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Carbon nanotubes and cubic silsesquioxanes nanohybrids as a new potential platform for dipyrone sensing

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ABSTRACT

This study reports the synthesis, characterization, and electroanalytical application of a nanohybrid platform based on carboxylated carbon nanotubes functionalized with octa(aminopropyl)silsesquioxane and copper(II) hexacyanoferrate(III) for dipyrone determination. The material, designated CNTmSCuH, was prepared through the coordination of Cu²⁺ ions onto the silsesquioxane-modified carbon nanotube surface, followed by reaction with hexacyanoferrate(III). Structural and surface characterization by FTIR-ATR, TEM, XPS, and N₂ physisorption confirmed the successful formation of the bimetallic complex, the presence of cubic nanostructures, Cu/Fe species, and mesoporous features. When incorporated into a graphite paste electrode, the CNTmSCuH/CPE exhibited well-defined electrochemical behavior associated with the Fe²⁺/Fe³⁺ redox couple and favorable stability under optimized conditions. The modified electrode showed electrocatalytic activity toward dipyrone oxidation, shifting the oxidation potential to lower values compared with the unmodified electrode. Under optimized conditions using 1.0 mol L⁻¹ KCl at pH 7.0 and a scan rate of 20 mV s⁻¹, the sensor presented a linear response from 5.0 × 10⁻⁴ to 5.0 × 10⁻³ mol L⁻¹ and a detection limit of 5.69 × 10⁻⁴ mol L⁻¹. The platform was successfully applied to commercial pharmaceutical samples by the standard addition method, demonstrating its potential for dipyrone sensing.

KEYWORDS: Copper (II) Hexacyanoferrate, Silsesquioxane, Dypirone, nanocomposite, electrocatalysis

1. INTRODUCTION

Silsesquioxanes are interesting materials for diverse fields because of their nanostructure and the possibility of modifying the properties of their functional groups[1]. In this context, these nanostructured materials have the general formula $(\text{RSiO}_{3/2})_n$, where R may represent a functional group or hydrogen[2, 3]. Furthermore, the inorganic-organic nature of silsesquioxanes enables their interaction with and immobilization on various substrates [4]. Among the many applications, POSS has been used flame retardant [5], liquid crystal devices[6], surface modifiers [7], catalysis and electrocatalysis [8, 9], coatings [10], adsorbents[11] among others.

From the perspective of electrocatalysis and sensing, silsesquioxanes have emerged as promising precursors due to their ability to interact with a wide variety of groups, thereby enabling numerous analytical applications [12]. In addition, silsesquioxanes exhibit several attractive properties, including high chemical and thermal stability, as well as biocompatibility [4]. Typical POSS monomers have a cubic octameric framework with eight organic groups at their corners, one or more of which may be reactive or polymerizable[13–15].

In this sense, CNTs are cylindrical macromolecules consisting of a hexagonal arrangement of sp^2 -hybridized carbon atoms and are suitable for sensing applications because they exhibit high thermal stability and excellent electronic properties, electrical conductivity, high surface area, and mechanical strength[16]. Additionally, CNTs can undergo a wide range of chemical modifications, allowing the introduction of functional groups such as hydroxyl, aldehyde, ketone, carboxylic acid, and amine groups, among others [17, 18].

The peripheral groups of the silsesquioxane can interact with the carboxylic and carbonyl groups present on the surface of carboxylated carbon nanotubes. These peripheral groups also enable the coordination of metal ions, acting as chelating sites and subsequently forming metallodendrimers. The reaction of these metallodendrimers with hexacyanoferrate(III) leads to the formation of electroactive materials, making them suitable for use in electrochemical sensors to detect target compounds[19].

Dipyrone (DP), or metamizole, is an analgesic and antipyretic drug with a limited anti-inflammatory effect, used in some countries because of its therapeutic effects and low toxicity. When used orally, DP is converted into several metabolites, including 4-methylaminoantipyrine (MAA) and 4-aminoantipyrine (AA). Its analgesic mechanism is not entirely understood because of the involvement of its metabolites [20, 21]. In the early 1970s, dipyrone began to be banned due to studies that correlated its use with cases of agranulocytosis, which led to the prohibition of this medication in several countries around the world [22]. In this context, a recent Brazilian study showed, based on a literature analysis, that this relationship is not fully justified and that further studies should be conducted to substantiate such prohibitions [23].

Regardless of the context presented, the detection and quantification of dipyrone are extremely important, both in situations where it is considered a contaminant and in those where analytical methods are intended for its quality control. Its determination can be carried out using ultra-high-performance liquid chromatography [24–26], thin-layer chromatography [27], spectrophotometry [28], and electrochemical sensors [9, 12]. In addition, several materials have been developed for the removal of this compound from different matrices [29–31].

In this context, the present study aims to synthesize and characterize a nanohybrid compound based on carboxylated carbon nanotubes functionalized with octa(aminopropyl)silsesquioxane, followed by the formation of copper(II) hexacyanoferrate(III), and to investigate its potential application as an electrocatalyst for the electrochemical determination of dipyrone in commercial pharmaceutical samples using cyclic voltammetry.

2. EXPERIMENTAL SECTION

2.1. Preparation of bimetallic complex on the NTCmS Surface.

The carboxylation process of carbon nanotubes was carried out according to methodologies reported in the literature[19] for the formation of CNTm. The synthesis of oct(aminopropyl)silsesquioxane hydrochloride salt (S) was carried out according to the methodology proposed by Feher et al.[32]. In this context, CNTmS was obtained in two steps. The first step was the neutralization of S, in which 0.5 g of S and 1.157 g NaHCO_3 (Synth, 99.7–100.7%) were dissolved in 25 mL of water and kept under stirring for 60h. In the second step, 1.0g of CNTm and 50 mg of dicyclohexylcarbodiimide (DCC) (Sigma-Aldrich, 99%) were added and refluxed with S for 24 h. This mixture was filtered and washed with water. The product obtained was designated as CNTmS.

Consequently, 0.5 g of NTCmS was added to 25 mL of a $1.0 \times 10^{-2} \text{ mol L}^{-1}$ CuCl_2 solution (Sigma-Aldrich, $\geq 98\%$) and the suspension was stirred for 2 h. The solid was collected by filtration, washed, dried at 60°C and labeled CNTmSCu. Finally, the CNTmSCu was stirred with 25 mL of a $1.0 \times 10^{-2} \text{ mol L}^{-1}$ potassium hexacyanoferrate (III) solution (Sigma-Aldrich, $\geq 98\%$) for 2 h. The product CNTmSCuH, is the solid phase obtained by filtration, washed, dried and stored in a desiccator with light protection.

2.2. Characterization

The CNTmSCuH was characterized by FTIR-ATR, TEM, XPS and BET analyzer. The Infrared spectra were recorded using a Perkin-Elmer FT-IR/ATR spectrometer. The measurements were performed with 64 scans at a resolution of $\pm 4 \text{ cm}^{-1}$, covering the spectral range from 4000 to 600 cm^{-1} . The Transmission Electron Microscopy images were obtained using the JEOL JEM-1400 Flash microscope (FAPESP Multi-User Equipment Program (EMU) (Process:2022/11494-3) at the Multi-User Electron Microscopy Laboratory of FMRP-USP. X-ray photoelectron spectroscopy (XPS) analysis was performed using a UNI-SPECS ultra-high vacuum (UHV) (Process: 2013/07296-2) surface analysis system (Berlin, Germany). Surface area and porosity measurements were conducted using nitrogen adsorption isotherms at liquid nitrogen temperature (77 K), analyzed with a Micromeritics ASAP 2010 pore analyzer. The specific surface area (SBET) was determined using the Brunauer–Emmett–Teller (BET) method.

