

## SUPERCAPACITANCE OF SINGLE-WALLED CARBON NANOTUBE-POLYANILINE COMPOSITES

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### Abstract

*In this paper, we report a facile electrochemical method to obtain polyaniline/single-wall carbon nanotubes (PANI/SWCNTs) composite electrodes by combining the electroreduction of diazonium salts and electropolymerization of conductive polymers. In a first step, the SWCNTs are covalently functionalized with p-nitroazobenzene functional group through the electrochemical reduction of the corresponding diazonium salt in order to provide anchors for the further polyaniline electrodeposition. The aniline oxidation remains possible on this grafted layer and PANI can easily be deposited afterwards. In situ monitoring of mass change during diazonium salt electroreduction and PANI electrodeposition was performed using an EQCM module. These measurements served to calculate the mass specific capacitance ( $F g^{-1}$ ) of the electrode material. It is shown that the electrochemically deposited composites exhibit excellent electrochemical charge storage properties making them promising electrode materials for high power supercapacitors.*

### 1 Introduction

Carbon nanotubes are attractive material for supercapacitors due to their unique one-dimensional mesoporous structure, high specific surface area, low resistivity and good chemical stability. [1,2]. However, the general specific capacitance of raw CNTs is usually less than  $100 F g^{-1}$ . On the other hand, electrically conducting polymers (ECPs) such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and their derivatives, are also interested electrode materials for supercapacitors due to the higher capacity they can provide from pseudocapacitance [3-6], but their cyclability and rate performance still needs to be improved. Therefore, conducting polymers are reported to modify CNTs so as to get both higher capacitance and better cycling performance [7,8]. Various strategies have been reported in the literature to enhance the interaction between the conducting polymer matrix and the nanotubes [9]. Surface functionalization of the CNTs surface has become the subject of research in recent years in order to improve its compatibility with various polymers. Several successful functionalization reactions for both SWCNTs and MWCNTs have been reported [10,11]. In this paper, we report an electrochemical method to obtain polyaniline/single-wall carbon nanotubes (PANI/SWCNTs) composite electrodes by combining the electroreduction of diazonium salts and electropolymerization of conductive polymers. In a first step, the SWCNTs are covalently functionalized with p-nitroazobenzene functional group through the electrochemical reduction of the corresponding diazonium salt in

order to provide anchors for the further electrodeposition of polyaniline. The aniline oxidation remains possible on the grafted layer, so that PANI can easily be deposited afterwards. In situ monitoring of mass change during diazonium salt electroreduction and PANI electrodeposition was performed using an EQCM module. These measurements served to calculate the mass specific capacitance ( $F g^{-1}$ ) of the electrode material. It is shown that the resulted PANI/SWCNTs composite exhibit higher specific capacitance as well as longer cycling life.

## 2 Materials and testing methods

### 2.1. 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<sup>®</sup> Catalytic Chemical Vapor Deposition (CVD) Method) were purchased from Aldrich. Anhydrous acetonitrile (99.8%, noted ACN) and tetra-n-butylammonium tetrafluoroborate (99%, noted TBATFB) were obtained from Aldrich and were used as received. Aniline (99.5%, Fluka) was used as supplied.

All of the electrochemical experiments were performed in air at room temperature and controlled by a potentiostat/galvanostat AutoLAB 128N. The electrochemical measurements were performed in a three-electrode electrochemical cell, in which a gold wire was served as a counter-electrode and a gold-coated quartz crystal electrode (geometric area of  $0.196 \text{ cm}^2$ ) modified with SWCNTs as the working electrode. Ag/AgCl<sub>sat</sub> and Ag/10 mM AgNO<sub>3</sub>, 0.1 M TBATFB electrodes served as reference electrodes for electrochemical experiments in aqueous and organic solvents, respectively. With the Sauerbrey equation shown in Eq. (1), the resonant frequency variation obtained from EQCM measurements could be transferred into the mass change of this electrode:

$$\Delta f = - \frac{2f_0^2}{A\sqrt{\rho_q \cdot \mu_q}} \cdot \Delta m \quad (1)$$

where  $\Delta f$  is the change in frequency, in Hz,  $f_0$  is the nominal resonant frequency of the crystal (6 MHz),  $\Delta m$  is the change in mass, in  $g/cm^2$ ,  $A$  is the area of the crystal in  $cm^2$ ,  $\rho_q$  is the density of quartz, in  $g/cm^3$  and  $\mu_q$  is the shear modulus of quartz, in  $g/cm \cdot s^2$ . For a 6 MHz crystal, the same equation can be reduced to:  $\Delta f = -\Delta m \cdot C_f$ , where  $C_f$  is  $0.0815 \text{ Hz/ng/cm}^2$ .

p-Nitroazobenzene diazonium tetrafluoroborate (p-NABDTFB) was prepared by standard diazotation of the corresponding amine with NaNO<sub>2</sub> in acidic medium as described in one of our previous studies [11].

