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ELECTROCHEMICAL CHARACTERIZATION OF GLASSY CARBON ELECTRODES MODIFIED WITH SWCNT FUNCTIONALIZED WITH DIAZONIUM SALT

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ABSTRACT

Although carbon nanotubes have unique properties, one of the biggest drawbacks in practice is the difficulty in forming dispersions of individual nanotubes in a given solvent. Covalent functionalization of carbon nanotubes allows the incorporation of chemical groups at the nanotube surface that, according to its polarity, facilitates the dispersibility in different solvents. In this work, singled-wall carbon nanotubes were functionalized by spontaneous grafting with a diazonium salt obtained from the 4-aminobenzoic acid to obtain SWCNT-pB. The nanomaterial obtained was characterized by several methodologies that the covalent incorporation of the functional groups. SWCNT-pB were dispersed in ethanol/water 50% V/V under ultrasonic treatment, and the exfoliation degree was evaluated by UV-Vis spectrophotometry. Under optimal conditions, SWCNT-pB dispersion was stable for more than 45 days. Glassy carbon electrodes (GCE) modified with the nanomaterial show significant increases in their capacitive current and a faradaic process due to redox species confined on the surface of SWCNT-pB whose anodic peak currents depend linearly with the scan rate. The modified electrodes also show a catalytic response towards ascorbic acid (AA) and notorious increments in the oxidation and reduction currents of H₂O₂. The stability of the dispersions and the excellent electrochemical responses obtained make this nanomaterial very interesting for its application in electrochemical detection.

Keywords: *Single-walled carbon nanotubes, diazonium salt, electrochemistry.*

1. INTRODUCTION

Although carbon nanotubes (CNT) have unique properties, one of the biggest drawbacks in practice is the difficulty in forming dispersions of individual nanotubes in a given solvent. Their hydrophobicity and large surface area make them poorly dispersible. Therefore, different methods have been developed to modify the surface properties of CNT and improve their dispersibility (Bollella & Katz, 2020). Covalent functionalization of CNT includes the chemical modification of the surface by oxidation of C with strong acids, reduction by alkali metals, and incorporating aryldiazonium salts (DS) (Pilan, 2021). The advantage of these methods lies in the better dispersibility and stability of functionalized

nanomaterials in different solvents provided by the polarity of the functional groups attached. In addition, the functionalization of CNT with DS makes it possible to achieve a high degree of functionalization by spontaneous grafting of the nanotubes. DS can be obtained from arylamines either in an acid medium or in isopentyl nitrite.

In this work, single-wall carbon nanotubes (SWCNT) were functionalized with the DS obtained from the 4-aminobenzoic acid, as shown in scheme 1. The nanomaterial obtained, SWCNT-pB, was characterized by several methodologies and applied to modify GCE. In addition, the electrochemical responses of different redox probes were analyzed at the modified electrodes to evaluate the possible application of these surfaces as electrochemical transducers for

developing electrochemical enzymatic (bio)sensors.

Scheme 1: SWCNT functionalization reaction.

2. MATERIALS AND METHODS

2.1. Reactives

It was used SWCNT of chirality (7, 6) containing more than 77% of nanotubes with (0.7 to 1.1) nm of diameter (Sigma-Aldrich, 704121-16). 4-aminobenzoic acid (pB), anhydrous N,N-dimethylformamide (DMF), acetonitrile, and isopentyl nitrite were also provided by Sigma-Aldrich. All the other reactives were of analytical degree. All solutions were prepared with ultrapure water (18 MΩ cm).

2.2 Functionalization of SWCNT

200.7 mg of SWCNT (16.725 mmol) were dispersed in 50 mL of DMF in an ultrasonic bath for 1 h and then with an ultrasonic probe for 30 min using cycles of 30 s with an amplitude of 60% in an ice bath. 2.7455 g (20.02 mmol) of pB were dissolved in 50 mL of deoxygenated DMF and added to the dispersion of SWCNTs under N₂ flow. To produce the DS, 2 mL of isopentyl nitrite were added. The reaction proceeded for 17 h at 60 °C under stirring. The reaction product was washed exhaustively with DMF and dimethyl ether, filtered under vacuum and dried in an oven to constant weight.

