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# Copper Hexacyanoferrate Formation on the Modified Silica Surface with DAB-Am-16 Dendrimer

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**Summary:** The third generation (G-3) polypropylenimine hexadecaamine dendrimer (DAB-Am-16) was grafted onto the silica gel surface. The modified silica interacts easily with $Cu^{2+}$ and then with potassium ferrocyanide to form copper hexacyanoferrate. The modified silica was characterized by the following techniques: Nuclear Magnetic Resonance (NMR), FTIR spectroscopy, Energy Dispersive X-ray (EDX) and Cyclic Voltammetry. The modified silica containing copper hexacyanoferrate (CuHCFSD) was tested for a voltammetric determination of nitrite using a modified graphite paste electrode.

**Keywords:** composites; copper hexacyanoferrate; polypropylenimine hexadecaamine dendrimer; silica gel; voltammetry cyclic

## Introduction

The term dendrimers[1] comes from the Greek "dendron" (tree) and meros (parts), thus referring to the tree appearance that is typical of these compounds. Dendrimers are monodisperse macromolecules of nanometric dimensions, highly branched and spherical, prepared by interactive synthesis methods.

These materials belong to a class of polymers; however, the structures differ substantially from the traditional linear polymers and are constructed from the monomers usually designated as $AB_n$[2] (where $n \geq 2$ is usually equal to 2 and 3), are highly branched and have three distinct structural characteristics: a core, multiple peripheral groups and branching units that connect to one another. Both peripheral groups and branching units are termed dendrons or "wedges".

There are two typical routes for synthesis of dendrimers: convergent and divergent routes, as shown in Figure 1. In the divergent method the branching units are attached one by one, multiplying the number of peripheral groups. The convergent method follows the opposite route: the skeleton is built step by step, starting from the end groups, which are attached to the core of the molecule to give a complete dendrimer. Usually, when the convergent route is used, the A group of the $AB_n$ monomer must be protected or requires activation to prevent a premature reaction with group B.

Currently, there are only two classes of dendrimers that are provided commercially, namely PAMAM polyamidoamine[3] and PPI polypropyleneimine.[4]

This class of polymers has received considerable attention, with the possibility for many applications in the encapsulation of substances,[5,6] "host-guest" systems,[7] catalyst systems,[8–10] liquid crystals,[11] mesoporous silicas as template,[12] due to its special structure and properties.

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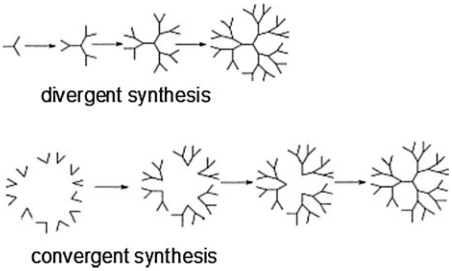

***Figure 1.***
Representative diagram of both synthesis routes commonly used in the preparation of dendrimers.

Another important feature of DAB-Am-16 is that the peripheral groups consist of $NH_2$ peripheral units and dipropylenetriamine (dpt), possibly acting as a binder for a variety of transition metals.[13–16]

Taking advantage of this important property, the objective is the immobilization of hexadecaamino poly(propylene)imine in the 3-chloropropyl silica gel (inorganic polymer). The choice of silica as support is due to its thermal and mechanical stability, in addition to the resistance to organic solvents. Both the presence of silanol groups (Si-OH), such as the area dimension and varied pores, enable obtaining chemically modified silicas with the most varied functional or inorganic groups.

The objective of this study was to prepare and characterize, by spectroscopic techniques, the DAB-Am-16 dendrimer grafted on the surface of the silica gel matrix, followed by reaction with cupric ions and then with potassium hexacyanoferrate, hence forming the hexacyanoferrate binuclear complex of copper on the silica surface. The aforementioned substance was chosen because it is electroactive and has good electrochemical stability and the ability to function as mediators of the electrons in the electrocatalysis of certain substances of biological interest, for example, L-ascorbic acid, citric acid, cysteine and N-acetylcysteine. As an application of the modified silica containing the binuclear complex, the electrocatalytic determination of nitrite was investigated.

## Experimental Part

### Materials and Methods

*Preparation of the 3-Chlopropyl Silica Gel*

All the reagents used in these syntheses were of analytical grade (p.a. Sigma-Aldrich, Merck) with water deionized using the Milli-Q Gradient model of Millipore.

