



The electrochemical effect of acid functionalisation of carbon nanotubes to be used in sensors development

F.C. Moraes ^{a,1}, M.F. Cabral ^{b,*}, L.H. Mascaro ^a, S.A.S. Machado ^b

^a Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13560-970 São Carlos, SP, Brazil

^b Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, 13560-970, São Carlos, SP, Brazil

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ABSTRACT

The electrochemical behaviour of multi-walled carbon nanotubes was compared with that of glassy carbon, and the differences were investigated by cyclic voltammetry and electrochemical impedance spectroscopy before and after acid pre-treatment. The electrochemical techniques showed that acid functionalisation significantly improves the electrocatalytic properties of carbon nanotubes. These electrocatalytic properties enhance the analytical signal, shift the oxidation peak potential to a less positive value, and the charge-transfer rate increase of both dopamine and $K_4[Fe(CN)_6]$. The functionalisation step and the resulting appearance of edge planes covered with different chemical groups were confirmed by FTIR measurements. Carbon nanotubes after acid pre-treatment are a potentially powerful analytical tool for sensor development.

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1. Introduction

The electrochemical behaviour of carbon materials is of great interest, particularly with respect to electron transfer reactivity [1]. Carbon materials differ from metals in several fundamental properties that make them attractive for electrochemical devices. Boron-doped diamond (BDD), pyrolytic graphite (PG), glassy carbon (GC), and carbon nanotubes (CNTs) have been used due to a number of particular advantages: a wide electrochemical potential window, good electrochemical properties, and interesting electrocatalytic compatibility with biological molecules [2–9].

Since their discovery in 1991 [10], carbon nanotubes (CNTs) have been the subject of numerous investigations owing to their extraordinary mechanical, chemical, and electronic properties [11,12]. The mechanism of charge transport of CNTs can vary from the semiconducting-type to the metallic-type depending on the radius, helical structure, and ability to mediate electron transfer reactions with electroactive species in solution [13,14].

The term CNTs includes both single-walled and multi-walled structures, which have characteristics that make them ideal choices for electroanalytical studies [15]. Structurally, single-walled carbon nanotubes (SWCNTs) can be approximated as a rolled-up graphene sheet several microns in length and have unique properties. Multi-walled carbon nanotubes (MWCNTs) can be thought of as several concentric tubes of graphene fitted one inside the other and are typically around 30 nm in diameter [16].

CNTs frequently show hollow bamboo-like defects associated with the termination of the inner shells, and pentagon–heptagon defects are also frequently found. It has been theoretically confirmed that many individual nanotubes have metallic characteristics [17].

CNTs are low-dimensional functional materials with a large surface-to-volume ratio and unique electronic properties. These materials have been studied intensively for several applications, particularly for solid-state chemical and biological sensors [18]. The development of electrochemical sensors is an area of rapid growth in materials science, and has led to a search for devices with improved reproducibility, sensitivity, and stability [19].

Electrochemical impedance spectroscopy (EIS) is an important technique used to elucidate electrochemical phenomena and bulk and interfacial electrical properties. Intrinsic material properties or specific processes that could affect the interfacial properties of an electrochemical system can potentially be studied by EIS [20]. The AC-impedance technique was chosen for the measurements for several reasons: it has low voltage perturbation, efficient separation in frequency domains (*i.e.*, diffusion and kinetic control), and conveniently allows for the simultaneous determination of electrochemical parameters [21,22].

Additionally, a sweep reversal method, cyclic voltammetry (CV), is extremely powerful and is among the most widely practiced of all electrochemical methods [23]. The ease of coupling of spectroscopy and electrochemical techniques provides additional information regarding the process through characterisation and monitoring of both the reactive intermediates and the products [24].

Numerous papers describe the use, modification, electronic and optical properties, functionalisation, assembled composites, and purification of carbon nanotubes [25–30]. The intrinsic powerful catalytic

* Corresponding author. Tel.: +55 16 3373 9924; fax: +55 16 3373 9952.

