



# Modified iron doped polyaniline/sulfonated carbon nanotubes for all symmetric solid-state supercapacitor



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## ABSTRACT

Electrode materials based on iron doped polyaniline (Fe-PANI) over the surface of sulfonated multi-walled carbon nanotubes (s-MCNTs) followed by freeze-drying treatment (FD-Fe-PANI@s-MCNTs) are dedicated for high performance electrochemical energy storage applications. The structure, morphology and thermal properties of the studied electrode samples are measured with different characterizing techniques. The N<sub>2</sub> sorption isotherm for (FD-Fe-PANI@s-MCNTs) shows high specific surface area 397.79 m<sup>2</sup> g<sup>-1</sup> calculated by Brunauer-Emmett-Teller (BET) method after the freeze-drying treatment. The electrochemical properties of the electrode samples are assessed by cyclic voltammetry and galvanostatic charge/discharge testes in the 1 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. The (FD-Fe-PANI@s-MCNTs) electrode with this high surface area shows high specific capacitance of 2105.64 F g<sup>-1</sup> at 1 A g<sup>-1</sup>. The symmetric solid-state supercapacitor device (SCs) based on (FD-Fe-PANI@s-MCNTs) electrode gave a specific capacitance of 776.85 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, energy density 13.55 Wh kg<sup>-1</sup>, power density 177.50 W kg<sup>-1</sup> and exhibit rate capability (≈ 59% retention at 20 A g<sup>-1</sup>). Furthermore, the symmetric supercapacitor device shows good cycling stability (91.6%) after 500 cycles at a scan rate 200 mV s<sup>-1</sup>, suggesting the potential application of (FD-Fe-PANI@s-MCNTs) for energy storage devices.

## 1. Introduction

High rate growth of consumer electronics sector led to an increasing demand for developing high efficient, low-cost and environmentally friendly energy storage devices [1–6]. Supercapacitor or ultra-capacitor can be considered the bridge between the batteries and traditional dielectric capacitor; they have high energy density than traditional capacitor but still lower than conventional batteries [7,8]. The ultra-capacitor can be divided into two basic types, non-Faradic electric double-layer capacitor (EDLCs) usually depending on carbon based materials and store energy physically according to electrostatic adsorption of accumulated charge [9–12], and Faradic pseudocapacitors (PCs) which can store energy chemically by redox reactions of materials in aqueous and non-aqueous electrolyte such as transition metal oxides and conducting polymers [13–15]. Conducting polymers, such as polythiophene, polyaniline, PEDOT, polypyrrole and other  $\pi$ -conjugated conducting polymers [16] have high electrochemical activity can widely be utilized as electrode materials in supercapacitor applications [17–19].

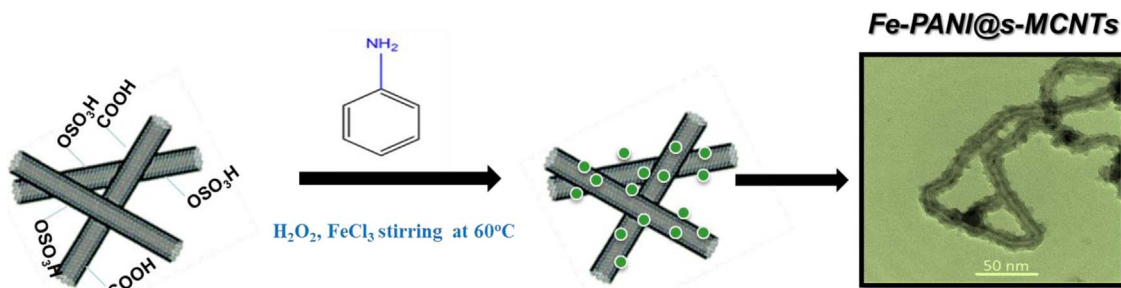
Among conducting polymers, polyaniline is considered as one of the

most promising materials in the area of energy storage applications, due to their controllable structure, low cost, environmental stability and easy handling [1,5,20,21]. The capacitive behavior in conducting polymers can be attributed to the reversible electrochemical doping-dedoping process which lead to store and release a lot of charge [22,23]. Indeed, when oxidation occurs, ions are transferred from the electrolyte to the polymer backbone. Then, when the reduction occurs the ions are released from this backbone into the electrolyte again; which means that the redox reaction in conducting polymer occurs throughout the bulk structure of the polymer and not just on the surface as in EDLCs [24,25]. So that, the specific capacitance of conducting polymers such as polyaniline is expected to be higher than any carbon-based materials which represented the EDLCs, while the carbon-based materials such as CNTs provide high electrochemical stability [26,27]. In this regards, the hybrid system which is consisting of polyaniline and carbon-based materials such as CNTs and graphene can provide high specific capacitance with high durability [28–34].

Nevertheless, the solubility of carbon nanotubes in water and other polar solvent provide a homogeneous dispersion of CNTs in polymer matrix such as polyaniline resulting in improve the electrochemical

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**Scheme 1.** Schematic diagram representing the one-pot formation of iron-doped polyaniline over the surface of sulfonated multi-walled carbon nanotubes (Fe-PANI@s-MCNTs).

properties of the hybrid material than pure one [34]. Sulfonic acid group is considered a promising functional group in the field of energy-storage [35], due to high proton conductivity and strong acidic than carboxylic group which provide a high solubility in polar solvent [36–38].