EIS measurements were carried out in the range of 10 kHz–10 mHz at open circuit potential ( $E_{oc}$ ).

### 2.2. Preparation of the modified electrodes

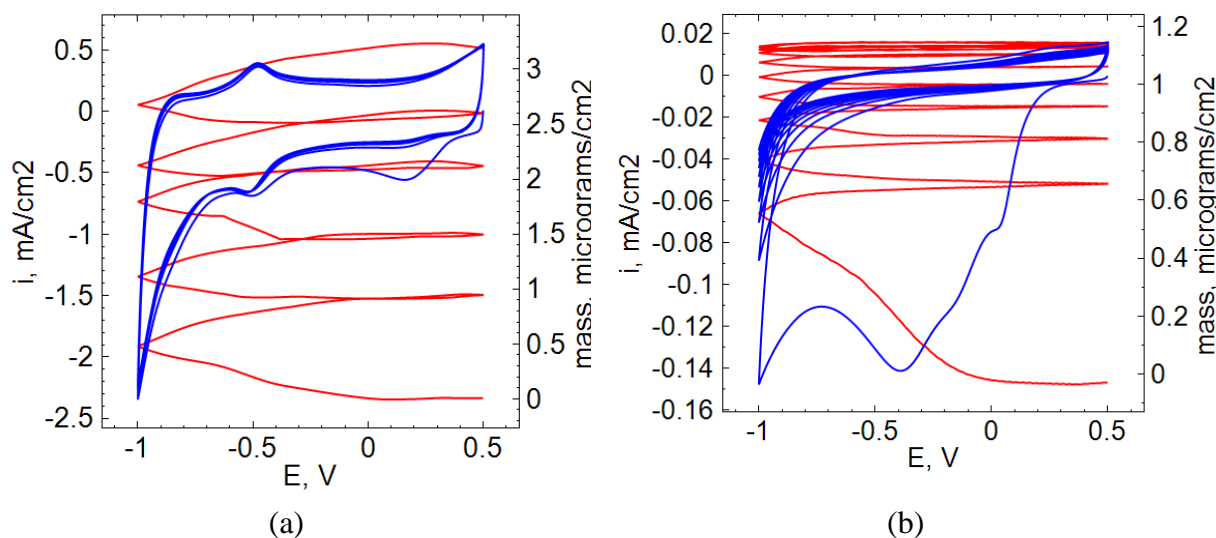
A SWCNTs-coated EQCM gold electrode (SWCNTs/Au) was prepared by dropping 100 $\mu$ L of a solution of 5 mg SWCNTs dispersed in 5 mL of dispersant (ACN) on the electrode surface. The electrode was dried in air and then rinsed thoroughly with double-distilled water. We observed a strong adherence of the sonicated SWCNTs on Au surface that allowed us to carry out the electrochemical studies similarly to modified electrodes, without loss of the immobilized material.

The surface derivatization of the SWCNTs electrodes with p-nitroazobenzene group was carried out in ACN solutions containing a 3 mM concentration of the diazonium salt and 0.1

M TBATFB either by cyclic voltammetry (CV) or under controlled-potential electrolysis (CPE) at imposed potentials more cathodic than diazonium salt electroreduction peak. The electrode was then removed from the grafting solution and rinsed with large volumes of ACN. Electrochemically functionalized carbon nanotube electrodes were denoted *NABSWCNTs*. The polyaniline / SWCNTs composite films were obtained by two different ways. One was to prepare these composite structures by electrogeneration of the PANI films directly at SWCNTs electrode surface and the second consisted in the electropolymerization of the monomer on the functionalized SWCNTs electrode. The PANI films were fabricated by electropolymerization from aqueous solutions consisting of 0.1M monomer and 0.1M H<sub>2</sub>SO<sub>4</sub>. Conventional CV electropolymerization was performed from -0.3 to 1V with a scan rate of 0.1V s<sup>-1</sup> for 10 cycles. The electrochemical characterisation of the composite and pure polymeric films was performed in 1 M H<sub>2</sub>SO<sub>4</sub>.