E-mail address: cabralmf@iqsc.usp.br (M.F. Cabral).

¹ F.C.M. and M.F.C. contributed equally to this work.

properties of MWCNTs represent a good alternative to the development of electroanalytical methods. In addition, depending on the nature of the electrochemical reaction and the kinetics of the electroodic process as compared to those of a possible coupled chemical reaction, the advantages of MWCNTs become even more important.

In this work, modifications promoted by an acid treatment used to functionalise multi-walled carbon nanotubes are discussed. The morphologic, catalytic, and physical aspects of these modifications will be analysed via cyclic voltammetry, surface characterization, electrochemical impedance spectroscopy, and infrared absorption techniques. To our best knowledge, the simultaneous studies of inner and outer sphere reaction at carbon functionalised materials modified electrode have not been reported.

2. Experimental

2.1. Apparatus and procedure

MWCNTs (purity of 90%, length 5–9 μm , diameter 110–170 nm) prepared by a CVD process were purchased from Sigma-Aldrich. Sulphuric acid was obtained from J. T. Baker, nitric acid was obtained from Merck, 2-(3,4-Dihydroxyphenyl)ethylamine hydrochloride (Dopamine – DA), $\text{K}_4[\text{Fe}(\text{CN})_6]$, and analytical grade reagent and chemicals were obtained from Sigma-Aldrich and used as received. The solutions were made with Barnstead nanopure water ($>18.2 \text{ M}\Omega$).

Cyclic voltammetry (CV) experiments were performed using an Autolab Type PGSTAT40 (Eco Chemie, Utrecht, Netherlands) potentiostat/galvanostat coupled to a personal computer and controlled with GPES 4.9 software. The electrochemical cell was assembled with a conventional three-electrode system: different carbon surfaces were used as the working electrode, Ag/AgCl ($\text{KCl } 3.0 \text{ mol L}^{-1}$) was the reference electrode, and a Pt plate was the auxiliary electrode. The working electrodes used here were composed of bare glassy carbon (GC) (3.0 mm diameter), glassy carbon modified with treated MWCNTs, or a glassy carbon modified with untreated MWCNTs. All experiments were carried out at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

EIS data were obtained using a PC-controlled FRA2 (Eco Chemie, Utrecht, Netherlands) coupled to an Autolab Type PGSTAT40 (Eco Chemie, Utrecht, Netherlands) potentiostat/galvanostat, scanning from 100 kHz to 40 mHz frequency range and 10 mV amplitude, with 10 data points per frequency decade. The measurements were carried out in the presence of $5.0 \text{ mmol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$ in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ as the supporting electrolyte and 5.0 mmol L^{-1} of dopamine (DA) in 0.2 phosphate buffer solution (pH 4.0). The impedance spectra were analysed with the simulation *Zview-Impedance software*[®], and the Randles equivalent circuit was used to fit the impedance spectroscopy and to determine electrical parameter values for each experiment.

Infrared analysis of micro-structural variations of treated MWCNT was performed. FTIR spectroscopy in a Nicolet 55XC FTIR spectrophotometer was used to obtain spectra in the range of 500–4000 cm^{-1} using potassium bromide (KBr) pellets. The samples were prepared by grinding dry material into KBr and adding 0.03 wt.% MWCNTs to all samples; this low concentration is necessary due to the high absorption of the nanotubes at a resolution of 4 cm^{-1} and 100 scans.

The morphologies of the MWCNTs were examined by means of a field emission gun with scanning electron microscopy (FEG–SEM) using a FEG–Zeiss model Supra 35VP (Zeiss, Germany) equipped with a high-resolution secondary electron detector (in-lens detector), operating at 6.0 kV and a point-to-point resolution of 3.8 nm. The samples were prepared by dropping a small amount of MWCNTs dispersion on a glassy carbon substrate and air-drying overnight.