The reaction of the DAB-Am-16 dendrimer with the 3-chloropropyl silica gel (SG) was performed starting from the idea that only one $NH_2$ group of the dendrimer would react with a Cl group of the silica chloropropyl. Figure 2 step (1) illustrates a schematic representation of the possible organofunctionalization for the formation of the 3-chloropropyl silica gel (SG). Step (2) illustrates a schematic representation of the dendrimer reaction with the silica gel matrix (SD).

$1.0 \times 10^{-3}$ mol of DAB-Am-16 was added to a three-mouth glass flask containing 10.0 g of 3-chloropropyl silica gel suspended in 25.0 ml of Methanol. The suspension was kept at reflux (69 °C) in a nitrogen atmosphere and stirring for 48 hours. The resulting solid was separated by a thin sintered plate funnel and washed several times with the solvent.

The solid phase was properly wrapped with a filter paper and transferred to a Soxhlet extractor and siphoned several times with dry toluene to eliminate the excess of unreacted alkoxysilanes. The resulting material was dried at 80°C and kept in a desiccator under vacuum. For the sake of brevity, the resulting material is designated SD.

*Formation of the Binuclear Complex with the Silica*

1.0 g of the modified silica (SD) was immersed in 25 mL of a solution of $1.0 \times 10^{-3}$mol $L^{-1}$ of copper ions ($CuCl_2.2H_2O$). This mixture was stirred for 30 minutes at room temperature, and then the solid phase was filtered and washed with bidistilled water. After extensive washing, the material was added to a solution containing $1.0 \times 10^{-3}$mol $L^{-1}$ of

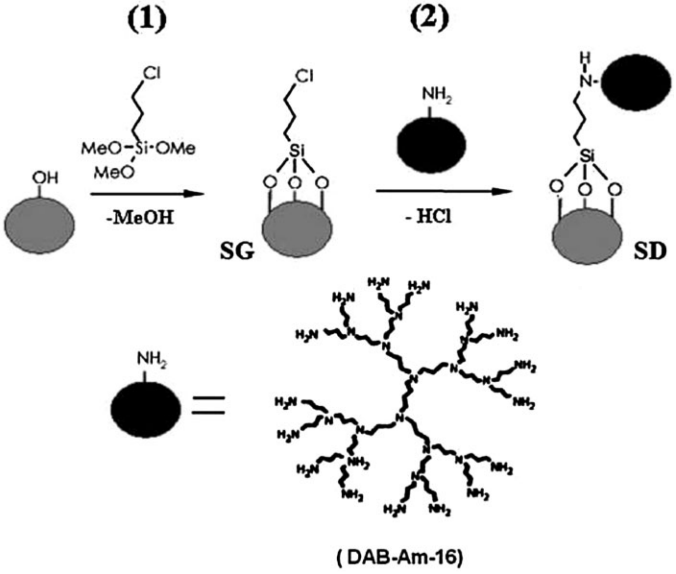

*Figure 2.*
Schematic representation of the stages in the modification process of the silica.

the potassium ferrocyanide $K_4[Fe(CN)_6]$ electroactive compound. The resulting material was washed with plenty of bidistilled water. The obtained compound was dried at 80°C for brevity, and is designated CuHCFSD.

## Results and Discussion

### Characterization Methods

*FTIR Spectroscopy*

The spectra in the infrared region were obtained using a Nicolet 5DXB FTIR spectrophotometer (Nicolet Instruments, Madison, WI). Approximately 150 mg of KBr (crystalline, spectroscopic grade of International Crystal Laboratories) was mixed with sample (1.0% w/w). 64 "sweeps" were collected for each sample with a resolution of 4 $cm^{-1}$. The presence of two bands at 2808 and 2944 $cm^{-1}$ both the $\nu$(CH), displaced by 46 and 11 $cm^{-1}$ for those found was assigned to the precursor SG. The largest displacement is depicted in Figure 3. Figure 3 illustrates the presence of two bands, when compared with the infrared spectrum of the silica gel (Figure 3A), located in the frequency of 2854 and 2955 $cm^{-1}$. The first two were ascribed to the symmetric stretching $\nu_s$(C-H). In the SD these two bands are displaced by 46 and 11 $cm^{-1}$, when compared to those found by the SG precursor, in addition to their very