### 3 Results and Discussion

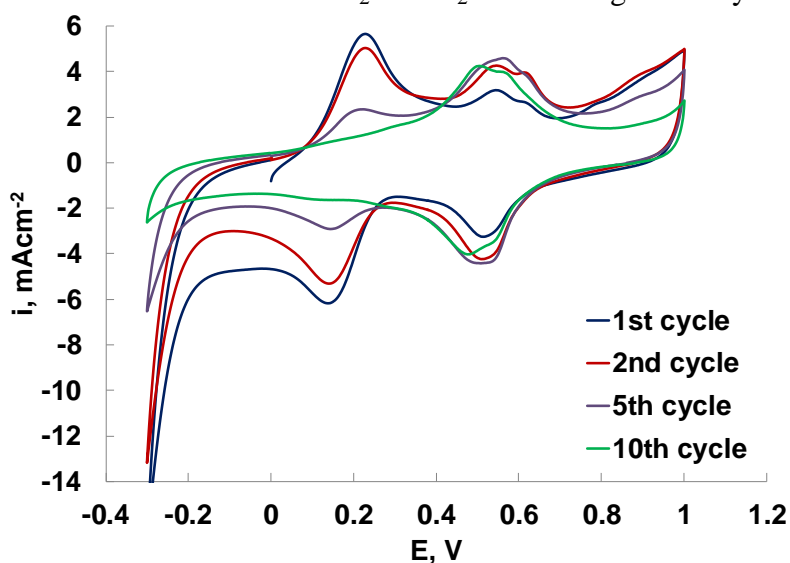
The CV studies of SWCNTs/Au electrodes in the *p*-NABDTFB solution allowed the establishment of the electrode potential to be used for the nanotubes functionalization. CVs recorded in solutions of 3 mM of the specified diazonium salt (+ 0.1 M TBATFB in ACN) at a SWCNTs electrode showed an irreversible cathodic process assigned to the reduction of the *p*-NABDTFB species. Thus, in figure 1(a) one can see one peak in the first cathodic scan (+0.15 V vs. Ag/Ag<sup>+</sup>) and then the electrode surface was passivated as indicated by the absence of cathodic peaks in this potential range for the further scans. By comparing the grafting process on SWCNTs/Au electrodes surface with the Au electrode surface (figure 1(b)), it was noted a shift towards positive values of the diazonium reduction peak for the former ones, meaning that the surface derivatization is easier to be performed. Figure 1 shows also the piezoelectric responses during the electrochemical reduction of the *p*-NABDTFB at both electrodes. According to the Sauerbrey equation, the mass accumulated at the SWCNTs/Au electrode surface is 3 times higher than for Au electrodes after 5 cycles.



**Figure 1.** The simultaneous current and piezoelectric responses during the reduction process of *p*-nitroazobenzene diazonium tetrafluoroborate using CV at (a) SWCNTs/Au – 5 cycles (a) and (b) Au – 10 cycles electrodes in mM NABDTFB in ACN having 0.1M TBATFB as supporting electrolyte (scan rate: 0.1 V s<sup>-1</sup>).

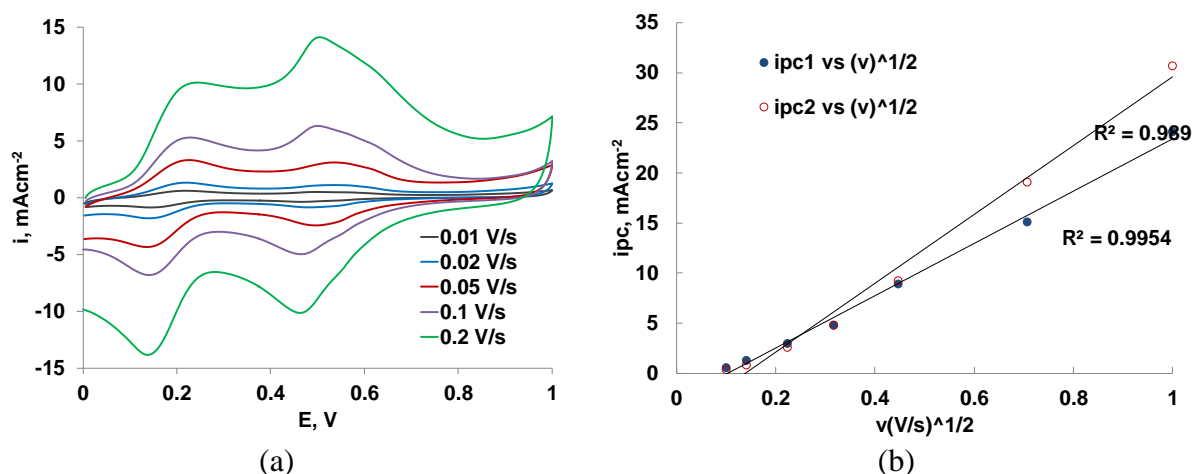
The voltammograms acquired at the *NABSWCNTs* grafted electrode in a pure electrolyte solution (1 M H<sub>2</sub>SO<sub>4</sub>) in the potential range (-0.3V ÷ 1V) exhibit during the first sweep in anodic potential range two very well defined oxidation processes showing a good

