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Growth and functionalization of CNTs on stainless steel electrodes for supercapacitor applications

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Abstract

Vertically aligned carbon nanotubes (VA-CNTs) were grown on stainless-steel (SS) substrates by RF plasma enhanced chemical vapour deposition (PECVD). Adhesion of the CNTs to the substrate improves after treating the SS substrates with HF acid and adding an Al_2O_3 layer of 20 nm that is required to support the metal catalyst. An optimal distribution of catalyst nanoparticles was required for a satisfactory CNT growth. In addition, the effect of a nitrogen plasma post-treatment of the obtained CNTs on the electrochemical properties of the electrodes has been investigated. SEM and Raman characterization provided morphological and structural information about the CNTs grown before and after the plasma treatment. Electrochemical measurements showed that the specific capacitance of the nanotubes increases from 44 to 137 $\mathrm{F g^{-1}}$ for untreated and nitrogen plasma treated CNTs, respectively, in 0.1 M Na_2SO_4 aqueous solution.

Keywords: CNTs nanotubes, supercapacitor, stainless steel, nitrogen plama, RFPECVD, HF acid

1. Introduction

Carbon nanotubes (CNTs) have extraordinary properties that come from their unique structure of graphite sheets rolled into tubes, because of these remarkable properties such as very high tensile, resilience, high electric current carrying capacity and heat transmission, many applications are proposed to make use of them [1]: nano-scale electronic devices [2], electrodes for secondary lithium batteries [3], and supercapacitors [4].

Supercapacitors or electric double layer capacitors (EDLCs) are attractive energy storage devices, particularly for applications that demand high power and long cycle life.

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[1] HM and SH equally contributed to this work.

Pores with an accessible size for the electrolyte ions play an essential role in charge accumulation devices. Due to the unique pore structure of aligned CNTs, with mainly mesopores (2–50 nm in diameter), a fast ionic transportation is achieved [5]. Therefore, most of their surface area can be available for the access of ions, in contrast to other forms of carbons with high surface area such as carbon powder or carbon fibers also used as electrode materials for supercapacitors. Thus, CNTs can improve the performance of EDLCs.

However, to properly take advantage of carbon nanotubes, some techniques should be applied to grow carbon nanotubes in specific locations, orientations, shapes and sizes. Synthesis of CNTs directly on conducting substrates, which can act as current collectors, will simplify the preparation of CNTs grown by chemical vapour deposition (CVD) on pre-coated substrates with metallic catalyst layer [6] and [7]. Stainless-steel (SS) is an attractive conducting substrate due to its inexpensiveness and good processability. The incorporation of CNTs can further improve its conductive and electrochemical properties.

In previous reports CNTs have been synthesized directly on a metallic substrate by PECVD without pre-coating of the metallic catalyst layer [8]. However, synthesis of CNTs on metallic or electrically conducting substrates proved rather difficult compared to that on insulators such as glass or silicon wafers [9].

Researchers have employed various kinds of CVD in the synthesis of carbon nanotubes on metal substrates: thermal CVD [6], dc-PECVD [10], microwave PECVD [11] and [12]. Emmenegger and co-workers [2] synthesized CNTs on aluminum substrates with thermal CVD and made EDLCs with them. But they coated the aluminum substrate with $FeNO_3$ by spin coating before CVD in order to provide nuclei for CNTs synthesis like on silicon wafer. Huang *et al* [10] synthesized carbon nanotubes on nickel substrates by hot filament aided dc-PECVD, and observed that the diameter of carbon nanotubes varied with plasma power. Also, CNTs were synthesized on nickel and stainless steel with MPECVD [11]. Wang and Yao [11] employed microwave PECVD to synthesize CNTs on SS.

Device performance would be dramatically improved if the CNTs were directly synthesized on a conducting substrate [13], this would avoid the transfer step of CNTs, prevent the use of any additional material that may increase the total mass of the electrode, and offer a lower contact resistance that improves the electron/thermal transport properties.

CNTs can be grown on various kinds of substrates such as Si, Cu, microelectrode arrays (MEAs), carbon fiber and quartz [14]. In this study, growth of CNTs was performed on Fe/Al_2O_3-coated SS substrates by PECVD, using acetylene (C_2H_2) as carbon source and cleaning the steel foils with hydrofluoric acid followed by a nitrogen plasma functionalization to increase the specific capacitance of the electrodes. RF plasma was used to grow these CNTs, AL_2O_3 was deposited by pulsed dc magnetron sputtering and Fe thin film was deposited by RF magnetron sputtering. A comparison between the properties of CNTs treated and untreated with nitrogen plasma is presented.