2.3 Equipment

During the syntheses, a Heischer model UP400S probe was used. In addition, a VCX 130W probe from Sonics and Materials with a 3 mm diameter titanium alloy micro-tip was employed to obtain the dispersions. Spectrophotometric determinations were carried out with a Shimadzu UV2600 spectrophotometer and a 0.1 cm optical path quartz cuvette. Raman spectra were obtained with a Horiba Jobin Yvon Model HR 800 UV Raman microscope with a LASER of 632.8 nm. A 100X objective lens (0.7 NA) focused the laser beam and collected the scattered Raman signal. The laser power used 0.48 mW and the acquisition time was 5 seconds for an average of 5 spectra per sample. Cyclic voltammetry (CV) was

performed with an Autolab PGSTAT128N potentiostat, and glassy carbon disk electrodes (GCE) of 3 mm diameter (Model CHI104, CH Instruments) were used as substrates. In all experiments, platinum wire and Ag/AgCl, 3M NaCl electrodes (Model RE-5B, BAS) were used as counter and reference electrodes, respectively. All reported potentials are referred to this reference electrode.

2.4 Surface modification

GCE was cleaned before each experiment by polishing with alumina powder 0.05 μm for 2 min, followed by sonication in deionized water for 30 s. The electrodes were electrochemically treated by CV applying fifteen consecutive cycles between -0.30 V and 0.80 V at 0.100 Vs⁻¹ in 0.10 M, pH 7.0 phosphate buffer (PBS). The electrodes were modified by drop coating with 10 μL of the SWCNT-pB dispersion. The solvent was allowed to evaporate.

3. RESULTS AND DISCUSSION:

Raman spectroscopy was used to characterize SWCNTs and to verify the chemical modification. Figure 1 shows the Raman spectra before (A) and after (B) functionalization. For the analysis, the spectra were adjusted using Lorentzian and Breit-Wigner-Fano (BWF) functions according to previous reports (Ojha *et al.*, 2019). From the analysis, a ratio of intensities between the D and G band (I_D/I_G) of (0.042±0.003) and (0.45±0.09) was determined for the SWCNT and SWCNT-pB, respectively. These values indicate an increase in the density of defects due to chemical functionalization. The FTIR spectra of SWCNTs-pB showed the bands corresponding to the symmetric and asymmetric stretching, 1384 and 1657 cm⁻¹ respectively, of the deprotonated carboxylic groups bound at the surface of the nanomaterial, confirming the presence of the chemical groups. From thermogravimetric analysis, a degree of functionalization of 21.3% was determined. SWCNTs-pB colloidal dispersions were prepared with 0.50 mg of the modified nanomaterial per mL of solvent (ethanol/water 50/50 V/V) applying ultrasonic treatment for different times, followed by ultracentrifugation at 15000 rpm to decant the impurities and agglomerated nanotubes. To analyze the effectiveness of the method and select the optimal conditions, the absorbance at 254 nm of 1/10 dilutions of the colloidal dispersions was measured, Figure 2.

Figure 1: Normalized Raman spectrum of (A) SWCNT and (B) SWCNT-pB obtained with a 632 nm laser.

Figure 2: Variation of Absorbance at 251 nm vs. ultrasound treatment time and pictures of the 1/10 dilutions of the supernatants obtained. The inset graph shows the UV-Vis absorption spectrum of the SWCNT-pB dispersion obtained with 20 min of treatment. Optical path 0.1 cm.

At short times of ultrasonic treatment, the absorbance is lower due to the fact that the SWCNTs-pB are agglomerated and decant during the centrifugation. Therefore, its concentration in the supernatant is lower. As the sonication time increases, the nanotubes exfoliated in the supernatant increments and absorbance accordingly. From these results 20 min of ultrasonic treatment was selected as the optimal time. The optimized colloidal dispersions were stable for at least 45 days.

