In this paper, the functionalization of single walled carbon nanotubes (SWCNTs) via electrochemical reduction of aryl diazonium salts in a manner that is similar to the one employed for glassy carbon surfaces is reported. The functionalization processes with diazonium salts can lead to further modifications of the nanotubes in order to facilitate their incorporation into polymer composite materials or use in sensors applications. The molecules used for SWCNTs functionalization were chosen for the opposite electronic effects of the aryl substituents and we observed that grafting behaviour depended on the electronic nature of the substituent. The functionalization of SWCNTs was evidenced using voltammetric methods by electrochemical signals related to the immobilized groups in their characteristic potential domain. For electrochemically inactive groups, where it was not possible to evidence the SWCNTs modification by direct electrochemistry methods, the functionalization of SWCNTs was probed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using \([\text{Fe(CN)}_6]^{3-/4-}\) as redox marker.

INTRODUCTION

Since the discovery in 1991 by Iijima, carbon nanotubes (CNTs) have become the subject of intense researches, due to their unique structural, electronic and mechanical properties and the potential applications in almost any aspect of nanotechnologies. For example, their biocompatibility, the good conductivity, the large specific area and the modifiable sidewall made CNTs ideal materials for constructing electrochemical sensors. Because of their excellent properties, CNTs can be also used as ideal reinforcing agents for high performance polymer composites. Since CNTs usually agglomerate due to Van der Waals force, they are extremely difficult to disperse and align in a polymer matrix. The functionalization of CNT is an effective way to prevent nanotube aggregation, which helps their better dispersion and stabilization within a polymer matrix. The recent development of methods to chemically functionalize CNTs has made it possible to solubilize and disperse CNTs in water, thus making possible their facile manipulation and processing in physiological environments. There are several approaches for functionalization of CNTs including defect functionalization, covalent functionalization and non-covalent functionalization. Obviously, the best functionalization route occurs through covalent coupling which ensures a stable strong grafting of the desired molecules. In this option, aryl diazonium salts are promising candidates for introducing molecular tools by surface modifications.

Electrochemical functionalization via electro-generation of radicals in the vicinity of the SWNTs sidewall shows several advantages over other reported derivatization methods. It is a clean and nondestructive chemical modification and it can be used for selective grafting of individual metallic nanotubes. Electrochemical functionalization involves the creation of an active species from a precursor in the vicinity of a working electrode.
The active species that is formed through charge transfer with the electrode (CNTs, in our case) has the tendency to react further with the precursor or to self-polymerize forming a coating on the nanotube surface. Depending on the electrochemical conditions and the precursor, the polymerization may or may not be accompanied by the formation of covalent bonds to the CNTs nanotubes. The electrochemical coupling can be achieved using different methods. Most common is the potentiostatic technique, wherein a constant potential is applied over an extended period of time. The appropriate potential to be applied can be estimated by performing cyclic voltammetry (CV) measurements.

In this paper we report the functionalization of SWCNTs with different functional groups via electrochemical reduction of aryl diazonium salts in a manner that is similar to the one employed for functionalization of glassy carbon (GC) surfaces. The functionalization processes with diazonium salts can lead to further modifications of the CNTs in order to facilitate their incorporation into polymer composite materials or their use in sensors applications.

Since their first application in electrochemistry by Britto et al., numerous papers dealing with the use of CNTs as electrodes have been reported. But very few cyclic voltammetry (CV) characterizations of CNTs have been described so far in the literature. The major problem is the immobilization of CNTs on the electrode surface because CNTs generally exist as highly tangled ropes and are insoluble in almost all solvents, which greatly hinder their capacity of forming uniform and stable films. To overcome this deficiency, CNTs are firstly dispersed or dissolved in various solutions or suspensions and immobilized on the surfaces of various substrates by physical or chemical methods.