2. Experimental setup

2.1. Cleaning of stainless steel substrates

SS plates (type austenitic 304) with a thickness of 0.100 mm were cut into $3 \times 3.5\ \mathrm{cm}^2$ rectangular pieces and cleaned in ultrasonic bath with acetone and ethanol sequentially for seven minutes, these pieces was dipping into 25% HF acid solution for seven minutes. Finally, the substrates were rinsed with distilled water and introduced in a CVD reactor.

2.2. Nucleation and carbon nanotubes growth

Prior to every vacuum process, the pressure in the reactor was lowered below 4×10^{-4} Pa to ensure clean deposition conditions. A thin layer (~20 nm) of Al_2O_3 was sputtered by pulsed dc reactive magnetron sputtering process on the substrates. Aluminum was used as a target. The deposition was performed under a flow of an Ar/O_2 gas mixture of 17/3 sccm, respectively, and 1 Pa of total pressure. The substrate was kept at room temperature and the pulsed-dc power was set to 90 W.

After introducing the SS substrate into the PECVD reactor [16], a 3 nm layer of Fe catalyst was RF-plasma sputtered under an Ar flow of 128 sccm and a total pressure of 2 Pa. Next, the reactor was evacuated and the catalyst was annealed up to 680 °C with a ramp time of 875 s in H_2 atmosphere (100 sccm, 200 Pa).

Afterwards, the sample was kept at this temperature for 120 s to form iron nanoparticles. Subsequently, the growth pressure of reactor was lowered to 100 Pa for 30 s, followed by the introduction of NH_3 (100 sccm, 80 Pa). Then, an RF plasma (50 W) was ignited and the carbon source (C_2H_2, 100 sccm, 100 Pa) was introduced; the growth was carried out for a total time of 1200 s.

2.3. Nitrogen plasma functionalization, electrochemical characterization and Raman spectroscopy

Radio frequency nitrogen plasma was used to remove amorphous carbon and decorate the surface of MWCNTs with nitrogen functionalities. The plasma treatment time was set to 120 s and the flow of pure nitrogen gas was set to 100 sccm.

Following the previous work in our research group [14–18], and [18], cyclic voltammetry was used to perform the electrochemical characterization. A 0.1 M Na_2SO_4 aqueous solution was used to analyze the charge storage capability of the CNTs electrodes. The experiments were carried out in a three-electrode cell at room temperature, using an Ag/AgCl electrode (3 M KCl internal solution) and a Pt-ring electrode as the reference and counter electrode, respectively. The geometrical area of the working electrode was set to a constant value of 1.0 cm^2.

The CNTs quality was evaluated by Raman Spectroscopy, using a micro-Raman system (Horiba LabRam HR800, Japan). A green laser (532 nm wavelength, 2.5 mW power) and a 50 LWD objective were used during the measurements.

3. Experimental results

3.1. Morphological characterization

The morphology and structure of multiwall carbon nanotubes (MWCNTs) were analyzed by field emission scanning electron microscopy (Nova Nano SEM 230 (FEI) at the nanotechnology platform of institute for Bioengineering of Catalonia (IBEC)). As already described in [19], it is very important to have an optimized size of catalyst particles. For example, if catalyst particles or islands are too large, the synthesis of CNTs would not be possible. Thus, in order to elucidate