reversibility. The further scans show decreased current intensity for the first pair of peaks compared to the first scan, but the second pair of waves present good reversibility and stability along the successive sweeps (figure 2). This behaviour indicates that after the first oxidation scan the classical reduction of  $\text{NO}_2$  to  $\text{NH}_2$  within the grafted layer may take place.



**Figure 2.** CVs ( $0.1\text{Vs}^{-1}$ ) of *NABSWCNTs* electrode (prepared in 3 mM *p*-NABDTFB + 0.1 M TBATFB solution in ACN) in 1M  $\text{H}_2\text{SO}_4$  aqueous solution in the potential range ( $-0.3\text{V} \div 1\text{V}$ )

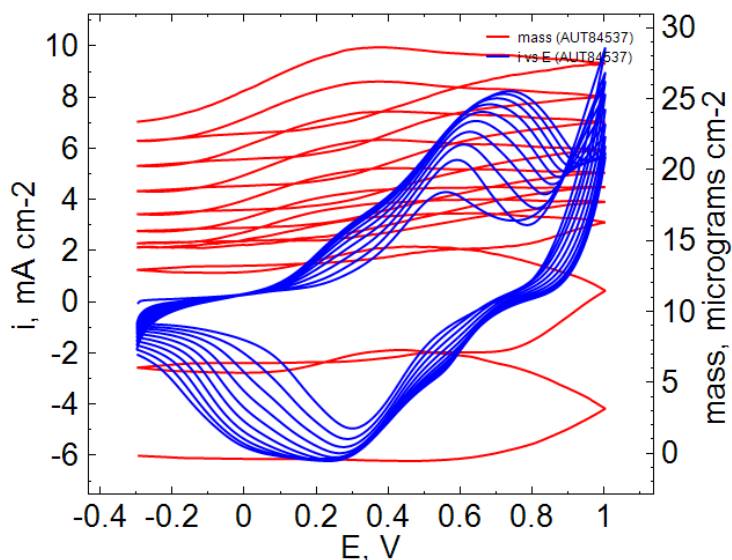
The electrochemical responses of *NABSWCNTs* electrodes at different scan rates in a narrower potential range were studied also in aqueous 1 M  $\text{H}_2\text{SO}_4$  solution. Figure 3 shows that the peak-to-peak separation when the scan is performed in ( $0\text{V} \div 1\text{V}$ ) potential range is around 70 mV for both redox processes and the ratio of anodic to cathodic peak currents is close to unity. Both pair of waves showed a good stability during cycling in this case and, also, a linear dependence of the current versus the square root of scan rate indicated a surface process. This film electroactivity strongly suggests that *NAB* moieties are grafted on the *SWCNTs* surface.



**Figure 3.** CVs for different scan rates (a) and the linear dependence of the cathodic peak currents on the square root of the scan rate (b) for *NABSWCNTs* electrodes (prepared in 3 mM *p*-NABDTFB + 0.1 M TBATFB solution in ACN) in 1M  $\text{H}_2\text{SO}_4$  aqueous solution

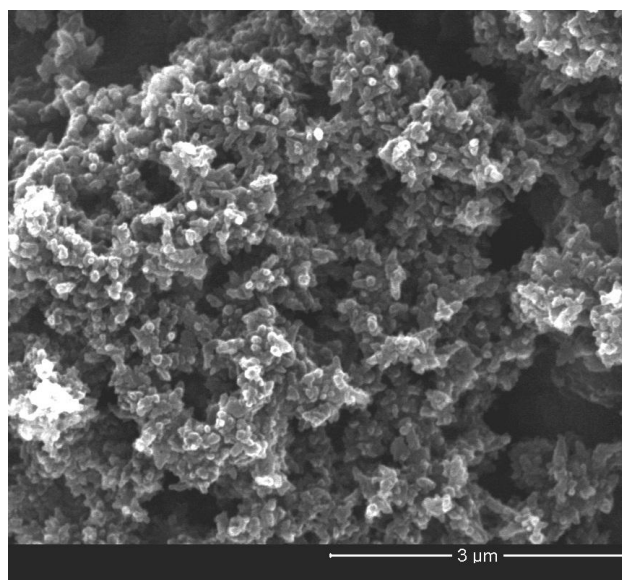
Polyaniline was then deposited at both *NABSWCNTs* and *SWCNTs* electrodes using cyclic voltammetry ( $0.1\text{Vs}^{-1}$ ) between  $-0.3\text{V}$  and  $1\text{V}$ . In the former approach, prior the aniline

