Investigation the effect of polyaniline modification of Carbon nanotubes/Nickel Foam based electrodes using in supercapacitors

F. Hekmat [a], B. Sohrabi[*, a], M. S. Rahmanifar [b]

[a] Department of Chemistry, Surface Chemistry Research Laboratory, Iran University of Science and Technology, P.O. Box 16846-13114, Tehran, Iran.
[b] Faculty of basic science, Shahed University, Tehran, Iran.

Abstract: supercapacitive performances of carbon nanotube (CNT) based electrodes, before and after electrochemical deposition of polyaniline (PANI) were compared. The PANI modified CNT/Nickel foam based electrodes were compared with the bare carbon nanotubes/Ni foam based electrodes. The modified electrode prepared by coating CNT based electrodes which were directly grown on a Ni-foam framework by a Chemical Vapor deposition (CVD) technique. The PANI modified electrode exhibits better capacitive performance and lower internal resistance than the bare CNT/Ni foam electrode. The specific capacitance of this CNT/PANI based electrode is 70 F/g which is 37 percent higher than the value of the CNT/Ni foam electrode before deposition of PANI. This work proposes that modification CNTs with PANI is a simple, effective and economical approach for preparing a suitable supercapacitor electrode which possess enhanced capacitance and rate performance.

Keywords: Supercapacitors, Carbon nanotubes, Polyaniline, Chemical vapor deposition

Introduction: Supercapacitors are expected to play a significant role in future hybrid electric vehicles, diesel engine starting systems, cordless power tools, and emergency safety systems, due to their high specific power, larger cycle life, low toxicity materials, operation over a wide temperature range, low cost per cycle, and tolerance of extreme environmental conditions [1, 2]. In contrast to batteries, supercapacitors generally store energy by highly reversible separation of electrical charge while batteries use chemical reactions.

Since their discovery in 1997 [3], electroactive polymers have attracted considerable attention as a family of novel organic electrochemical materials. Able to store and release charge during their redox processes, electroactive

polymers have been investigated for energy storage technologies including supercapacitors [4, 5]. In order to improve the electrochemical utilization (and hence capacitance) and rate capability of electroactive polymers nanostructures have been developed in these electrode materials. Specially, incorporating CNTs and electroactive polymers to fabricate nanocomposites is an efficient approach to fulfill this goal. Combining the pseudocapacitance of electroactive polymers with the high conductivity and high mesoporosity of CNTs, the resultant CNT/electroactive polymer nanocomposites possess enhanced capacitance and rate performance. In this study, CNT based electrodes were investigated and the characteristics before and after deposition of PANI.

Experimental:

Electrodes:

First, Ni foam with dimensions of 1cm*1cm*1.5mm (purchased from Wuzhou HGP Advanced Materials Technology corp., Ltd) was degreased in acetone ultrasound and rinsed in ethanol solution, then dried. The CNTs were synthesized directly on Nickel foam in a quartz tube furnace chemical vapor deposition (CVD) system using an easy single step approach. The Ni were reduced in a gas mixture of 10% Hydrogen and 90% Argon at 500 °C for 1 hr. CNTs were then grown by catalytic pyrolysis of 10% acetylene and 20% hydrogen in an Argon carrier gas for 10 min at 650 °C in a quart tube reactor. The grown CNTs on Ni foam framework (Ni foam-CNTs) were directly used as an electrode for making supercapacitors. To preparing another electrode, the PANI film was electrochemically deposited on Ni foam-CNT electrode applying at 50 mV/s in the 0.1 M aniline solution containing 0.3 M oxalic acid. The growths of PANI film were carried out in the potential range between 0.25 and 1 V applying 5 cycles [6]. Finally, after film growth, the PANI coated electrodes were rinsed with doubly-distilled water and then dried in air. The grown CNT/PANI composites on Ni foam framework (Ni foam-CNTs) were directly used as an electrode for making supercapacitors.

Experimental techniques and instrumental details:

The microstructure was observed by using a scanning electron microscope (SEM) (TESCAN, VEGA, Czech Republic). Different electrochemical techniques were used to characterize the capacitive performance, and internal resistance of supercapacitor electrodes. Electrochemical characterizations were carried out by an electrochemical

workstation (electroanalyzer system SAMA 500, Iran) in 1M Na_2SO_4 aqueous solution (pH=5) at room temperature in a three electrode configuration using a saturated Ag/AgCl as the reference electrode and a graphite counter electrode. The electrochemical impedance spectroscopy (EIS) measurements were conducted by a Auto lab PGSTATE 30 model controlled by computer and Nova 1.7 software, applying an alternating current in the frequency range from 10 kHz to 0.1 Hz with 14 mV amplitude on the dc voltage of -0.4 V.

Result and discussion

The PANI film growth recorded on CNT/Ni foam based electrode in 0.1M aniline containing oxalic acid solution (0.3 M) were shown in Fig. 1.

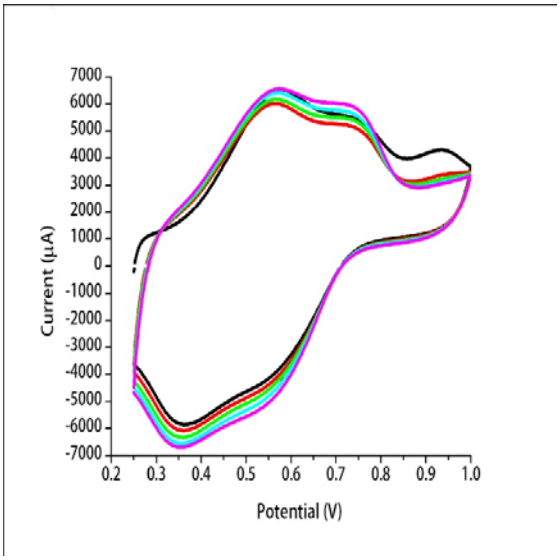


Fig. 1. The polymer film growth on CNT/Ni foam based electrode in 0.1M aniline containing oxalic acid solution (0.3 M), scan rate: 50mV/s.