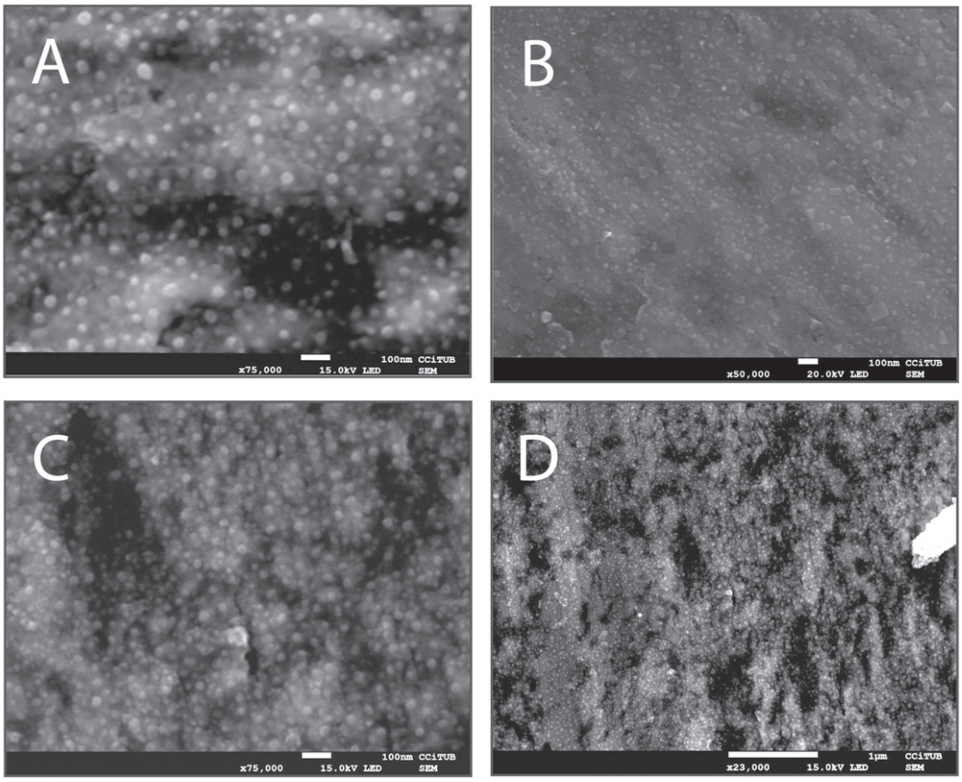

Figure 1. SEM images, formation of iron nanoparticles on Al_2O_3 coated SS under the same conditions of annealing temperature and thickness of iron and alumina film. The annealing times were: (a) 500 s, (b) 750 s, (c) and (d) 875 s

the optimal size of the nanoparticles to grow CNTs with suitable characteristics, a series of samples with iron particles on SS were treated at different annealing times (see figure 1).

The diameter of nanotubes grown by PECVD is dependent on the annealing time and on the thickness of the previously deposited iron film. In our experiments, we fixed the Fe film thickness to 3 nm. The most favorable result corresponds to the thinnest and dense nanoparticles (figure 1(c)). It was obtained using 875 s annealing time. Under this condition, the average diameter of the particles was 19.8 nm, while the other diameters were 24.5 nm and 105 nm for 750 s and 500 s annealing time, respectively.

CNTs were grown all over the metal substrate with high density and homogeneity by PECVD process (see figure 2(a)). The inset in figure 2(a) shows vertically aligned carbon nanotubes with catalyst particles at the tips. The HF acid treatment increases the surface roughness of the substrates by the formation of a nanoscale structure, constituted by small islands that enhance the adherence and act as template for CNTs formation [19].

After the plasma treatment the nanotubes remain vertically aligned and the amorphous carbon has been removed from their surface (see figure 2(b)). The inset image in figure 2(b) clearly shows that after the nitrogen plasma treatment, the tips of the nanotubes are agglomerated in comparison to untreated ones.

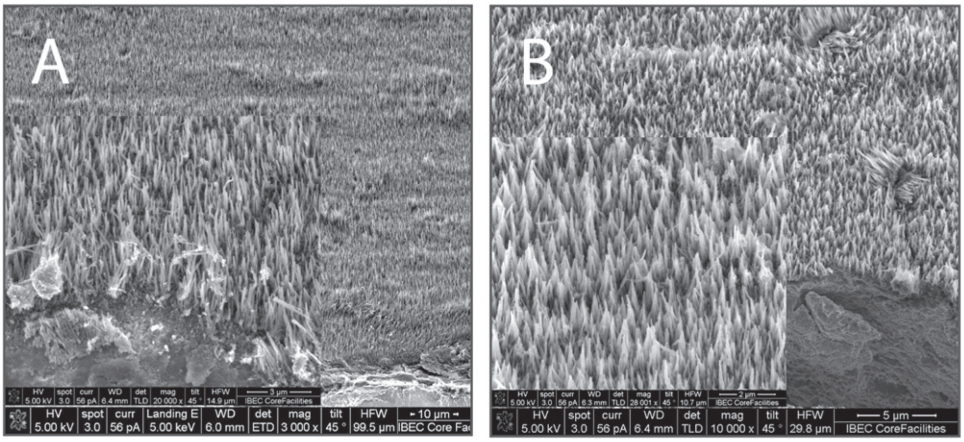

Figure 2. SEM images of CNTs grown on SS by PECVD. (a) Untreated (b) nitrogen plasma treated.