electropolymerization, the NABCNTs electrodes were electrochemically reduced in 1M H<sub>2</sub>SO<sub>4</sub> aqueous solutions in order to modify the nitro grafted groups to amine functionality. Figure 4 shows the current versus potential and the accumulated mass versus potential. The accumulated mass in the electrodeposition step resulted from EQCM experiments was used to calculate the mass of the polymer electrodeposited at SWCNTs electrodes during 10 cycles from 0.1M aniline in 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution.



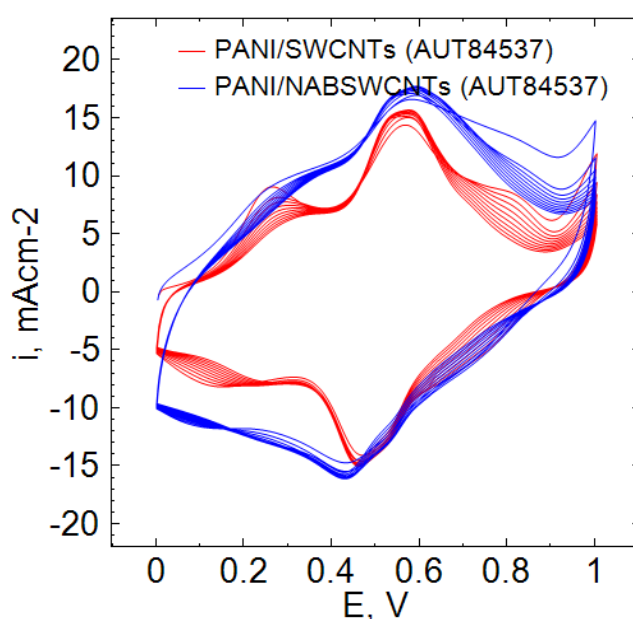
**Figure 4.** The simultaneous current and piezoelectric responses during the electrodeposition of PANI at NABSWCNTs electrodes using CV at a scan rate of 0.1 V s<sup>-1</sup>.

The composite electrodes were also examined by SEM. From figure 5, it can be seen that all polymer is dispersed on the nanotubes, keeping the advantage of the entangled network of the nanotubes that allows a good access of the electrolyte to the active polymer material. Such a texture of the capacitor electrodes is optimal for the fast ion diffusion and migration in the polymer so that the electrode performance should be improved.



**Figure 5.** SEM image of the surface of PANI/SWCNTs deposit formed by potential cycling showing the nanoporous network of PANI coated SWCNTs.

