

Preparation and Voltammetric Behavior of a Hybrid Silsesquioxane Chemically Modified with 4-amino-5-(4-pyridyl)-4H-1,2,4-triazole-3-thiol (APTT) and Copper Hexacyanoferrate(III): A Sensor of Nitrite.

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The hybrid materials properties are different from those displayed by their precursors, and new properties (e.g., electrical, magnetic) are acquired resulting from the synergy between organic and inorganic components. In this context a wide variety of building blocks of inorganic and organic hybrids are now available [1]. Among the hybrid materials, the new class of inorganic-organic silica based, called of silsesquioxanes offer many applications in different field, that is extremamly described in recent review [2]. This work describes the preparation, and voltammetric behavior and application of a hybrid nanocomposite (CuHSA) formed by octa(3-chloropropyl)octasilsesquioxane (S) functionalized with 4-amino-5-(4-pyridyl)-4H-1,2,4-triazole-3-thiol (APTT) (SA). For the synthesis of octa(3-chloropropyl)silsesquioxane (S) and functionalization with APTT an analogue procedure described in the literature with any modifications was followed [3].

The preparation of hybrid silsesquioxane was carried out by two stages. At the first stage, the SA adsorbs Cu^{2+} and the second step the composite formed (CuSA) reacts with hexacyanoferrate forming a new composite (CuHSA). The precursors and CuHSA were initially characterized by Fourier transform infrared spectra (FTIR) and Scanning Electron Microscopy (SEM) and cyclic voltammetry.

The cyclic voltammogram of the modified electrode containing CuHSA showed only one redox pair with $E^{0'} = 0.75 \text{ V}$ attributed to the redox process of the $\text{Fe}^{\text{II}}(\text{CN})_6/\text{Fe}^{\text{III}}(\text{CN})_6$ in the presence of binuclear complex formed. After rigorous voltammetric studies, such as : influence of different electrolyte support, concentration, pH and scan rate the composite was tested in the electrocatalytic determination of sodium nitrite. Figure 1 illustrates the voltammetric behavior of the graphite paste electrode modified with CuHSA for the electro-oxidation of nitrite in 1.0 mol L^{-1} KCl.

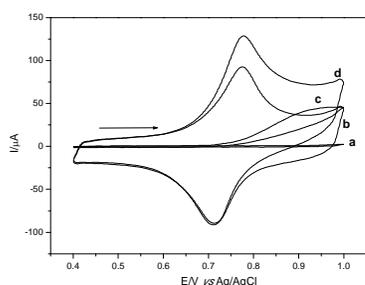


Figure 1. Cyclic voltammograms: a) of the graphite paste electrode, b) of the graphite paste electrode modified with CuHSA, c) of the graphite paste electrode in $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of sodium nitrite, d) of the graphite paste electrode modified with CuHSA in $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of nitrite ($\text{KCl } 1.0 \text{ mol L}^{-1}$; $\nu = 20 \text{ mV s}^{-1}$; pH 7.0; 20%(w/w)).

Figure 1 also illustrates that anodic current increase is proportional to the increasing concentration of nitrite and this intensity increase of anodic current clearly shows the electrocatalytic

oxidation of sodium nitrite by CuHSA.

The graphite paste electrode in a solution of $\text{KCl } 1.0 \text{ mol L}^{-1}$ in the absence and presence of nitrite did not show a redox pair in the potential range studied between 0.4 and 1.0 V (curve a and b, respectively). After the addition of nitrite there was an increase in the anodic peak intensity (curve d) when compared with the graphite paste electrode modified with CuHSA (curve c). There was an increase in the anodic current intensity of the peak at 0.77 V and a small shift to more negative potentials as showed by Figure 2.

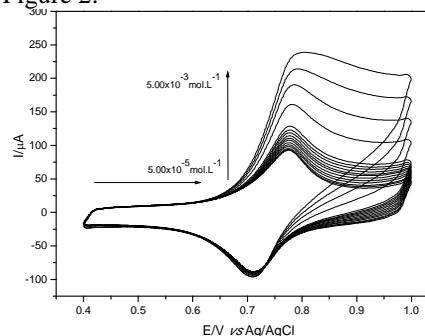


Figure 2. Cyclic voltammograms of the applications of varying concentrations of nitrite using graphite paste electrode modified with CuHSA ($\text{KCl } 1.0 \text{ mol L}^{-1}$; $\nu = 20 \text{ mV s}^{-1}$; pH 7.0; 20% (w/w)).

Figure 3 illustrates the analytical curve of the sodium nitrite concentration as a function of anodic current for the peak. The modified electrode showed a linear response of 1.0×10^{-5} to $5.0 \times 10^{-3} \text{ mol L}^{-1}$ and an equation corresponding to $Y(\mu\text{A}) = 76.51 + 30.005$ [sodium nitrite] with a correlation coefficient of $r = 0.997$. The method has a detection limit of $3.57 \times 10^{-4} \text{ mol L}^{-1}$, standard deviation of 1.5% for $n=3$ with an amperometric sensitivity $30.00 \text{ mA/mol L}^{-1}$ to nitrite. The modified electrodes were stable during all studies. The reproducibility was satisfactory for the investigated concentration range (RSD 2.3%) for nitrite.

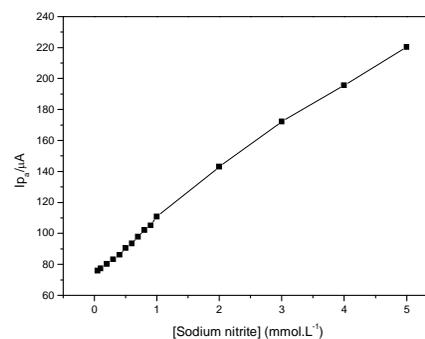


Figure 3. Analytical curve of the anodic peak for the determination of sodium nitrite using graphite paste electrode modified with CuHSA ($\text{KCl } 1.0 \text{ mol L}^{-1}$; $\nu = 20 \text{ mV s}^{-1}$; pH 7.0; 20%(w/w)).

Acknowledgements

The authors are grateful for Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - Procs. 2012/05438-1 and 2012/11306-0).

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