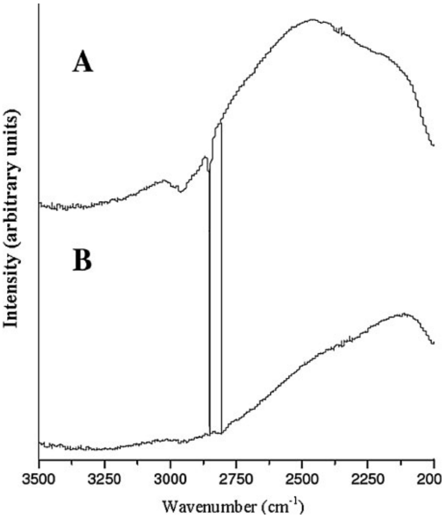

*Figure 3.*
Spectrum in the Infrared region of A) SG and B) SD.

low intensities. In the 3000-2950 cm$^{-1}$ region there is a weak band ascribed to the -$CH_2$ group and another weak band ascribed to the symmetric angular deformation in the Si-$CH_2$[17] group.

The infrared spectrum of the composite (CuHCFSD) obtained exhibited a band at 2090 cm$^{-1}$, ascribed to the stretching $\nu$(C≡N) characteristic of copper hexacyanoferrate [18] and a band at 1108 cm$^{-1}$ ascribed to the stretching $\nu$(Si-O-Si) characteristic of SG precursor as shown in Figure 4.

### NMR in the Solid State

The magnetic resonance spectra of $^{29}$Si (59.6 MHz) and $^{13}$C (75.4 MHz) were obtained using an INOVA 300-Varian spectrophotometer with a zirconia rotor. The experiment with $^{29}$Si was performed using an acquisition time of 0.005, a pulse of 84.4°, with 156 replications, a rotation rate of 2300 and a mean time of 2h. The $^{13}$C was carried out using an acquisition time of 0.0050 s, pulse of 28.4°, with 13,300 replications, a rotation rate of 6000 and mean time of 15h.

The NMR of $^{29}$Si of 3-chloropropyl silica gel (SG) showed 3 peaks at -76.48, -103.32, -111.51 ppm, as shown in Figure 5. The peak at -76.48 ppm was ascribed to $Si(OSi)_3(R)$ where R is the organic group of chloropropyltrimethoxysilane. The other two resonances at -103.32 ppm and -111.51 ppm were ascribed to units $Q_3$ [$Si(OSi)_3(OH)$] and $Q_4$ [$Si(OSi)_4$] that are present in the silica, respectively.

The NMR of $^{13}$C of SG presented 4 types of very well defined resonance peaks at 10.18, 26.52, 46.27 and 49.99 ppm. The peaks at 10.18, 26.52 and 46.27 ppm were ascribed to carbons (C1), (C2) and (C3) in $(\text{-O-Si})_3SiCH_2(1)CH_2(2)CH_2(3)Cl$. The peak at 49.99 ppm was ascribed to the methoxy group [17] as shown in Figure 6.

In the composite SD there is a single string of chains or segments -$CH_2$-$CH_2$-$CH_2$- for each generation that is isolated from each other by a trivalent nitrogen atom. The existence of numerous resonances with very close chemical shifts is due to the groups -$CH_2$-$CH_2$-$CH_2$- of each generation of dendrimer. These resonances in the solid state can undergo superposition, widening and even show coinciding signs with that reported by the SG matrix.[20] In accordance with the experimental conditions related to the sensitivity of the device,