In this paper, the preparation of the SWCNTs electrodes basically consists of casting the GC electrode with a drop of the SWCNTs-dispersion, followed by a drying step. This preparation method allowed us to carry out electrochemical studies, similarly to modified electrodes, without loss of the immobilized material. In order to establish the electrochemical behaviour of covalently attached aryl layers obtained by different kinds of diazonium derivatives electrochemically reduced on the SWCNTs surface, the selection of the molecules to be grafted was done both for their electroactivity after grafting and the contrasted electronegativity (i.e., electro-withdrawing nitro group, electro-donating aminophenyl group) of the substituents. Thus, the following diazonium salts were studied: \( p\)-nitrophenyl diazonium tetrafluoroborate (NBDTFB); \( p\)-tolyldiazonium tetrafluoroborate (TDTFB) and 4-diazo-\( N\)-phenylaniline tetrafluoroborate (DPATFB), respectively.

**EXPERIMENTAL**

**Reagents solutions and instrumentation**

All aqueous solutions were prepared with bidistilled water. Single-walled carbon nanotubes, 0.7-1.11 nm diameter (Produced by CoMoCAT® Catalytic Chemical Vapor Deposition (CVD) Method) were purchased from Aldrich. Anhydrous acetonitrile (99.8%, noted ACN), tetra-n-butylammonium tetrafluoroborate (99%, noted TBATFB), K\(_3\)Fe(CN)\(_6\) (99%), NaCl (99%), were obtained from Aldrich and were used as received.

All electrochemical measurements including CV and EIS were performed with a 128N Autolab potentiostat. A three-electrode configuration consisting of bare or modified GC (Metrohm, disks, diameter 2 mm) as working electrodes, Hg/Hg\(_2\)Cl\(_2\) (3M KCl) and Ag/10 mM AgNO\(_3, 0.1\) M TBATFB as reference electrodes for electrochemical experiments in aqueous and organic solvents, respectively, and a Pt wire as counter electrode was used.

EIS measurements were carried out in the range of 10 kHz–10 mHz at the constant potential of 0.22 V, which is the formal potential of the Fe(CN)\(_6\)\(^{3-}\)/Fe(CN)\(_6\)\(^{4-}\) redox probe vs Hg/Hg\(_2\)Cl\(_2\) (3M KCl). All solutions were deoxygenated by bubbling high purity Ar for 15 min prior to experiments.

\[ \text{Scheme 1} – \text{The synthesis of the diazonium salts (2) a-c: (The synthesis of the diazonium salts (2): (p-nitrophenyl diazonium tetrafluoroborate: NBDTFB, p-tolyldiazonium tetrafluoroborate: TDTFB, 4-diazo-N-phenylaniline tetrafluoroborate: DPATFB).} \]
SWCNTs polishing the electrode was thoroughly rinsed with water and polished in 0.05µm alumina slurry on a microcloth pad. After being cooled and washed with cold 5% fluoroboric acid solution maintaining the temperature near 0-5 °C. The mixture was then cooled to below 0 °C in a salt/ice bath. The precipitate was collected on a sintered glass filter which had been washed with cold 5% fluoroboric acid followed by ice-cold ethanol and ethyl ether. The products were air-dried and stored at room temperature in a vacuum desiccator.

Preparation of GC-SWCNT modified electrodes

Prior to electrode modification, the electrode surface was vacuum desiccated. The SWCNTs electrodes were obtained by depositing a drop of a SWCNTs-dispersion (obtained by sonication of 5 mg of SWCNTs in 5mL ACN) on the GC electrode surface and evaporating the solvent after the drop addition. Once the solvent has been evaporated, a strongly adherent SWCNTs film resulted on GC surface. The change in the electroactive surface of the electrodes obtained by SWCNTs deposition on the GC electrode surface can be observed by the voltammetric signal of [Fe(CN)6]3-/4- redox couple.

RESULTS AND DISCUSSION

In this paper we report the functionalization of SWCNTs with different functional groups via electrochemical reduction of aryl diazonium salts in a manner that is similar to the one employed for functionalization of GC surfaces. The selected molecules used for SWCNTs functionalization were chosen both for the opposite electronic effects of the aryl substituents and their electroactivity after grafting. We observed that electrochemistry can be an advantageous technique for qualitative analysis of grafting on SWCNTs, the functionalization of SWCNTs with electroactive groups (i.e., nitrophenyl and N-phenylaniline groups) being evidenced using voltammetric methods by electrochemical signals related to the immobilized groups in their characteristic potential domain.