Fig. 2a shows the SEM images of CNTs directly grown on porous Ni foam. Obviously, the entangled CNTs were well grown on the surface of Ni foam framework.

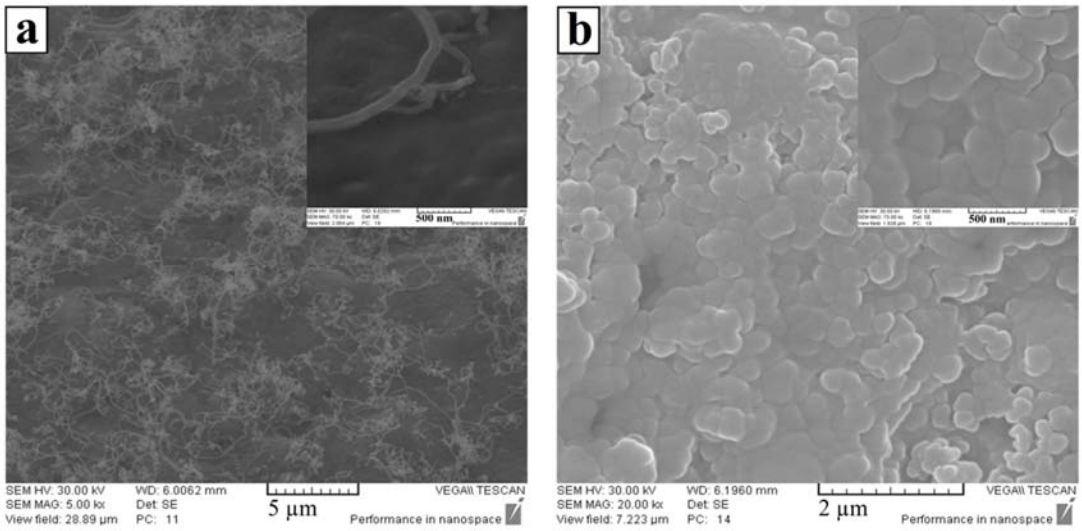
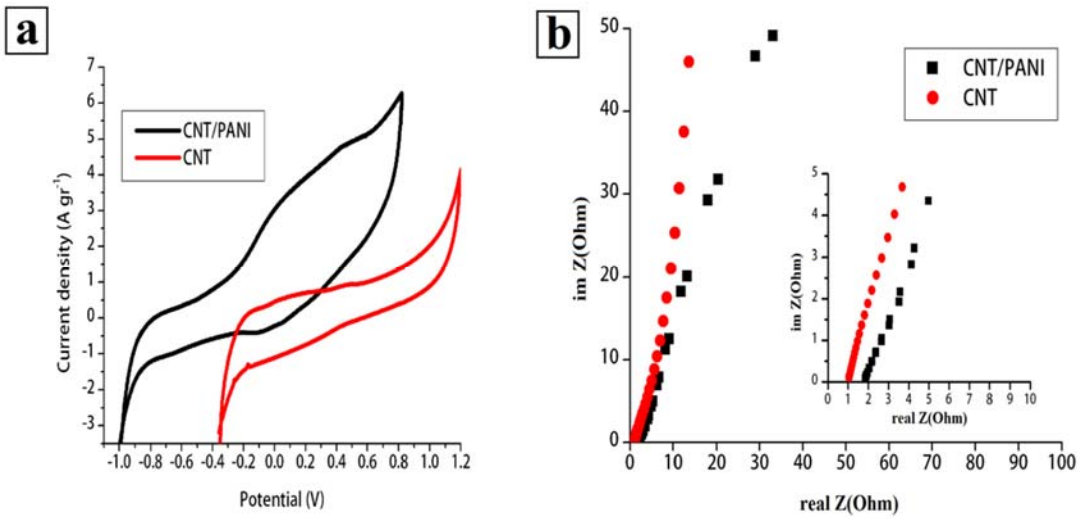


Fig. 2. (a) SEM morphologies of CNTs grown on the Ni foam, inset: high magnification of CNTs which shown in Fig. 1a. (b) SEM images of PANI where electrochemically deposited on CNT/Ni foam, inset: high magnification of PANI deposited on CNTs

Fig. 3a illustrates the CV curves of as prepared electrodes. Voltagrams present regular shapes at relatively high scan rate (100 mV/s), indicating well-developed capacitive properties. The electrode which modified by PANI exhibits higher specific capacitance (70 F/g), because its CV curves cover a much larger area, compared to another electrode (51.7 F/g). Fig. 2b shows the Nyquist plots indicated that the electrode which is modified by PANI exhibits higher internal resistance (~ 1.87 Ω/cm^2), than another electrode (~1.04 Ω/cm^2).



Fiq. 3. (a) CV curves taken at 100mV/s; (b) Nyquist plots (0.01 ~ 100000 Hz), inset is a local amplified image at high frequencies.

The above experimental results indicate that the electrode with the Ni foam-CNT/PANI has a significant high specific capacitance. This can be mainly attributed to the combination of the pseudocapacitance of electroactive polymers with the high conductivity and high mesoporosity of CNTs, the resultant CNT/electroactive polymer nanocomposites possess enhanced capacitance and rate performance.

Conclusions

In conclusion, the present process provides an effective approach for improving the capacitive performance of CNT based electrodes, which were directly deposited on current collector in a simple way. It presents higher electrochemical capacitance and better capacitive performance at very high current densities.

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