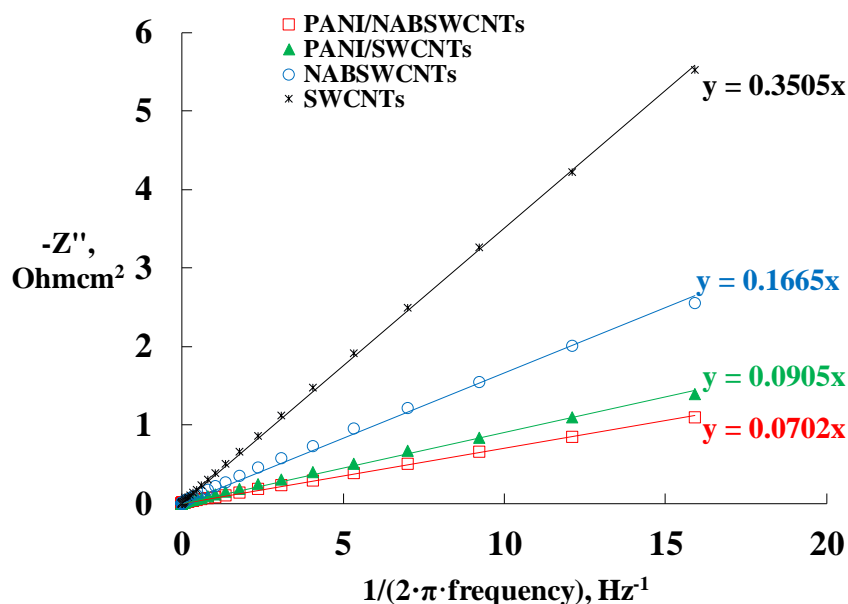
The comparative stability upon cycling of PANI/SWCNTs and PANI/NABSWCNTs modified electrodes with approximately the same thickness was studied. The electroactivity in 1M H<sub>2</sub>SO<sub>4</sub> of PANI/SWCNTs and PANI/NABSWCNTs composite films is presented figure 6 (the films were obtained in similar conditions: 10 sequential cycles, at a scan rate of 0.1 V/s, in the potential range -0.3V÷1V, from 0.1M monomer and 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution). In contrast with the electrochemical response of the PANI film obtained at SWCNTs electrode, the PANI/NABSWCNTs modified electrode shows less electroactivity loss. The current intensity remains almost unchanged after 10 cycles, in contrast with the gradual decrease observed for the first and third peak intensities for the SWCNTs electrode modified only with a PANI coating. Also, it can be seen that PANI/NABSWCNTs modified electrode provides a more rectangular curve which is convenient for capacitance calculations. Considering these results, we can state that the PANI deposited on a NABSWCNTs electrode is most likely grafted to the reduced nitroazobenzene organic layer.



**Figure 6.** CVs of PANI/NABSWCNTs and PANI/SWCNTs composite films electrodes (mass of composite 133  $\mu$ g and 130  $\mu$ g, respectively) at the scanning rate of 0.1V/s in 1 M H<sub>2</sub>SO<sub>4</sub> solution

The composite films were also studied by EIS. The Nyquist plots for SWCNTs, PANI/SWCNTs, NABSWCNTs and PANI/NABSWCNTs systems are featured by a vertical trend at low frequencies, indicating a capacitive behaviour. The capacitances of the electrode materials were calculated, according to the equation:  $C = -1/(2\pi f Z''')$  ( $f$  = frequency;  $Z'''$  = imaginary impedance) from the slope of the linear correlation between the imaginary impedance and the reciprocal of the frequency at low frequencies (see figure 7). Compared with similarly grown PANI/SWCNTs films, the composite PANI/NABSWCNTs films exhibit not only a higher stability upon cycling, but also a higher capacitance.





**Figure 7.** Capacitance evaluation plot for SWCNTs, PANI/SWCNTs, NABSWCNTs and PANI/NABSWCNTs electrodes (NABSWCNTs electrodes were obtained by the SWCNTs electrodes electroreduction for 5 cycles in a 3mM NABDTFB solution in (0.5V ÷ -1V) potential range)

Modified electrode	Slope of $-Z'' = f(1/2\pi\text{frequency})$	C [F cm <sup>-2</sup> ]	C [F g <sup>-1</sup> ]
SWCNTs	0.3505	2.85	895
PANI/SWCNTs	0.1665	6.01	1831
NABSWCNTs	0.0905	11.05	2609
PANI/NABSWCNTs	0.0702	14.25	3441

**Table 1.** Capacitance evaluation values for SWCNTs, PANI/SWCNTs, NABSWCNTs and PANI/NABSWCNTs electrodes (NABSWCNTs electrodes were obtained by the SWCNTs electrodes electroreduction for 5 cycles in (0.5V ÷ -1V) potential range in a 3 mM NABDTFB solution)

#### 4 Conclusions

By adding an intermediate layer by electrochemical reduction of the p-nitroazobenzene diazonium salt, we have shown that a strongly stable conducting PANI film can be electrodeposited on SWCNTs electrode surface. SEM examination confirms the presence of well-distributed, networked nanotubes that are individually coated with polyaniline in the composite, forming a highly porous structure.

Compared with similarly grown PANI/SWCNTs films, the PANI/NABSWCNTs composite films were more stable during repetitive cycling.

In situ monitoring of mass change during diazonium salt electroreduction and PANI electrodeposition was performed using an EQCM module. These measurements served to calculate the mass specific capacitance (F g<sup>-1</sup>) of the electrode material. Capacitance values as high as 3441 F g<sup>-1</sup> are obtained for PANI/NABSWCNTs composites. These findings illustrate the exceptional benefits to be gained by application of the studied composites in supercapacitor domain.

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