3.2. Raman spectroscopy

The samples show the characteristic D and G bands of CNTs. The G mode (1550–1600 cm^{-1}), is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. Therefore, band broadening and decreasing in intensity means graphite content in the sample decreases.

The D band (1330-13600 cm^{-1}) is directly related to structural disorder coming from amorphous carbon and defects [20, 21]. D″ appears near 1500 cm^{-1} wave number and is related to stacking defects in the graphene layer [18]; after the plasma treatment the area of this band increased considerably. I band was more prominent around 1230 cm^{-1} after nitrogen plasma treatment and is attributed to impurities in the graphite lattice and incorporation of nitrogen in CNTs [17]. After the plasma treatment a very small shift in the D band position of nitrogen-CNTs was observed, because the treatment is mainly specific to removal of amorphous carbon.

The ratio between D and G bands $R = I_D/I_G$ is used to evaluate the extension of defects on the surface of CNTs [22] when the number of structural defects decreases, so does the ratio between D and G bands. The ration after the nitrogen plasma treatment increases from 1.05 to 1.09. Figure 3 shows the corresponding G and D peaks for untreated and plasma-treated samples grown by PECVD.

The intensity between the G and D peaks before and after the treatment resulted to be quite similar. This strongly suggests that our carbon nanotubes are characterized by high structural defects.

3.3. Electrochemical characterization

Electrochemical properties analysis of MWCNTs before and after the nitrogen plasma treatment indicates that nitrogen functionalities enhance the charge storage properties of the CNTs in accordance with previous results [17]. Specific capacitance of the samples was calculated from the cyclic voltammograms using equation (1)

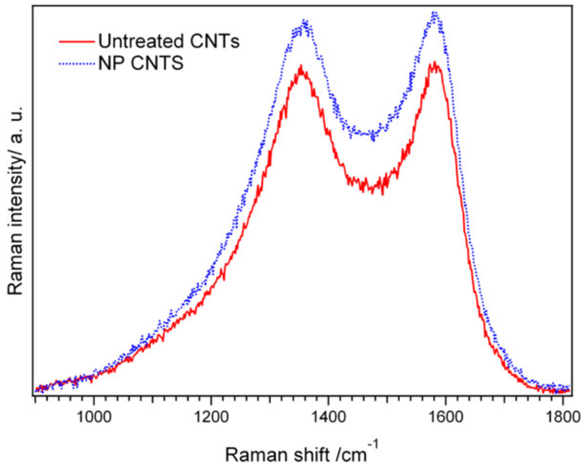

Figure 3. Raman spectra of samples treated (NP) and untreated with nitrogen plasma.

$$C_s = \left(\frac{q_a + |q_c|}{2m\Delta V}\right) \tag{1}$$

Where C_s is the specific capacitance in $F \cdot g^{-1}$, ΔV is the voltage window in V and m is the mass of the active material in g, q_a and q_c are the anodic and cathodic charge in C, respectively.

The wettability is further improved through the removal of amorphous carbon by the plasma, the production of numerous defects sites and the introduction of new functional groups such as quaternary and pyrrolic-like nitrogen introduced by the treatment, allowing the increase of CNTs charge storage capability, as shown in a previous study [17]. Therefore, the specific capacitance increases from $44\,F \cdot g^{-1}$ for untreated MWCNTs up to $137.6\,F \cdot g^{-1}$ for nitrogen plasma treated MWCNTs.

Figure 4(a) shows the specific capacitance at different scan rates, in which the specific capacitance of nitrogen-plasma treated sample at $10\,mVs^{-1}$ scan rate is almost three times higher than for the untreated sample. The enhanced capacitance of the treated CNTs may come on the one hand, due to the removal of amorphous carbon that increases the surface area and, on the other hand, due to plasma etching that increases the number of defects on the CNTs surface. Figure 4(b) shows cyclic voltammograms of treated and untreated samples at a scan rate of $150\,mVs^{-1}$.

