotto, *Int. J. Electrochem. Sci.*, 6 (2011) 1175
3. C. S. Mattos, M. O. Firmino, D. R. do Carmo and N. R. Stradiotto, *Int. J. Electrochem. Sci.*, 3 (2008) 338
4. H. S. El-Desoky and M. M. Ghoneim, *Talanta*, 84 (2011) 223
5. A. Salimi, K. Abdi and G. -R. Khayatiyan, *Electrochim. Acta*, 49 (2004) 413
6. M. H. Pournaghi-Azar and R. E. Sabzi, *J. Electroanal. Chem.* 543 (2003) 115.
7. H. Razmi, Es. Habibi, *Electroanalysis*, 21 (2009) 867
8. H. Razmi and K. Heidari, *Electrochim. Acta*, 50 (2005) 4048
9. D. R. do Carmo, R. M. da Silva and N. R. Stradiotto, *J. Braz. Chem. Soc.*, 14 (2003) 616
10. R. E. Sabzi, *J. Braz. Chem. Soc.*, 16 (2005) 1262
11. M. H. Pournaghi-Azar and H. Nahalparvari, *J. Electroanal. Chem.*, 583 (2005) 307
12. H. Razmi and M. Harasi. *Int. J. Electrochem. Sci.*, 3 (2008) 82
13. H. Razmi, M. Agazadeh and B. Habibi-A, *J. Electroanal. Chem.*, 547 (2003) 25
14. W. T. Suarez, L. H. Marcolino Jr. And O. Fatibello-Filho, *Microchem. J.*, 82 (2006) 163
15. T. H. Degefa, B. S. Chandravanshi and H. Alemu, *Electroanalysis*, 11 (1999) 1305
16. E. Shams, F. Alibeygi and R. Torabi, *Electroanalysis*, 18 (2006) 773
17. M. Jaafariasl, E. Shams and M. K. Amini, *Electrochim. Acta*, 56 (2011) 4390
18. R. Torabi, E. Shams, M. A. Zolfigol and S. Afshar, *Anal. Lett.*, 39 (2006) 2643
19. D. R. do Carmo, S. Gabriel Jr., U. O. Bicalho, C. A. Picon and L. L. Paim, *Macromol. Symp.*, 299/300 (2011) 206
20. E. Shams, A. Babaei, A. R. Taheri and M. Kooshki, *Bioelectrochemistry*, 75 (2009) 83
21. R. P. Tomkiewicz, E. M. App, G. T. De Sanctis, M. Coffiner, P. Mães, B. K. Rubin and M. King, *Pulm. Pharm.*, 8 (1995) 259
22. G. S. Caravajal, D. E. Leyden and G. R. Quinting, *Anal. Chem.*, 60 (1988) 1776
23. J. J. Yang, I. S. EL-Nahhal and G. E. Maciel, *J. Non-Crystall. Sol.*, 209 (1997) 19
24. C. Fulcher, M. A. Crowell, R. Bayliss, K. B. Holland and J. R. Jezorek, *Anal. Chim. Acta*, 129 (1981) 29
25. R. K. Iler, *The chemistry of silica*. John Willey & Sons, New York, USA, (1979)

26. J. R. Hernandez and E. Reguera, *J. Chem. Crystall.*, 34 (2004) 30
27. D. Engel and E. W. Grabner, *Bunseng. Phys. Chem.*, 89 (1985) 982
28. D. R. Carmo, R. M. Silva and N. R. Stradiotto, *Eclét. Quím.*, 27 (2002) 197
29. A.J. Bard and L. R. Faulkner, *Electrochemical methods: Fundamentals and Applications*, 2nd ed., John Wiley, New York, USA, (2001)
30. T. R. Ralph, M. L. Hitchman, J. P. Millington and F. C. Wash, *J. Electroanal. Chem.*, 375 (1994) 1
31. D. R. Carmo, R. M. Silva and N. R. Stradiotto, *Portug. Electrochim. Acta*, 23 (2005) 457