The electrochemical response of GCE modified with the optimized dispersion was analyzed by CV. Figure 3 shows the voltammograms obtained at GCE/SWCNT-pB in H_2SO_4 0.5 M at different scan rates. The CVs exhibit a notorious increment of the capacitive

current and several anodic and cathodic peaks between 0.0 and 0.8 V. The peak currents at 0.440 V were found to vary linearly with the scan rate, indicating that the redox process was due to redox species confined on the surface of SWCNT-pB. The anodic (E_{pa}) and cathodic (E_{pc}) peak potentials of this process negatively shifted with increasing pH. The peak position depended linearly on the pH range between 2.0 and 10.0, according to the equation $E_p = (0.51 \pm 0.01) \text{ V} - (0.060 \pm 0.001) \text{ pH}$. The slope value is very close to the theoretical one at 25 °C (0.059 V pH^{-1}) and indicates that the redox process involves the same number of protons as electrons transferred. The peaks observed at GCE/SWCNT-pB electrodes might correspond to a redox process of carboxylic acid groups present at the nanotube surface. The $-\text{COOH}$ groups are reduced to $-\text{CH}_2\text{OH}$ in a four proton/four-electron process. However, the redox processes of quinoid and pyrone groups can not be discarded, and further characterizations should be done for a deeper analysis of the nature of the functional groups at the SWCNT surface.

Figure 3: Cyclic Voltammograms obtained at GCE/SWCNT-pB in H_2SO_4 0.5 M at different scan rates. The inset shows the variation of the peak current at 0.440 V vs. v .

Ascorbic acid (AA) and H_2O_2 are widely used to evaluate the electrochemical response at CNT-modified electrodes. Figure 4 shows the CVs of AA obtained at GCE/SWCNT-pB with the colloidal dispersion prepared with different sonication times. Compared with bare GCE, the electrooxidation of AA exhibits a decrease of the peak potential as increase the sonication time. In addition, an increment of both capacitive current and peak current of AA is observed due to the increase in the amount of SWCNT-pB deposited on the electrode's surface. The remarkable diminution of the oxidation potential for AA is due

to the catalytic effect of the nanotubes, as it was described by another author (Eguílaz *et al.*, 2016).

Figure 4: A) Cyclic Voltammograms of ascorbic acid 1×10^{-3} M in phosphate buffer 0.1M pH 7.0 at GCE/SWCNT-pB, v : 100 mVs^{-1} .

In the field of enzymatic biosensors, the detection of H_2O_2 is very important since this molecule is the by-product of reactions catalyzed by oxidase enzymes.

Figure 5: Hydrodynamic voltammogram of 5.0×10^{-4} M H_2O_2 at GCE/SWCNT-pB. Inset: Calibration plot at -0.050 V (open symbol) and $+0.400$ V (full symbol). Supporting electrolyte phosphate buffer 0.1M pH 7.0

Figure 5 shows the hydrodynamic voltammogram and calibration plots for H_2O_2 . The notorious reduction and oxidation currents are associated with the increment of the electroactive area of the electrode, while the decrease of oxidation potential to the presence of carboxylic groups of the functionalized nanotubes.

4. CONCLUSIONS:

SWCNTs were functionalized by spontaneous grafting of the DS from 4-aminobenzoic acid. Raman and thermogravimetry demonstrated the functionalization. FTIR evidenced the presence of carboxylic groups at the SWCNT surface. The dispersion of the SWCNT-pB was optimized in ethanol/water 50% V/V, selecting 20 min of sonication treatment for further studies. The dispersion was stable for more than 45 days. The modified electrodes show significant increases in their capacity, catalytic response towards AA, and notorious increments in the oxidation and reduction currents for H_2O_2 .

The electrochemical responses obtained, the stability of the dispersions, and the reproducibility of the system are promising for the immobilization of redox enzymes to develop enzyme biosensors.

5. ACKNOWLEDGMENTS:

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