Untreated CNTs present quite regular curves, with the typical rectangular shape characteristic of the ideal double layer capacitor behaviour without Faradaic reactions [23]. On the other hand, the voltammograms for the nitrogen plasma treated sample show a slight deviation from this shape, which is related to the contribution of pseudo capacitance in the total capacitance of the electrode [16]. In addition, the deposition of a thin supporting oxide layer (Al_2O_3) shows an increase in the specific capacitance (see table 1). Therefore, a significant improvement in capacitance and adhesion is obtained when using HF acid and Al_2O_3 in combination.

Furthermore, both electrodes show regular shaped cyclic voltammograms without clear redox peaks at different scan rates (from $10\,mVs^{-1}$ to $150\,mVs^{-1}$), which is important for super capacitive applications (see figure 4(c))

The cycling stability of the obtained electrodes was studied applying galvanostatic charge/discharge cycles with a constant current density of $0.5\,mA\,cm^{-2}$ in a potential window from 0 to

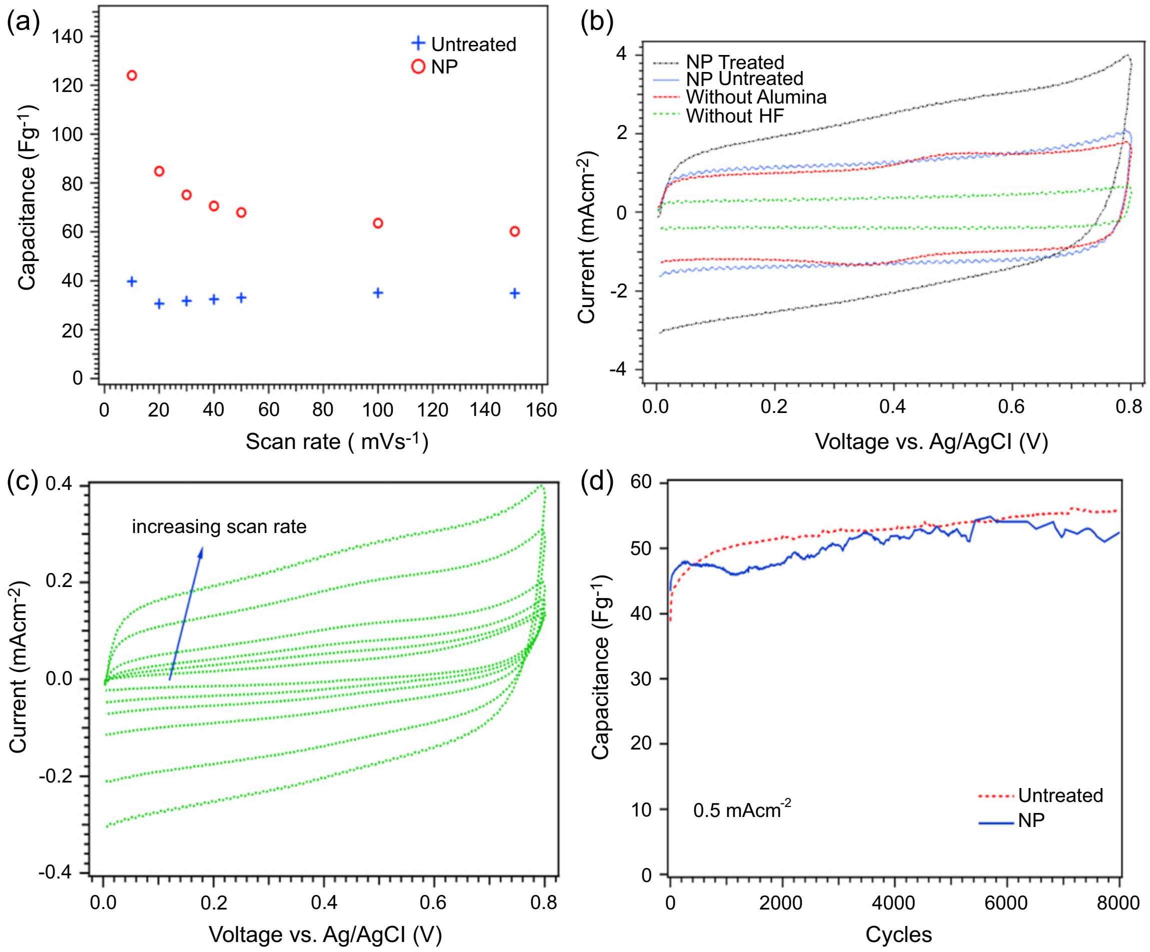

Figure 4. (a) Specific capacitance at different scan rates, (b) comparison between the cyclic voltammograms of PECVD samples treated (NP) and untreated with nitrogen plasma at scan rate of 150 mV · s^{-1}, (c) cyclic voltammetry of nitrogen plasma treated CNTs at different scan rates (10, 20, 30, 50, 100, 150 mVs^{-1}), (d) charge discharge cycling stability of untreated and nitrogen plasma treated CNTs.