2.3. Electrochemical measurements

The electrochemical measurements were performed using a three-electrode configuration, with a graphite paste electrode modified with 20% (w/w) CNTmSCuH (labeled as CNTmSCuH/CPE) as the working electrode, a platinum electrode as the auxiliary electrode, and an Ag/AgCl (saturated) reference electrode. The measurements were

carried out using an Autolab PGSTAT302N potentiostat/galvanostat controlled by NOVA software. The electrochemical system was optimized by evaluating the effects of the supporting electrolyte, its concentration, pH, and scan rate on the electrochemical parameters.

The electrochemical behavior of DP was investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with successive aliquot additions. In this context, CV was performed within a potential window from -0.2 V to 1.1 V at a scan rate of 20 mV s^{-1} , whereas EIS measurements were performed at an Edc of -0.2 V and an Eac of 10 mV over a frequency range from 1×10^4 to $1 \times 10^{-2} \text{ Hz}$.

The applicability of the CNTmSCuH/CPE for DP determination in real samples was evaluated using commercial pharmaceutical formulations and the standard addition method. Appropriate aliquots of each sample were introduced into an electrochemical cell containing 20 mL of $1.0 \text{ mol L}^{-1} \text{ KCl}$ to obtain an initial DP concentration of $1.0 \times 10^{-3} \text{ mol L}^{-1}$. Subsequently, successive $500 \mu\text{L}$ aliquots of a standard DP solution were added to the electrochemical cell, and the analytical response was recorded after each addition.

3. RESULTS AND DISCUSSION

3.1. Vibrational Spectroscopy

The vibrational spectroscopy was performed by the FT-IR/ATR spectra of the formation of bimetallic complexes on the surface of CNTmS (Fig. 1). In both spectra, characteristic bands of hydroxyl groups (νOH) at $3500\text{--}3750 \text{ cm}^{-1}$, originating from functional groups on the CNT and/or water incorporated into the lattices[33], are observed.

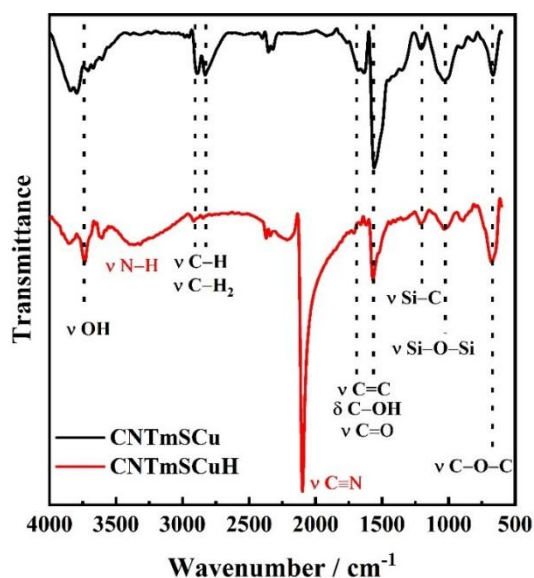


Figure 1 - FT-IR/ATR spectrum of CNTmSCu(–) and CNTmSCuH (–)

Thereafter, the bands at 2985 and 2865 cm^{-1} are associated with the CH_2 and CH_3 groups ($\nu_{\text{C-H}}$) of the CNT structures and ramifications of S[19, 34, 35]. The region between 1800 and 1600 cm^{-1} presents overlapping bands

corresponding to the respective precursors, such as the $\nu_{\text{C=O}}$ band at 1750 cm^{-1} of carbonyl groups and shoulders indicating C–OH bonds[19, 33, 34]. The band at 1550 cm^{-1} could be attributed to $\delta_{\text{N-H}}$ of the terminal groups of S[35, 36] and to the vibrational mode $\nu_{\text{C=C}}$ of the hexagonal skeleton of the nanotube walls [33]. The vibrational modes at 1100 , 1275 , and 770 cm^{-1} are assigned to $\nu_{\text{Si-O-Si}}$ and $\nu_{\text{Si-C}}$ vibrations of the inorganic core of S [35–38]. At 600 cm^{-1} , the $\nu_{\text{C-O-C}}$ vibration of ether groups is shown.

The band at 2095 cm^{-1} is characteristic of the vibrational mode $\nu_{\text{C}\equiv\text{N}}$, corresponding to copper (II) hexacyanoferrate (III). This confirms the efficiency of the functionalization of CNTmSCuH from NTCmSCu. Furthermore, CNTmSCuH presented a band assigned to $\nu_{\text{N-H}}$ at 3100 cm^{-1} , which is related to the formed product[19, 39–41].

3.2. Morphological characterization

Transmission electron microscopy (TEM) micrographs of CNTmSCu (A) and CNTmSCuH (B) are shown in Fig. 2. In Fig. 2A, a tangled CNT structure is observed, with S indicated by small spherical structures. In this image, it can be observed that Cu^{2+} adsorption does not cause any structural or morphological changes in CNTmS. In contrast, the formation of copper (II) hexacyanoferrate (III) (Fig. 2B) reveals new cubic structures that differ from the spherical structures of S. These new structures have a diameter of $38.16 \pm 9.89\text{ nm}$ and are associated with S at multiple points, indicating that there is a synergistic interaction between these compounds.

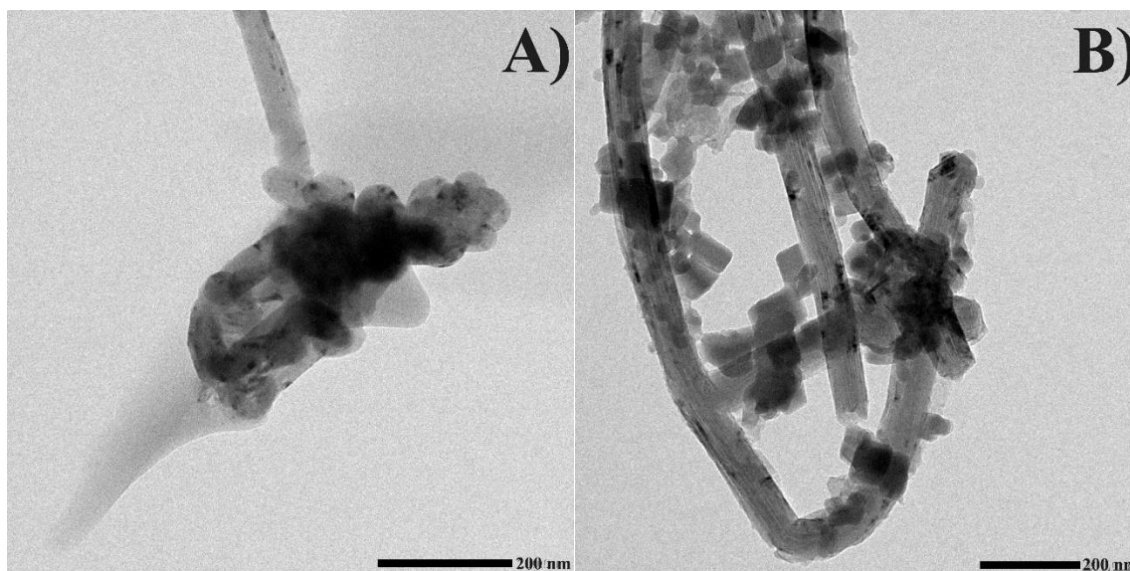


Figure 2 – TEM of A) NTCmSCu and B) NTCmSCuH

3.3. Surface Chemical Composition and Oxidation States of CNTmSCuH

The semi-quantitative XPS technique was used to determine the composition and oxidation states of the metallic elements present in NTCmSCu and NTCmSCuH. Fig. 3 shows the survey spectrum (Fig. 3A) and the high-resolution

spectra for NTCmSCuH, which revealed the presence of Si, C, O, N, Fe, and Cu. The semi-quantitative analysis and the elemental composition of each sample are presented in Table 1.