In order to modify SWCNTs with the mentioned diazonium salts, we deposited sonicated SWCNTs on a GC electrode and performed cyclic voltammetry or controlled-potential electrolysis in ACN electrolytic solution with millimolar concentrations of diazonium salts. The cyclic voltammograms recorded in solutions of 5mM of the specified diazonium salts (+ 0.1 M TBATFB in ACN) at a SWCNTs electrode (Fig. 1) showed an irreversible cathodic process assigned to the reduction of the diazonium species. The reduction potential values correlate well with electron-donating or electron-withdrawing properties of the diazonium substituents: the more electron-withdrawing is the substituent, the more shifted towards positive values is the reduction potential. From the studied diazonium salts, DPADTFB is the most difficult to reduce. It can be seen that after the first scan the electrode presents a blocking effect toward the reduction of diazonium in solution because, in this potential range, no electroactive relay continues to reduce. It can be seen that after the first scan the electrode presents a blocking effect toward the reduction of diazonium in solution because, in this potential range, no electroactive relay continues to exist for the grafted molecules. In fact, in the case of DPADTFB salt, because of the electronic transfer, diazonium reduction is still observed after the first scan but the signal is slightly visible. Performing several scans leads to a more difficult electron transfer induced by thicker layers formed on the electrode surface. When grafting occurs on SWCNTs, the diazonium reduction peak presented a shift towards positive values in respect with GC electrodes meaning that the surface derivatization is easier to be performed (as shown in Fig. 1 for N-phenylaniline grafting). The values of the potentials for the reduction peak (noted as Ep) for studied salts on SWCNTs and GC electrodes are summarized in Table 1.
Fig. 1 – Successive cycling (0.1 V/s, 5 cycles) of (a) SWCNTs electrode and (b) GC electrode in 5 mM DPADTFB solutions + 0.1 M TBATFB in ACN.

Table 1
The values of the Ep potentials for electrochemical grafting of the studied diazonium salts on SWCNTs and GC electrodes (values obtained at a potential scan rate of 0.1 V/s)

<table>
<thead>
<tr>
<th>Diazonium salt</th>
<th>NBDFB</th>
<th>TDTFB</th>
<th>DPAFDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP, V for SWCNTs</td>
<td>+0.28</td>
<td>0</td>
<td>-0.25</td>
</tr>
<tr>
<td>EP, V for GC</td>
<td>-0.22</td>
<td>-0.5</td>
<td>-0.57</td>
</tr>
</tbody>
</table>

Fig. 2 – TEM image of SWCNTs functionalized using 5mM NBDFB salt in 0.1 M TBATFB in ACN.
After electrochemical modification, the SWNTs were first examined by transmission electron microscopy (TEM). Structural characterization by this technique showed that for all the considered aryl diazonium salts, the tubular structure is maintained after functionalization. TEM images for SWCNTs functionalized using 5mM NBTFB salt in 0.1 M TBATFB in ACN is presented in Fig. 2.

The cyclic voltammetry study was performed also by potential scanning on a long potential range and in Fig. 3 are presented the successive CVs obtained during this procedure in the case of NBDTFB (Fig. 2a) and DPATFB (Fig. 2b) salts. The associated response for the diazonium reduction appears at the same potential and becomes very low starting with the 2nd cycle as in the case of the short potential range scanning. In this case, the voltammetric responses of the nitrophenyl group reduction and N-phenylaniline oxidation are also seen during electrografting.

Thus, grafting of p-nitrophenyl and N-phenylaniline functional groups at the SWCNTs electrode surface can be proved by the reversible wave observed in the CV of the electrode transferred to a pure electrolyte solution. Therefore, after grafting, nanotubes were released from the GC before being intensively washed with ACN and deposited on the cleaned surface of a GC for CV analysis. The voltammetric signal of the nitrophenyl group should be observed at the cathodic potential of approximately -1.6 V (for a scan rate of 0.1 V/s), nitrobenzene being reversibly reduced, in aprotic medium, by one electron to its stable radical-anion.