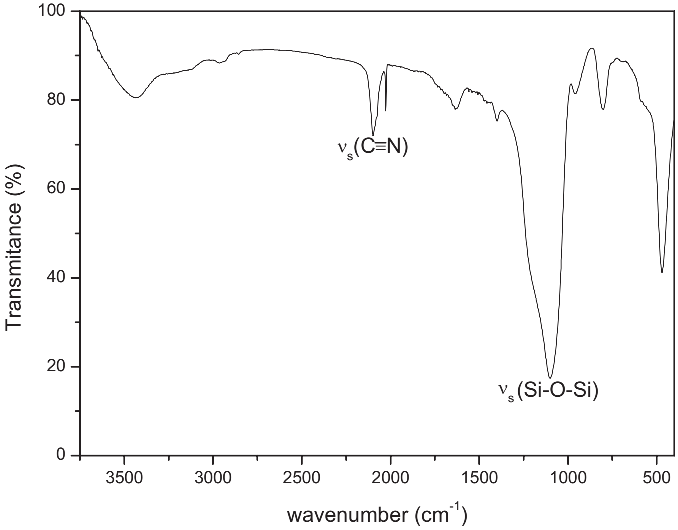

**Figure 4.**
Spectrum in the Infrared region of CuHCFSD.

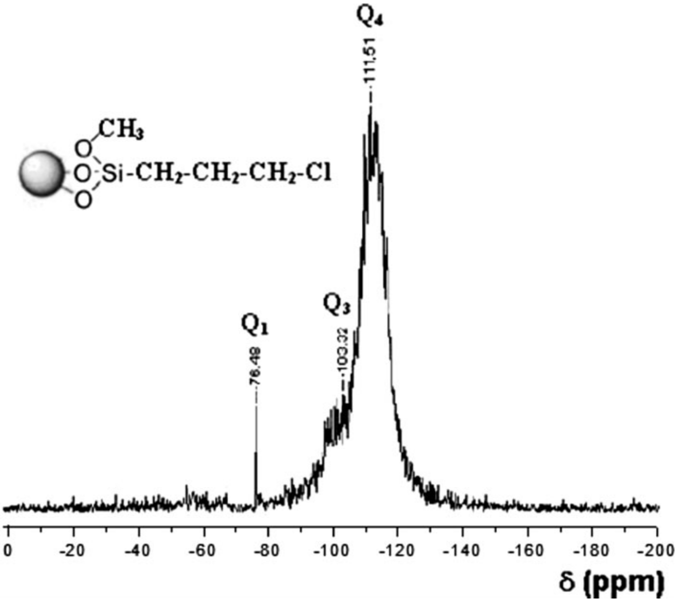

***Figure 5.***
NMR Spectrum of $^{29}$Si in the solid state for SG.

the attributions were ascribed in agreement with the literature[20] and the resonances obtained are illustrated in Figure 7, where the asterisks (*) were tentatively ascribed to each one in agreement with the dendritic structure presented in this same Figure.

In the NMR of $^{13}$C shown in Figure 7, the carbon 3 (C3) is exactly the coordination site of the chemical bond between the dendrimer and the functionalized silica (see Figure 6), whose resonance peak was shifted to higher magnetic fields.