Table 1 - XPS peak binding energy assignments and functional groups for NTCmSCuH

Element	CNTmSCu	Binding Energy		CNTmSCuH	Binding Energy	
Si 2p	4.0%	102.4 eV	Si-C	2.8%	102.5 eV	Si-C
		103.2 eV	Si-O		103.4 eV	Si-O
C 1s	78.5%	284.8 eV	C-C, C=C, C-H	80.9%	284.8 eV	C-C, C=C, C-H
		285.6 eV	C-OH		285.4 eV	C-OH
		286.6 eV	C-O-C		286.2 eV	C-O-C
		288.0 eV	C=O		287.0 eV	C-O
		288.8 eV	O=C-OH, O-C=O		288.3 eV	C=O
					289.2 eV	O=C-OH, O-C=O
O 1s	14.6%	531.8 eV	Si-O, Cu-O	11.1%	531.3 eV	Si-O, Cu-O, Fe-O
		532.4 eV	C=O		532.5 eV	C=O
		533.4 eV	C-OH		533.8 eV	C-OH
N 1s	2.8%	400.4 eV	N-(C=O)-O, Imide	4.6%	398.4 eV	C=N-C, Imine
		401.9 eV	C-NH ₃		400.3 eV	N-(C=O)-O, Imide
					402.1 eV	C-NH ₃
Fe 2p				0.20%	708.7 eV	Fe2p _{3/2} (Fe ²⁺)
					721.6 eV	Fe2p _{1/2} (Fe ²⁺)
					710.2 eV	Fe2p _{3/2} (Fe ³⁺)
					723.8 eV	Fe2p _{1/2} (Fe ³⁺)
Cu 2p (Cu ²⁺ /Cu ⁺)	0.5%	934.8 eV	Cu 2p _{3/2} (Cu ²⁺)	0.33%	936.4 eV	Cu 2p _{3/2} (Cu ²⁺)
		954.7 eV	Cu 2p _{1/2} (Cu ²⁺)		955.1 eV	Cu 2p _{1/2} (Cu ²⁺)
		942.8 eV	Satellite		933.0 eV	Cu 2p _{3/2} (Cu ⁺)
		963.3 eV	Satellite		953.7 eV	Cu 2p _{1/2} (Cu ⁺)
					942.8 eV	Satellite
					963.3 eV	Satellite

The Si 2p spectrum (Fig. 3B) revealed two distinct components: the Si-C bond, corresponding to the propyl groups of S, and the Si-O bond of the cage structure (T8) of the inorganic core [36, 42]. In this context, the observed decrease from 4.0% to 2.8% is related to the inclusion of new functional groups during the formation of CNTmSCuH.

The C 1s spectrum (Fig. 3C) showed characteristic components between 284 and 290 eV, labeled as C-C, C=C, C-H, C-OH, C-O-C, C-O, C=O, O-C=OH, and O-C=O, originating from the structure of the S-functionalized carbon nanotubes [43–45]. The formation of the bimetallic complex led to the appearance of additional C-O groups, indicating that copper (II) hexacyanoferrate (III) also interacts with the CNTs via carbonyl or hydroxyl groups.

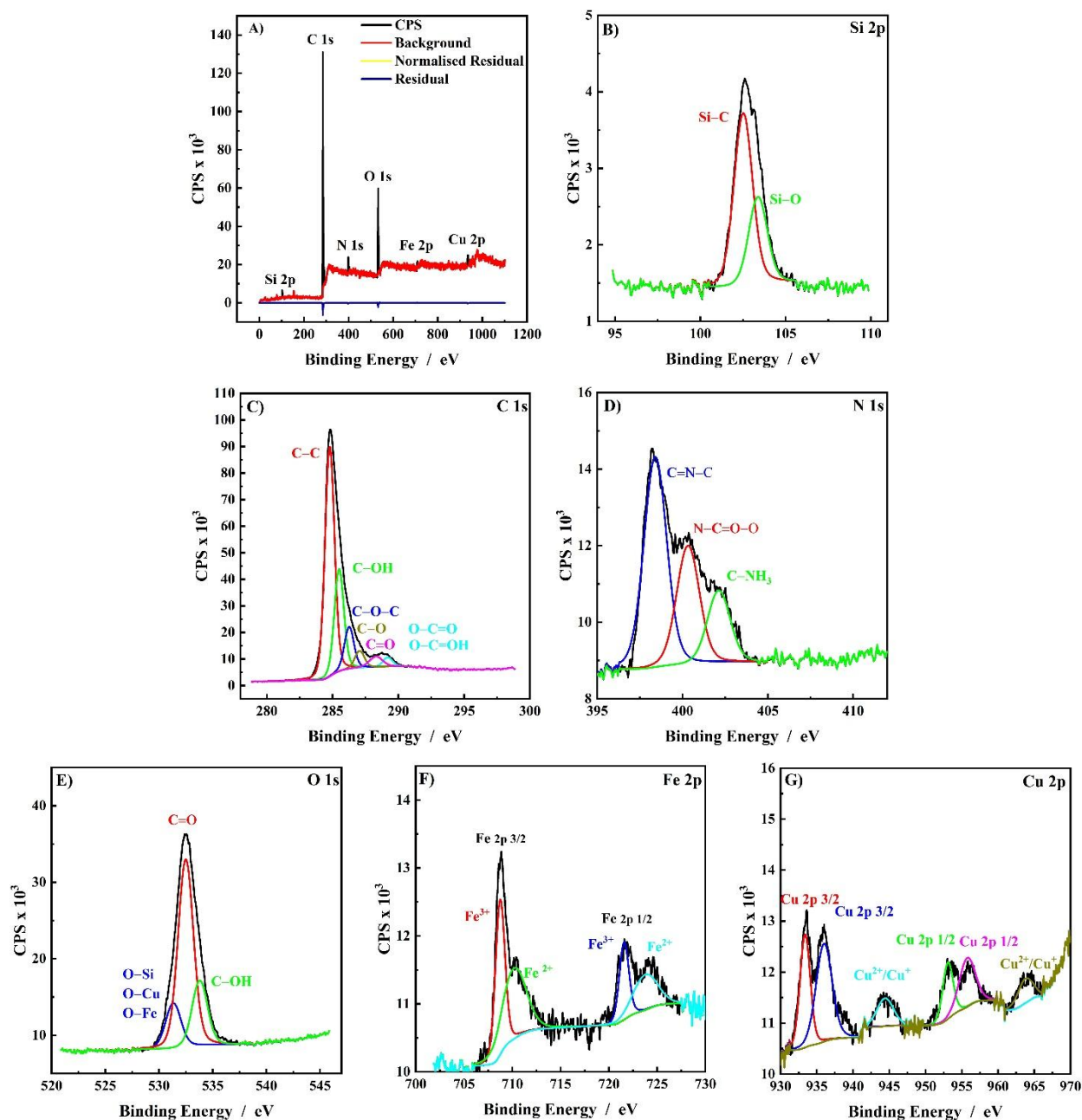


Figure 3 – XPS: A) survey spectrum, B) Si 2p, C) C 1s, D) N 1s, E) O 1s, F) Fe 2p, and G) Cu 2p for NTCmSCuH

The N 1s spectra (Fig. 3D) showed two components: C-NH₃ (401.9 eV) and C(O)-N-H (400.4 eV), corresponding to the interaction of S with the nanotubes and to the amine groups at the ends of S[36, 46]. The formation of the bimetallic complex is evidenced by the formation of imine groups, C=N=C (398.4 eV). In the O 1s spectrum (Fig. 3E), components related to metal-oxygen bonds (Si-O, Cu-O, Fe-O) are observed, in addition to carbonyl and carboxyl groups (C=O and C-OH) [19, 36, 39, 43–45].