Electrochemical study of the modified NBSWCNTs is presented in Fig. 4. During the first scan, we observed that the reduction peak appeared strongly shifted towards the cathodic potentials with a peak potential of −1.8 V. This wave corresponds to the grafted electroactive nitrophenyl groups. The reversibility could not be evidenced, but the material appeared highly stable during successive scans (same peak positions starting with 2nd cycle).

**Fig. 3** – Successive cycling (0.1 V/s, 5 cycles) of SWCNTs electrode in the potential ranges of (a) (0.4 ÷ -2V) electrode in 5 mM NBDTFB solution and (b) (1 ÷ -1V) electrode in 5 mM DPADTFB solution.

**Fig. 4** – CV measurements at the transfer in the supporting electrolyte solution (ACN + 0.1 M TBATFB) for (a) NBSWCNTs (0.2 V/s) and (b) DPASWCNTs (0.01 V/s) modified electrodes obtained by potentiodynamic grafting for 5 cycles in 5 mM diazonium salt solution.
As shown in Fig. 4(b), strong modifications of the CV shapes were obtained in anodic potentials domain for the diphenylamine groups. These new waves observed were in agreement with the previous grafts of this compound on a GC electrode and confirmed that grafting occurred on SWCNTs. DPASWCNTs showed stable and reversible redox systems corresponding to the oxidation of the amine groups at the surface of the nanotubes. The first wave showed higher current density with well-defined peaks. Then, the second scans in showed decreased intensities compared to the first peaks, but the obtained large waves presented good reversibility and stability along the successive sweeps (Fig. 4b). The losses of intensity after the first scan and the apparition of new redox waves may indicate that the grafted groups are the subject to chemical modification after the first oxidation (i.e. coupling reactions). Concerning the grafting quantities, similar trends were observed as for NBDTFB and DPADTFB. Surface densities estimated for DPADTFB compound by integrating waves in second sweep of CV are presented in Table 2. The surface functionalization by DPA films becomes higher as the electrolysis potential for film formation becomes more negative until a potential of -0.6V. By using potentials for film formation more cathodic than -0.6V, reduction of the aryl radical as an alternative reaction pathway to surface coupling can become favourable. However, it is known that charge value does not represent necessarily what is observed with film thickness measurements and that overgrafting may be produced by subsequent radical addition on the deposited layer. Also, those values should be considered cautiously due to the fact that all redox centres may not be electrochemically available.

It is well known that the CV of soluble electroactive species provides a convenient tool to study the presence of grafted films and their blocking properties. p-Tolyl functional group is not electroactive, hence it was not possible to evidence the SWCNTs modification by direct electrochemistry methods. Therefore, the functionalized SWCNTs obtained by electrochemical reduction of diazonium salts were characterized by CV and EIS using [Fe(CN)₆]³⁻/⁴⁻ as redox probe. The influence of the diazonium reduction time at the potential corresponding to cathodic peak (Eₚ) was also studied. As presented in Fig. 5(a), the [Fe(CN)₆]³⁻/⁴⁻ couple in 0.1 M NaCl aqueous solution presents a reversible system with ∆Ep = 70mV on bare GC electrode. The various diazonium layers on the GC electrode exhibit different blocking behavior for oxidation and reduction reactions of the Fe(CN)₆³⁻/⁴⁻ redox system. It was observed that in the case of GC modification with p-tolyl groups for a grafting time higher than 60 seconds at Ep = -0.5V, the Fe(CN)₆³⁻/⁴⁻ response is strongly suppressed. In the case of SWCNTs electrodes, firstly, it should be emphasized that, proportionally to the amount of deposited material, the current densities obtained at the bare SWCNTs (Fig. 5b) are extremely high. The high intensity values denote not only an increasing electrode surface after SWCNT deposition, but also point out the huge capacitive behaviour of the SWCNTs. As expected, [Fe(CN)₆]³⁻/⁴⁻ exhibits a well-defined redox peaks at SWCNTs electrode. However, with the modification of SWCNTs films, the redox currents decrease and the peak shapes become poor, due to the blocking of [Fe(CN)₆]³⁻/⁴⁻ from the electrode surface by grafted groups on the sidewall of SWNTs. Results from Fig. 5b show that the blocking effects increase with increasing reduction time. This trend, actually, was observed for all grafted layers and demonstrates that it is possible to obtain relative control of the SWCNTs degree of functionalization by controlling the diazonium reduction time.
The electrochemical impedance spectra of \([\text{Fe(CN)}_6]^{3-/4-}\) at these electrodes were also studied. The Nyquist plot of \([\text{Fe(CN)}_6]^{3-/4-}\) at GC is characteristic of a semicircle at high frequencies and a straight line with a slope of about 1 at low frequencies, corresponding to the kinetical and the diffusional processes, respectively. At functionalized GC, an obviously larger semicircle at high frequencies and a depressed straight line at low frequencies appear parallel with that at GC (Fig. 6(a)). This suggests that the diffusional behavior of \([\text{Fe(CN)}_6]^{3-/4-}\) at TGC is similar to that at GC. These conclusions are supported by the Bode plots ($\phi$ (phase angle) vs. log f (frequency)) (see Fig. 6(c)). At GC a symmetrical peak with a maximum value of 30° at about 3000 Hz is observed, corresponding to the relaxation process of the GC | solution interface. With the modification of p-tolyl films,
this relaxation completely disappears and a new one situated at 65 Hz appears, reflecting the replacement of the GC | solution interface by the p-tolyl films | solution interface.