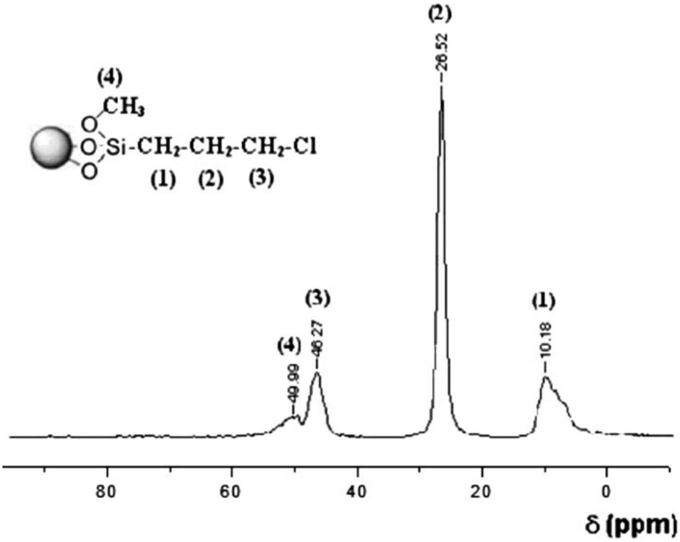

***Figure 6.***
NMR spectrum of $^{13}$C in the solid state for SG.

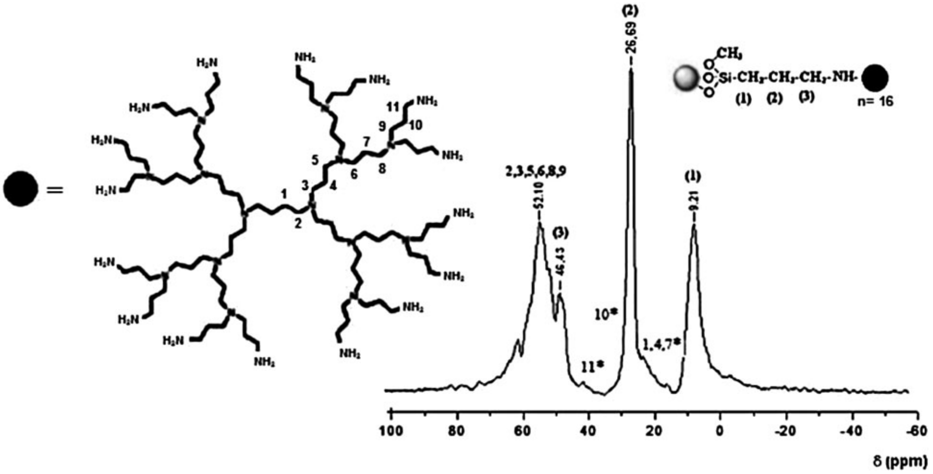

***Figure 7.***
NMR spectrum of $^{13}C$ in the solid state for SD.

The NMR of $^{29}Si$ of the SD, shown in Figure 8, showed 3 peaks at -78.48, -100.65, -112.33 ppm. The first was ascribed to the units $Si(OSi)_3(R)$ where R is the organic group, the other two peaks were ascribed to the $Q_3$ species $[(Si(OSi)_3(OH)]$ and $Q_4$ $[Si(OSi)_4]$, respectively, which showed a small shift that can be ascribed to a possible effect of magnetic susceptibility produced by the dendrimer molecule [19].

*Energy Dispersive X-Ray (EDX)*

The EDX was performed in a Jeol JTSM T-330 electron microscope. The samples, of a thickness of about 20 to 30 nm, were metallized in a BAL-TEC SCD 050 metal-

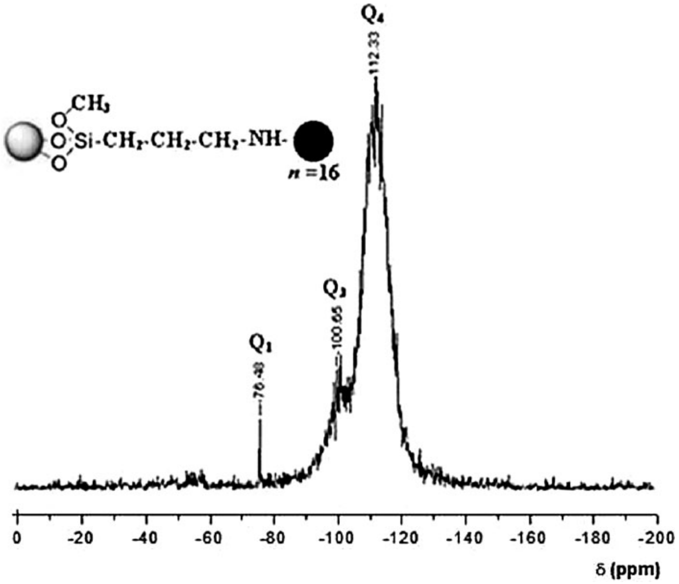

***Figure 8.***
NMR spectrum of $^{29}Si$ in the solid state for SD.

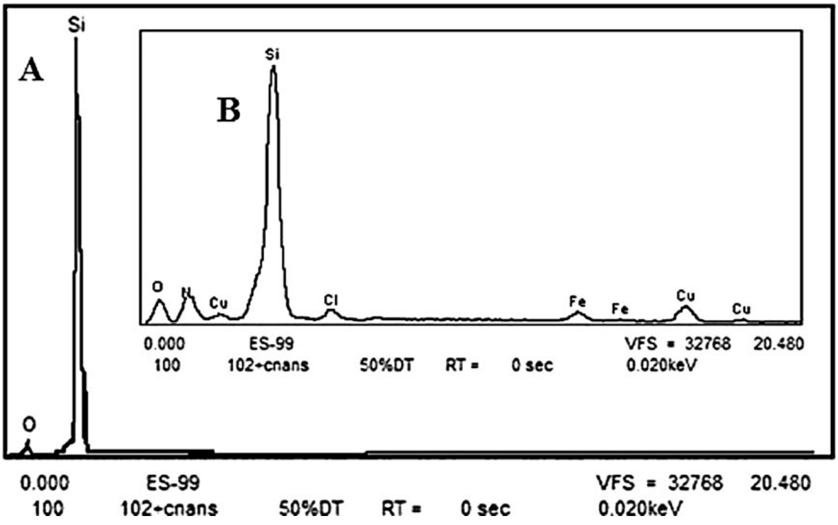

*Figure 9.*
Energy Dispersive X-ray (EDX) analysis: of A) SD and B) CuHCFSD.

lizer, for 120 s. Figure 9 presents the EDX for the A) SD and B) CuHCFSD. The absence of chlorine can be observed in this analysis, however, in the EDX of CuHCFSD it clear a presence of chlorine and copper, due the used copper chlorine in the reaction with SD. It was also detected iron, which makes clear the formation of copper hexacyanoferrate with dendrimer supported on the silica gel surface.