The Fe_{2p} spectra (Fig. 3F) exhibited peaks corresponding to the $\text{Fe}_{2p\ 3/2}$ and $\text{Fe}_{2p\ 1/2}$ states, with the Fe^{3+} and Fe^{2+} oxidation states present in the $[\text{Fe}(\text{CN})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{4+}$ ions, respectively [19, 39, 47]. The Cu/Fe metal ratio was 1.65. The Cu_{2p} spectra (Fig. 3G) showed two peaks corresponding to $\text{Cu}_{2p\ 3/2}$ and $\text{Cu}_{2p\ 1/2}$ [48, 49]. The deconvolution of these peaks is linked to the Cu^+ and Cu^{2+} oxidation states, as well as to the observed satellite peaks [50].

3.4. Surface area and porosity analysis

The nitrogen adsorption–desorption measurements presented in Fig. 4 for CNTmSCu and CNTmSCuH exhibit Type IV isotherms [51, 52] with H3-type hysteresis loops [53]. In this context, both materials are mesoporous, with an average pore diameter of approximately 10 nm and pore sizes ranging from 2 to 100 nm. The narrow hysteresis loops observed at high relative pressures, together with a pronounced increase in the adsorbed volume, suggest that the porous structures arise from aggregates or agglomerates of particles, leading to the formation of slit-shaped pores [54–56].

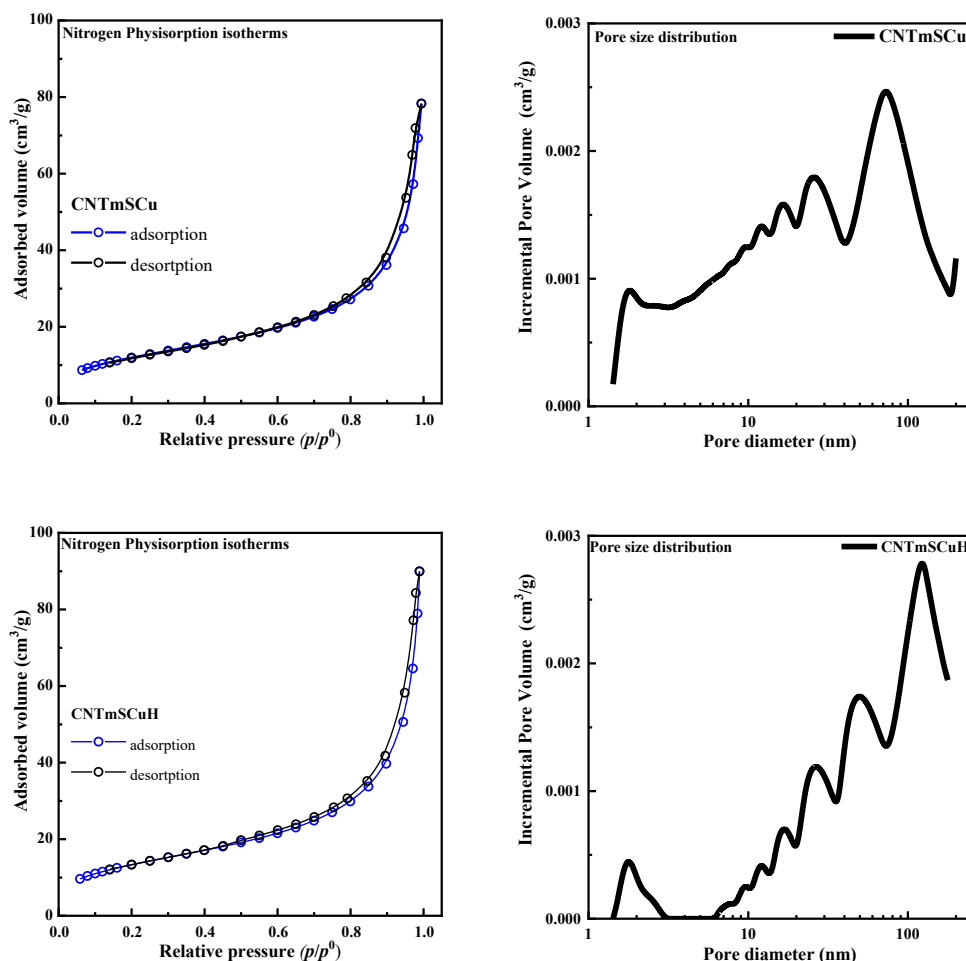


Figure 4. Nitrogen adsorption–desorption isotherms and pore size distribution graphs for: (a) CNTmSCu; (b) CNTmSCuH

BET surface area increased from 44.7 m² g⁻¹ for CNTmSCu to 49.3 m² g⁻¹ for CNTmSCuH (Table 2). These results suggest that the formation of copper(II) hexacyanoferrate(III) did not significantly block the accessible porous structure. Instead, the incorporation of the electroactive species may have promoted surface roughening or rearrangement of the particle aggregates, increasing the accessible surface and interparticle pore volume.

Table 2 – Surface analysis parameters for the CNTmSCu, CNTmSCuH samples from the nitrogen adsorption isotherms.

Sample	Surface area, S_{BET} (m ² /g)	Average pore diameter, I_p (nm)	Pore volume, V_p (cm ³ /g)
CNTmSCu	44.7	9.6	0.107
CNTmSCuH	49.3	9.9	0.122

3.5. Electrochemical optimization

The electrochemical behavior of the CNTmSCuH/CPE system is shown in Fig. 5. The voltammograms presented in Figs. 5A and 5B show the voltammetric profiles of the working electrode in different supporting electrolytes. Two distinct electrochemical processes can be identified. The first is associated to pair Cu⁺/Cu²⁺, not very well defined and a low current (~ 0.200 V)[19] and second pair (II) related to the Fe²⁺/Fe³⁺ pair ([Fe²⁺(CN)₆]⁴⁻/[Fe³⁺(CN)₆]³⁻) present in the copper(II) hexacyanoferrate complex with E^{0'} = 0.745 V (KCl 1.0 mol L⁻¹, v = 20 mV s⁻¹). Additionally, a shoulder was observed in 0.500V, that can be explained by another copper species in the nanohybrid composite.

Alkali metal cations and NH₄⁺ can intercalate into the structure of copper hexacyanoferrate to maintain charge neutrality[34, 57]. The nature of the electrolyte affects the formal potential (E^{0'}) and current intensity. In this context, the sequence of E^{0'} values were NH₄⁺ (0.800 V) > K⁺ (0.745 V) = Li⁺ (0.745 V) > Na⁺ (0.680 V). This fact can be explained by hydrated radio relations and the interstitial lattice [58]. Due to their affinity with these cations, the better response to CNTmSCuH/CPE was observed for electrolytes containing K⁺ and NH₄⁺ due to similar values for hydrated ratios[12].

Successively, the voltammogram at different KCl concentrations (1.0 x 10⁻³ to 2.0 mol L⁻¹) are presented in Fig. 5C. The increase in [K⁺] caused a shift in the formal potentials toward more positive values (from 0.687 to 0.749 V), and an increase in the current values was also observed, indicating that the observed processes are strongly related to the supporting electrolyte concentration [8, 39, 58]. By modifying the Nernst equation, a relationship can be established between E^{0'} and log[K⁺]. This relationship is presented in Fig. 5D, with the linear equation E^{0'} = 0.060 log[K⁺] + 0.747 (R² = 0.996), and the slope suggests a quasi-Nernstian process involving the transfer of one electron [19, 39]. Owing to the higher financial costs associated with higher concentrations of the supporting electrolyte, a concentration of 1.0 mol L⁻¹ KCl was chosen for the optimized conditions.