Table 1. The capacitance of EDLC made from carbon nanotubes.

Sample	Capacitance Fg^{-1}
No HF acid, with Al2O3	11,68
No Al2O3, with acid	35,5
SS treated, NP untreated	44,1
SS treated, NP treated	137,6

0.8 V during 10 000 cycles. The specific capacitance was calculated from the discharge curve using equation (2).

$$C_s = \left(\frac{I}{(\Delta V/\Delta t)\cdot m}\right) \tag{2}$$

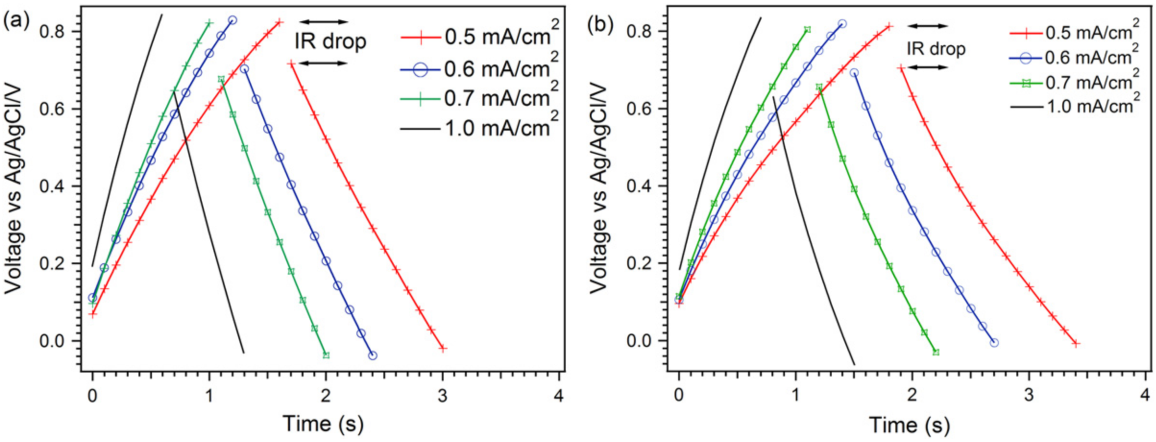

Figure 5. Charge/discharge curves at different current densities, (a) for untreated CNTs (b) for nitrogen plasma treated CNTs.

Where C_s is the specific capacitance in Fg^{-1}, ΔV is the voltage during the discharge curve in V, I is the current in A, t is the discharge time in s, and m has the same meaning and units as in equation (1).

Figure 4(d) shows the cycling stability of CNTs electrodes in the voltage range of 0 to 0.8 V at a current density of $0.5\,\mathrm{mA\,cm^{-2}}$. As observed, there is a rise in the capacitance after some cycles. This initial increase in capacitance with cycle number is due to electrochemical oxidation processes at the CNTs surface that convert them from a hydrophobic to a hydrophilic state [24]. It is evident that there is almost no decrease in capacitance for both treated and untreated samples even after 8000 cycles. Figure 5 shows the cycling stability of nanocomposite electrodes.

4. Conclusions

A proper pretreatment of the SS substrate was found to be very important for the successful synthesis of CNTs. The role of HF acid is essential to improve the growth, capacitance and attachment of CNTs on SS substrate. Adhesion of the CNTs to the substrate improves after treating the SS substrates with HF acid and adding an Al_2O_3 layer of 20 nm that is required to support the metal catalyst. In addition, optimum size and distribution of catalyst nanoparticles for the CNTs growth was obtained for an annealing time of 875 s. Raman spectroscopy results show that structural disorder increases with nitrogen introduction. Electrochemical measures showed an increase in the specific capacitance after nitrogen plasma treatment from 44 to $137\,\mathrm{F \cdot g^{-1}}$ which is maintained even after 8000 cycles. This enhanced capacitance is achieved by the introduction of new functional groups, which improve the wettability and increase the number of the defects sites on the CNTs, as well as an increase of the electrode surface area.

Acknowledgments

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