The composite CuHCFSD was also characterized by cyclic voltammetry using an electrode carbon paste containing the modified silica (20% m/m). The electro-

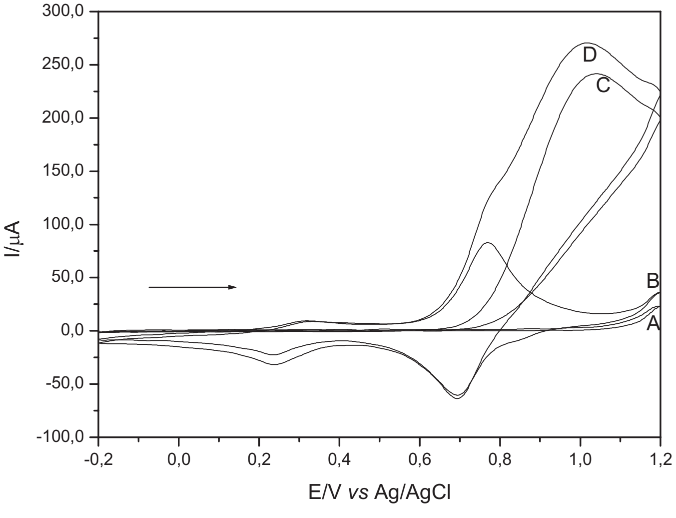

*Figure 10.*
Cyclic voltammogram of the graphite paste electrode: A) graphite paste without modifier; B) graphite paste with dendrimer modified silica, C) graphite paste without dendrimer modified silica + sodium nitrite; D) graphite paste with dendrimer modified silica + nitrite sodium (nitrite $=5.0 \times 10^{-4}$ mol $L^{-1}$; KCl 1.0 mol $L^{-1}$; pH 7; $v = 40$ mV $s^{-1}$).

chemical studies were performed on a scale ranging from -0.1 to 1.2 V (*vs* Ag/AgCl). The cyclic voltammogram of CuHCFSD exhibited two redox pairs (Figure 10B) with a mean potential (Em); $(Em)_1 = 0.28$ V and $(Em)_2 = 0.72$ V *vs* Ag/AgCl (KCl =1.0 $molL^{-1}$; $v = 40$ $mVs^{-1}$) ascribed to the redox processes $Cu^{(I)}/Cu^{(II)}$ and $Fe^{(II)}(CN)_6$ / $Fe^{(III)}(CN)_6$, respectively. Recent tests have shown that this electrode can be used in the detection of millimolar concentrations of Nitrite, as shown in the voltammogram inserted in Figure 10D. Figure 10 displays cyclic voltammograms of CuHCFSD in absence (curve B) and presence (curve D) of nitrite. The carbon paste electrode displays no redox peaks in the potencial range from -0.2 to 1.2 in abcense of nitrite (curve A), but exhibit an oxidation peak at 0.76 V (see curve C). After the addition of nitrite, a substantial enhancement of the anodic peak current is observed (curve D). The anodic peak current increased in proportion to the analyte concentration. This increase in anodic current indicates a moderade electrocatalytic oxidation of nitrite by CuHCFSD. The Fe(III) produced during the anodic scan chemically oxidizes these compounds while it is reduced to the Fe(II), which will be again oxidized to the Fe(III) electrochemically. The electrochemical oxidation of nitrite can be written as proposed by Guidelli e Casella.[21,22]

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad (1)$$

And the proposed catalytic process at interface electrolyte solution at 0.76 V can be described as:

$$\begin{aligned} & Cu^{II}[Fe^{III}(CN)_6] + NO_2^- + H_2O \\ & \rightarrow NO_3^- + 2H^+ + e^- \\ & + Cu^{II}[Fe^{II}(CN)_6] \text{ (electrode interface)} \end{aligned} \qquad (2)$$

In addition biological substances such as cysteine, N- acetylcysteine and citric acid do not interfere in the redox process.

## Conclusion

The functionalization of 3-chloropropyl silica gel (SG) with the dendrimer Hexadecaamino Poly(propylene)imine (DAB-Am-16) was successfully carried out. The studies of FTIR, NMR in the solid state together with EDX confirm the modification of the silica with the (DAB-Am-16) dendrimer. In a two-step synthesis, the modified silica allowed forming the binuclear complex (CuHCFSD), that was also characterized by FTIR and cyclic voltammetry. The composite (CuHCFSD) obtained, proved to be very promising in its use as sensors not only for the detection of nitrite, but also for other substances of biological interest.

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