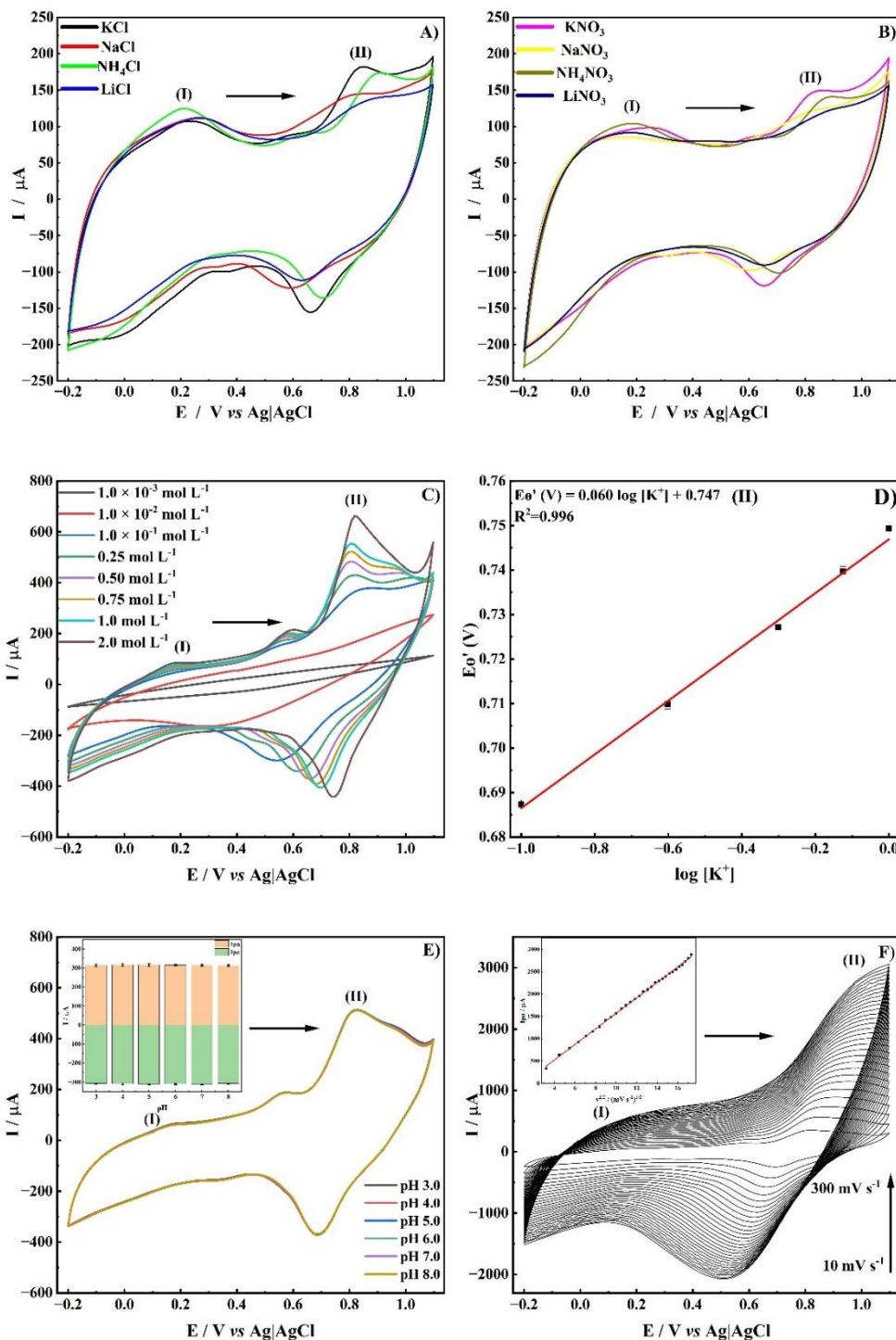


Figure 5 - Cyclic voltammograms of the CPE-CNTmSCuH electrode in different supporting electrolytes: A) chlorides and B) nitrates (1.0 mol L⁻¹, $v = 20$ mV s⁻¹). C) Voltammograms in KCl at concentrations from 0.001 to 2.0 mol L⁻¹ ($v = 20$ mV s⁻¹). D) Relationship between the mean potential (E_0') and the logarithm of K⁺ concentration E) Cyclic voltammograms at pH values from 3.0 to 8.0 (KCl 1.0 mol L⁻¹, $v = 20$ mV s⁻¹), insert: relationship between pH and I_p . F) Cyclic voltammograms varying the scan rate from 10 to 300 mV s⁻¹ in KCl 1.0 mol L⁻¹, insert: relationship between I_p and $v^{1/2}$.

The effect of pH (3.0 to 8.0) on the system was evaluated using the voltammograms shown in Fig. 5E. The $E^{\ominus'}$ for redox pair (II) remained constant at 0.745 V. The variation in pH did not increase the intensities of the cathodic or anodic peaks. The insert in Fig. 5C demonstrated good electrochemical stability of CNTmSCuH and no statistically significant contribution of pH to these responses. Based on these considerations, the pH values chosen for the next steps was pH 7.0 because the possibility of being used for electrochemical determination of pharmaceutical compounds on different medio.

The scan rate effect is presented in Fig. 5F. In this context, despite the increase in scan rate, $E^{\ominus'}$ remained close to 0.74 V; however, an increase in the separation between the oxidation and reduction peaks (ΔE_p) was observed. A linear relationship between the anodic peak current and $v^{1/2}$ was observed, indicating that the process is *quasi-reversible* and diffusion controlled [19]. In this sense, the voltammogram obtained at a scan rate of 20 mV s⁻¹ exhibited the best voltammetric profile; therefore, this scan rate was selected as the optimal parameter for the present system.

Still considering the contribution of the scan rate, it is possible to evaluate the parameters involved in the charge-transfer process. The Laviron equation was employed to determine the charge-transfer coefficient (α) and the heterogeneous electron-transfer rate constant (k_s)[59]. The equation for anodic peak is below described (Eq. 1)

$$E_{pa} = E^{\ominus'} + \frac{2.303RT}{(1-\alpha)nF} \log \left[\frac{(1-\alpha)nFv}{RTk_s} \right] \quad (\text{Eq. 1})$$

where E_{pa} is the anodic peak potential, $E^{\ominus'}$ is the formal potential, α is the charge-transfer coefficient, k_s is the heterogeneous electron-transfer rate constant, n is the number of electrons, v is the scan rate, and R , T , and F are the gas constant, temperature, and Faraday constant, respectively. The Fig. 6 exhibits the relationship between $E^{\ominus'}$ and $\log v$. The slope of the empirical equation can be related to Eq. 2 to determine the charge-transfer coefficient. Similarly, the intercept can be correlated with Eq. 3 to determine k_s .

$$\frac{dE_{pa}}{d \log v} = \frac{2.303RT}{(1-\alpha)nF} \quad (\text{Eq. 2})$$

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log \left(\frac{RT}{nFv} \right) - \frac{\alpha(1-\alpha)nF\Delta E_p}{2.303RT} \quad (\text{Eq. 3})$$

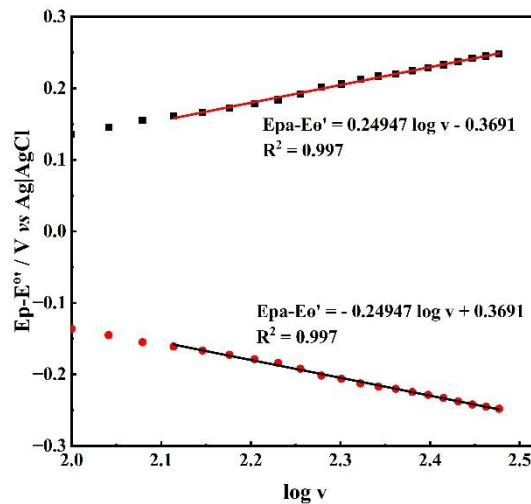


Figure 6. Dependence of the anodic and cathodic peak current intensity on the square root of the scan rate

By correlating the slope of the linear relationship between $E_{pa} - E^{\circ'}$ and $\log \nu$ with the Laviron equation, a charge-transfer coefficient (α) of 0.763 was obtained, assuming a one-electron process at 298 K. Similarly, after converting the scan rate to V s^{-1} , the intercept was used to determine the apparent heterogeneous electron-transfer rate constant (k_s), which was estimated to be 0.28 s^{-1} . These results are consistent with a quasi-reversible electron-transfer process at the CNTmSCuH/CPE interface.