In the case of SWCNTs electrodes, the complete disappearance of the relaxation process suggests that the electrochemical reactions of $\text{[Fe(CN)₆]}^{3-/4-}$ take place at the surface of SWNTs instead of GC. The appearance of the peak in Bode diagrams for functionalized SWCNTs at the same position with SWCNTs confirms that the capacitive property of the nanotubes was kept after functionalization (Fig. 6(d)). Nevertheless, differences appear between the structures of these films, i.e. the TSWCNTs2 films might have denser and more regular structures than the TSWCNTs1 films. This is supported firstly by the higher maximum in the Bode plot at the TSWCNTs2 films (approx. 73°) than that at the TSWCNTs1 films (approx. 67°). This fact suggests that the TSWCNTs2 films | solution interface is closer to a pure capacitor than the TSWCNTs1 films | solution interface, i.e. structures of the TSWCNTs2 films should be denser and more regular than those of the TSWCNTs1 films. The narrower distribution of the maximum at the TSWCNTs2 films than that at the TSWCNTs1 films indicates, also, that the former ones should have a denser and more regular structure.

**CONCLUSIONS**

Electrochemical reduction of aryl diazonium salts has been presented as a promising method of functionalization of SWCNTs. We report the functionalization of SWCNTs in a manner that is similar to the one employed for functionalization of GC surfaces. As in the case of functionalization of GC electrodes, it was shown that substituents directly act upon the diazonium reactivity and their effect may be directly monitored through the potential peak value during the diazonium reduction. The reduction wave is correlated with the electronic groups located on the para position of the aryl diazonium salts. This is an important point to predict the grafting behaviour, especially when the subsequent grafted molecules are not electrochemical active. When grafting occurs on SWCNTs the diazonium reduction peak presented a shift of 0.3 - 0.5 V towards positive values in respect with GC, meaning that the grafting is easier to be performed on SWCNTs surface. The functionalization of SWCNTs with electroactive groups was evidenced by CV in the potential domain characteristic for the grafted group reduction and oxidation, respectively. For electrochemically inactive groups, where it was not possible to evidence the SWCNTs modification by direct electrochemistry methods, the functionalization of SWCNTs was probed by CV and EIS using $\text{[Fe(CN)₆]}^{3-/4-}$ as redox marker.

The functionalization processes with diazonium salts can lead to further modifications of the nanotubes in order to facilitate their incorporation into polymer composite materials and will perhaps permit molecular electronic application.

*Acknowledgements:* Authors recognise financial support from the European Social Fund through POSDRU/89/1.5/S/15478 project: “Postdoctoral Program for Advanced Research in the field of nanomaterials”.

**REFERENCES**