To prepare the samples for transmission electron microscopy (STEM VG-603 with Cs correction – with a 300 kV differential potential) a small amount of the powder was dispersed in anhydrous isopropanol in an ultrasound bath. Then, a freshly prepared dispersion was added drop wise onto a copper grid.

2.2. Treatment of MWCNTs

The mixture consisted of 1.0 g MWCNT (as received – untreated) in 500 mL of a 1:3 volume concentrated solution of $\text{HNO}_3/\text{H}_2\text{SO}_4$. The content was kept under magnetic stirring at room temperature for 12 h and subsequently filtered. They were then filtered through a 0.45 μm Millipore nylon filter membrane. The resulting MWCNTs (treated) were continuously washed using purified water until the pH of the filtrate was neutral, and then dried overnight in a vacuum oven at 120 $^\circ\text{C}$.

2.3. Preparation of the electrodes

The GC electrode surface was polished with 0.5 μm alumina slurries, rinsed thoroughly with double distilled water, subject to an ultrasonic stirring bath for 3 min in acetone and 3 min in water, and air-dried. After that, 1.0 mg of treated or untreated MWCNTs were dispersed using ultrasonic stirring for 20 min in 1.0 mL dimethylformamide (DMF) to prepare the GC/MWCNT electrodes. Then 10 μL of this dispersion (each batch) was dropped on the cleaned GC electrode surface and the solvent was evaporated under an infrared heat lamp.

3. Results and discussion

3.1. Morphology and structural characterisation of carbon nanotubes

The FEG–SEM images show that untreated MWCNTs (Fig. 1A) have lengths and diameters of approximately 10 μm and 250 nm, respectively, and that the nanotubes have carbon protective caps on the ends. After the treatment with a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ for 12 h (Fig. 1C), the nanotubes were significantly modified as evidenced by the removal of their protective caps and significant alteration to their sidewalls. The length and the diameter also considerably decreased. The image shown in Fig. 1C indicates that the sulphonic treatment promoted the rupture of the nanotubes in the MWCNTs, diminishing their size and increasing the amount of edge planes exposed. These FEG–SEM observations are in agreement with the theory that acid treatment attacks the sidewall of the MWCNTs and increases the population of the edge plans [16].

These proposals were confirmed through transmission electron microscopy (TEM) analysis. Fig. 1B, which shows the protective caps while the Fig. 1D shows that after the acid treatment these caps were removed. This finding confirms the efficiency of the oxidant treatment that is proposed in several literature papers [9,13,15,28,30]. The image presented in Fig. 1D is compatible with the proposed orientation increasing the amount of edge planes on the substrate. The presence of edge planes promotes the electrochemical reactions rates at the nanoscale [16].

Typical FTIR spectra are shown in Fig. 2 for untreated (dotted line) and treated (full line) MWCNT samples. Chemical treatments such as wet oxidation in $\text{HNO}_3/\text{H}_2\text{SO}_4$ can functionalise the carbon surface with anchor groups such as hydroxyl (–OH), carboxyl (–COOH), and carbonyl (–C=O) [31].

The peak at 3432 cm^{-1} corresponds to hydroxyl groups, which are always present in CNT samples. The region around 2900 cm^{-1} indicates a stretch oscillation from CH_2 – CH_3 groups, with an increased intensity observed in treated carbon nanotubes, indicating the rupture of nanotubes sidewalls after the acid treatment.

Both samples showed absorption peaks in the IR region around 1650 cm^{-1} ascribed to the oscillation of carboxylic groups. It should be noted that the untreated MWCNTs were initially purified to remove traces of the catalytic metallic nanoparticles originating from the nanotubes production process. Thus, the presence of carboxylic groups in these commercial MWCNT was expected. The carboxylic peaks (1650 cm^{-1}) remain present in the spectra independent of the surface chemical treatment [32], but chemical treatment with the acid

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