3.6. Stability and reproducibility under optimization conditions

The stability of the CPE–CNTmSCuH electrode was evaluated over two-time scales, as shown in Figure 7. The first profile corresponds to the short-term behavior of the modified electrode within a single day of analysis, indicating that the electrochemical response was maintained during repeated measurements under the same experimental conditions. The second profile shows the behavior of the system over five consecutive days, demonstrating that the modified electrode preserved its response over time and suggesting adequate stability for analytical applications.

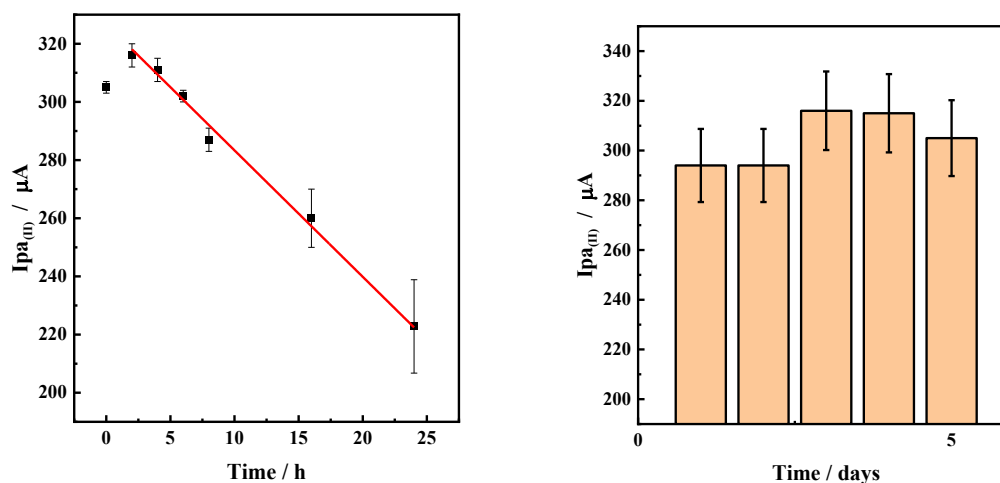


Figure 7 – Stability evaluation of the CPE–CNTmSCuH electrode: A) short-term stability assessed over one day and B) reproducibility monitored over five days.

3.7. Electrochemical behavior of CNTmSCuH/CPE under presence of DP

Under the optimized conditions ($1.0 \text{ mol L}^{-1} \text{ KCl}$, $\nu = 20 \text{ mV s}^{-1}$, pH 7.0), DP was added to the system to verify the electrocatalytic activity of CPE–CNTmSCuH. Fig. 8 shows the electrochemical behavior of the system after the addition of DP ($5 \times 10^{-3} \text{ mol L}^{-1}$).

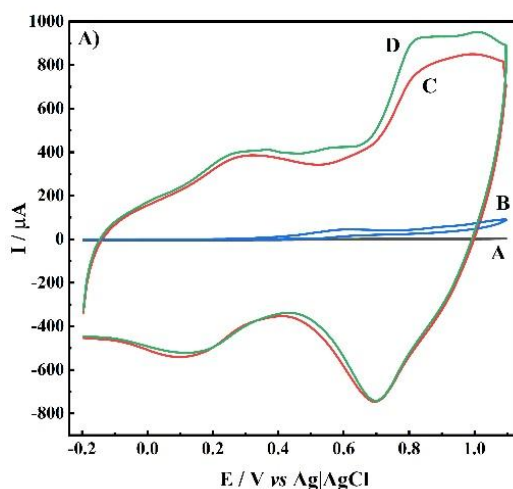


Figure 8. A) Cyclic voltammograms for detection of DP: (a) CPE; (b) CPE in the presence of 5.0×10^{-3} mol L $^{-1}$ of DP; (c) CPE–CNTmSCuH (d) CPE–CNTmSCuH in the presence of 5.0×10^{-3} mol L $^{-1}$ of DP (1.0 mol L $^{-1}$ KCl; $v = 20$ mV s $^{-1}$). B) Cyclic voltammograms for CPE–CNTmSCuH with add of 1.0×10^{-4} to 5.0×10^{-3} mol L $^{-1}$ (1.0 mol L $^{-1}$ KCl; $v = 20$ mV s $^{-1}$) C) Analytical curve of DP for the second peak of CPE–CNTmSCuH.

Voltammograms A and B (Fig. 8A) refer to the CPE electrode without the modifier, where A is the voltammogram obtained in the absence of the analyte, and B refers to the voltammogram obtained in the presence of the analyte; a characteristic peak corresponding to DP oxidation can be observed at 0.597 V. Similarly, voltammograms C and D refer to the CPE–CNTmSCuH electrode, where C is the voltammogram obtained in the absence of the analyte, and D corresponds to that obtained in the presence of the analyte. A shift in the DP oxidation potential to 0.539 V was observed, indicating that the modifier acts as an electrocatalyst for DP oxidation.

Fig. 9 presents the impedance profile of CNTmSCuH/CPE in the presence and absence of DP. The EIS response in the absence of DP reveals the charge-transfer process associated with the Fe $^{2+}$ /Fe $^{3+}$ redox couple, more specifically the reduction process, evaluated at a DC potential (E_{dc}) of -0.200 V, allowing a better evaluation of the experimental data and the subsequent construction of an equivalent circuit. Analysis of the Nyquist plot (Fig. 9A) reveals a significant decrease in the charge-transfer resistance of the system in the presence of DP, as evidenced by the reduction in the diameter of the experimentally obtained semicircle.

The series resistance (R_s) and charge-transfer resistance (R_{ct}) of the system were obtained from the high- and low-frequency plateaus of the Bode plot (Fig. 9B)[60]. In this context, the R_s value was approximately 80Ω both in the absence and presence of DP, indicating that this parameter remained unchanged. In contrast, R_{ct} decreased from 1185 to 1000Ω , corresponding to a ΔR_{ct} of 185Ω . This decrease indicates that the presence of DP facilitates charge transfer at the CNTmSCuH/CPE interface, supporting its electrocatalytic activity. Through the analysis of the imaginary components, the capacitive contribution can be described as a non-ideal capacitor, with a constant-phase exponent of 0.718 in both cases and pseudo capacitance values of 1.09 mF s $^{-1}$ before and 1.22 mF s $^{-1}$ after the addition of DP.

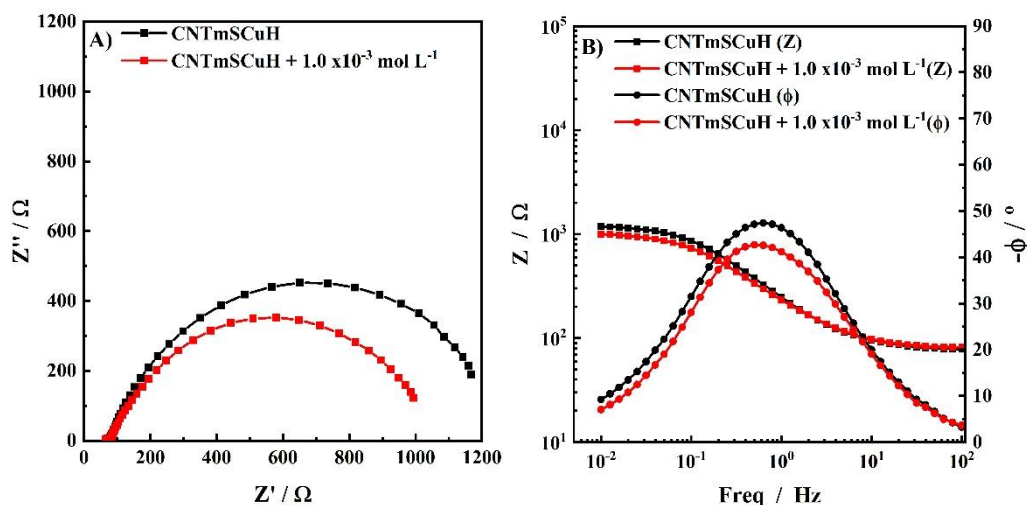
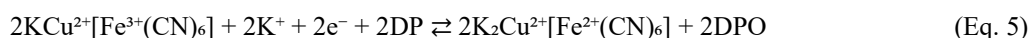
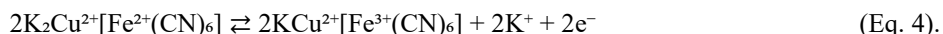


Figure 9. Electrochemical impedance spectra of CPE–CNTmSCuH in the absence and presence of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ DP: (A) Nyquist plots and (B) Bode plots of the impedance modulus (Z , square symbols) and phase angle (ϕ , circular symbols). Measurements were performed in 1.0 mol L^{-1} KCl at $EDC = -0.200 \text{ V}$

Thus, as mentioned above, the decrease in R_{ct} (Fig. 9A) in the presence of the analyte indicates the electrocatalytic effect of CNTmSCuH observed by cyclic voltammetry (Fig. 8). Therefore, a possible reaction mechanism describing the system can be proposed (Eqs. 4 and 5).



The DP oxidation process begins at the electrode surface with the adsorption of this species. From an interfacial perspective, the N_2 physisorption measurements indicate the presence of mesopores in the CNTmSCuH structure, which is consistent with the non-ideal behavior observed by EIS, as evidenced by the exponential factor of the constant-phase element (0.718). In this context, copper(II) hexacyanoferrate acts as an electron mediator, i.e., it mediates the transfer of one electron from DP to form the oxidized species, denoted as DPO in Eq. 5. To maintain the electroneutrality of the bimetallic complex structure, cations from the supporting electrolyte are intercalated into the cavities of the complex, resulting in an increase in pseudocapacitance through this process [61].

Figure 10 presents the voltammograms obtained after successive additions of DP aliquots (Fig. 10A) and the relationship between the oxidation peak current and DP concentration (Fig. 10B). The increase in current was observed specifically in the previously mentioned shoulder region. Accordingly, the analytical curve $I_{pa}(DP) = 291.11 + 19336.5[DP]$ ($R^2 = 0.996$) was obtained over a linear range from 5.0×10^{-4} to $5.0 \times 10^{-3} \text{ mol L}^{-1}$. The voltammetric sensitivity, determined from the slope of the calibration curve, was $19,336.5 \mu\text{A L mol}^{-1}$ ($0.01934 \text{ A L mol}^{-1}$). The limit of detection, calculated as three times the standard error of the intercept divided by the slope of the calibration curve, was $5.69 \times 10^{-4} \text{ mol L}^{-1}$.

The Table 3 presents representative electroanalytical methods, including the electrode material, technique, linear concentration range, and limit of detection. This comparison provides a broader assessment of the CNTmSCuH/CPE performance, particularly regarding its working concentration range, voltammetric sensitivity, ease of electrode preparation, and suitability for the determination of DP in pharmaceutical and aqueous samples.

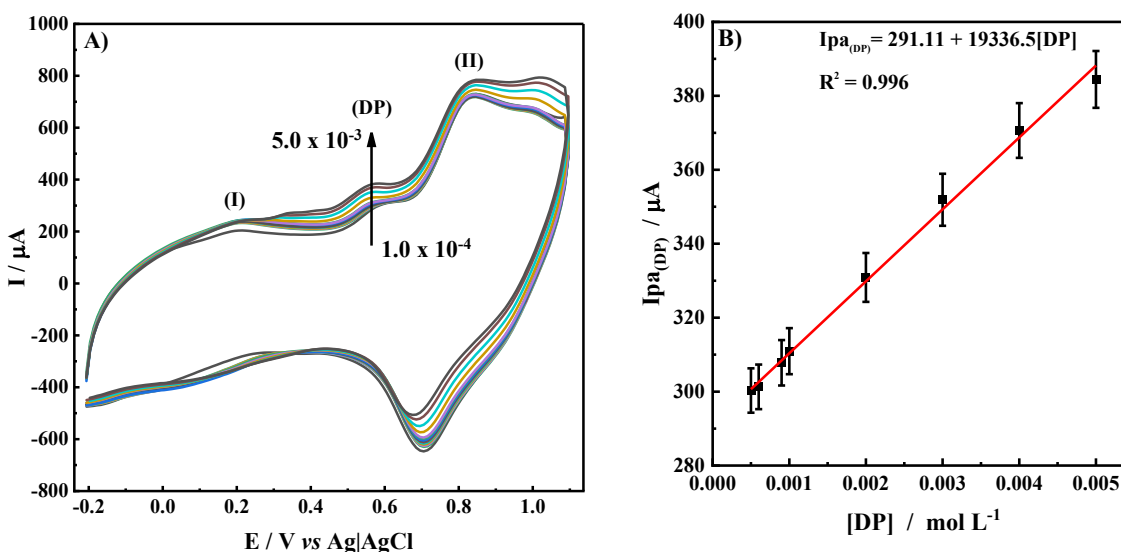


Figure 10. (A) Cyclic voltammograms obtained using the CNTmSCuH/CPE, at dipyrone (DP) concentrations ranging from 1.0×10^{-4} to 5.0×10^{-3} mol L⁻¹ (1.0 mol L^{-1} KCl, $v = 20 \text{ mV s}^{-1}$, pH 7.0). (B) Corresponding calibration curve of the anodic peak current of DP, $I_{(DP)}$, as a function of DP concentration.

Table 3. Comparison of the analytical performance of different electrochemical sensors reported for DP, including the electrode configuration, electroanalytical technique, linear range, limit of detection (LOD)

Electrode/sensor	Technique	Linear range (mol L ⁻¹)	LOD (mol L ⁻¹)	
Tubular PVC membrane electrode supported on a graphite conductor	FIA–potentiometry	8.0×10^{-4} – 1.0×10^{-1}	9.0×10^{-4}	[62]
DAB-AM-16/ Ni^{2+} /silica-modified graphite paste electrode	Cyclic voltammetry	3.0×10^{-4} – 6.0×10^{-3}	4.79×10^{-4}	[12]
Titanium phosphate/nickel hexacyanoferrate-modified graphite paste electrode	Cyclic voltammetry	3.0×10^{-4} – 8.0×10^{-3}	3.75×10^{-4}	[63]
POSS/ Ni^{2+} /silica-modified graphite paste electrode	Cyclic voltammetry	1.0×10^{-4} – 2.0×10^{-3}	9.17×10^{-5}	[12]
Metamizole-selective PVC membrane electrode	Potentiometry	1.0×10^{-4} – 1.0×10^{-2}	4.58×10^{-5}	[64]
Reactive Blue 4/amine-functionalized silica-modified carbon paste electrode	Cyclic voltammetry	4.99×10^{-5} – 4.40×10^{-4}	2.20×10^{-5}	[65]
CNTmSCuH/CPE	Cyclic voltammetry	5.0×10^{-4} – 5.0×10^{-3}	5.69×10^{-4}	This work

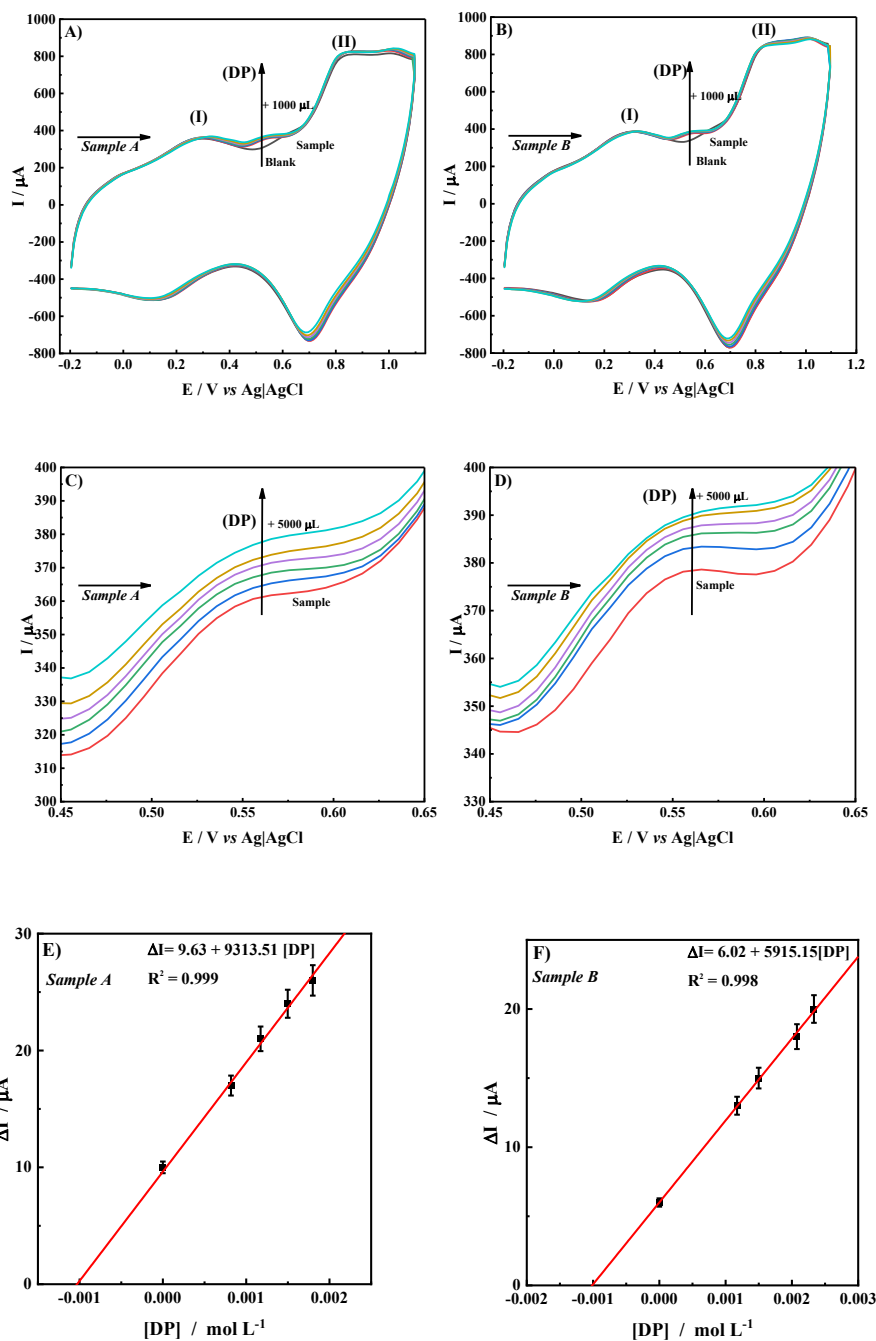


Figure 11. Cyclic voltammograms obtained using the CPE–CNTmSCuH electrode in 1.0 mol L^{-1} KCl at a scan rate of 20 mV s^{-1} for (A) sample A and (B) sample B. Enlarged views of the DP oxidation region during the standard-addition experiments for (C) sample A and (D) sample B, obtained after successive $1000 \mu L$ additions of a $1.0 \times 10^{-2} \text{ mol L}^{-1}$ DP standard solution. Corresponding standard-addition curves for (E) sample A and (F) sample B.

Pharmaceutical samples are composed of complex matrices with possible interferents; as an alternative to suppress these interferents in this type of matrix, the standard addition technique is employed. In this sense, Figure 11 presents the voltammograms and the standard addition curves in samples of two commercial syrups (Sample A and Sample B). Sample A (Medley) is composed of DP (500 mg/mL), citric acid, acerola flavor, sodium benzoate, disodium erythrosine red, sodium edetate, dibasic sodium phosphate heptahydrate, sodium metabisulfite, sucrose, sorbitol, and purified water. Sample B (Neoquímica) is composed of DP (500 mg/mL), disodium edetate, sorbitol, sodium metabisulfite, and water.

The voltammograms obtained for samples A and B are presented in Fig. 11A and 11B, respectively. The addition of each sample resulted in the appearance of the shoulder previously attributed to DP, with a shift toward more cathodic potentials, as discussed above. However, to better evaluate the increase in current, the DP oxidation region was enlarged, as shown in Fig. 11C and 11D. The red curve represents the response obtained after sample addition, whereas the subsequent curves correspond to successive 1000 μL additions of the DP standard solution. For construction of the standard-addition curves, the current response recorded before the addition of the standard was subtracted from the responses obtained after each addition, resulting in ΔI_{pa} . This analytical signal was then correlated with the added DP concentration, yielding the standard-addition curves for sample A (Fig. 11E) and sample B (Fig. 11F). From the extrapolation of the fitted lines and after accounting for the dilution used to prepare the $1.0 \times 10^{-3} \text{ mol L}^{-1}$ sample solutions, DP concentrations of 515 ± 26.25 and $509 \pm 25.45 \text{ mg mL}^{-1}$ were determined for samples A and B, respectively.

4. CONCLUSIONS

The CNTmSCuH material was successfully synthesized and characterized. Vibrational spectroscopy provided evidence of the formation of the copper(II) hexacyanoferrate(III) complex, while transmission electron microscopy confirmed the presence of cubic nanostructures. The semiquantitative elemental analysis revealed an appropriate relationship between Cu and Fe and also supported the presence of the functional groups identified by spectroscopic characterization. In addition, N_2 physisorption measurements demonstrated the mesoporous nature of the material. The CNTmSCuH/CPE exhibited favorable electrochemical behavior, diffusion-controlled charge transfer, and clear electrocatalytic activity toward dipyrone oxidation. Under optimized experimental conditions, the proposed platform showed satisfactory analytical performance, with a linear response over a useful concentration range and successful application to the determination of dipyrone in commercial pharmaceutical samples using the standard addition method. Therefore, these results highlight the potential of this nanohybrid material as a promising electrochemical sensor for dipyrone determination and encourage its further investigation for the analysis of other compounds of analytical and pharmaceutical interest.

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Authors' Contribution

Pablo C. Soto: sample collection and processing, data editing, writing and original draft preparation.

Thiago N. M. Cervantes: sample collection and processing, validation, data editing and writing.

Alexsandro dos S. Felipe: Resources, Writing - Review & Editing.

Newton L. D. Filho: Resources, Writing - Review & Editing.

Valmor R. Mastelaro: Investigation, Data Curation, Formal Analysis;

Fábio S. de Vicente : data curation, Resources, Formal analysis, Writing - Review & Editing;

Devaney R. do Carmo: supervision, conceptualization, data editing, validation, writing, funding acquisition and final edition

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