Here in, based upon the above considerations a simple and efficient synthetic method is followed for the formation of iron doped protonated polyaniline over the surface of multi-walled carbon nanotubes functionalized by sulfonic acid ( $\text{SO}_3\text{H}$ ) groups. The sulfonated multi-walled carbon nanotubes (s-MCNTs) were performed by one-pot synthesis method. After that, the aniline monomer is oxidized by using  $\text{H}_2\text{O}_2$  and transition metal catalyst ( $\text{FeCl}_3$ ) in the presence of functionalized multi-walled carbon nanotubes under acidic condition, resulting in the formation of Fe-doped protonated polyaniline at warm temperature over the surface of carbon nanotubes (Fe-PANI@s-MCNTs). This shows that, (i) the metal ion ( $\text{Fe}^{3+}$ ) acts as a conducting tunnel for charge transfer between polyaniline and s-MCNTs, and (ii) further improves the conductivity of the electrode material. Finally, the freeze-drying treatment was carried out to the above products to get high surface area of the nano composite and improve the electrochemical performance.

## 2. Experimental

### 2.1. Materials

The aniline monomer (99%), analytical grade  $\text{H}_2\text{SO}_4$  (98%),  $\text{HNO}_3$  (55%),  $\text{H}_2\text{O}_2$  (30%) aqueous solution, Xylene and HCl (33%) were purchased from El-Nasr Pharmaceutical company, Egypt. Anhydrous iron (III) oxide was purchased from (SRL 98%, India) and (DMF) Dimethyl formamide was purchased (S D Fine-Chem Limited, India). Finally, the Ferrocene was purchased from (Sigma-Aldrich). The aniline monomer was purified prior to use and all the remaining reactants were used as received.

### 2.2. Synthesis of sulfonated multi-walled carbon nanotubes (s-MCNTs)

Firstly, the MCNTs was synthesized by the floating catalyst chemical vapor deposition (FCCVD) method by using Ferrocene as a catalyst and xylene as a hydrocarbon source in the presence of Argon as a carrier gas. For further details see elsewhere [39,40]. The purification and functionalization process was done by one-step chemical reaction method started by 1 g from as-prepared MCNTs was mixed with 200 ml of ( $\text{H}_2\text{SO}_4/\text{HNO}_3$  3:1) solution by ultrasonic bath for 4 h at room temperature. After that, the reaction solution was diluted by adding 200 ml from warm distilled water and heated at  $100^\circ\text{C}$  for another 4 h with magnetic stirring and rest to be cooling for 24 h see (Fig. S1, Supplementary file). Finally, the precipitate was filtered and washed by distilled water several time and dried at  $80^\circ\text{C}$  for 24 h to get multi-walled carbon nanotubes functionalized by sulfonic acid groups (s-MCNTs).

### 2.3. Synthesis of iron-doped PANI (Fe-PANI) and iron-doped PANI at the surface of sulfonated multi-walled carbon nanotubes (Fe-PANI@s-MCNTs)

The Fe and  $\text{H}^+$  co-doped polyaniline was prepared by oxidative polymerization method of aromatic aniline monomer by using anhydrous iron (III) chloride as a mild oxidizing agent in the presence of  $\text{H}_2\text{O}_2$ . Typically, aniline monomer (10.9 mmol) was dissolved in  $1\text{ mol L}^{-1}\text{HCl}$  and heated at  $60^\circ\text{C}$  for half an hour with continuance magnetic stirring. After that,  $\text{H}_2\text{O}_2$  (0.1625 mol) was added slowly to the above mixture followed by adding anhydrous iron (III) chloride (4.93 mmol) with continuance stirring overnight at room temperature. The final filtered precipitates were carefully washed with distilled water several times until the filtrate turned clear and get finally (Fe-PANI) sample see (Fig. S2). While, for iron doped polyaniline at the surface of sulfonated multi-walled carbon nanotubes (Fe-PANI@s-MCNTs) a certain amount of s-MCNTs and the remaining weight from the aniline monomer were dispersed in  $1\text{ mol L}^{-1}\text{HCl}$  by using ultrasonic bath for 15 mints and heated at  $60^\circ\text{C}$  for 30 mints with continuance magnetic stirring. After that, continue with the same procedure like in (Fe-PANI) to get finally (Fe-PANI@s-MCNTs) sample see [scheme 1](#).

### 2.4. The freeze-drying treatment (Lyophilization process) of iron doped PANI at the surface of sulfonated multi-walled carbon nanotubes (FD-Fe-PANI@s-MCNTs)

In a typical, a mixture of Fe-PANI@s-MCNTs and distilled water was prepared by ultrasonically for a few minutes in ultrasonic bath followed by stirring for 1 h to get a homogenous mixture then the mixture was frozen in a cold bath by using liquid nitrogen to start the drying process. In this condition, the solvent was sublimated by using a vacuum pump for a day to get finally (FD-Fe-PANI@s-MCNTs) see [Scheme 1](#).

### 2.5. Materials characterizations

The microstructures were examined with a high-resolution transmission electron microscope (HR-TEM, FEI Philips Tecnai G2 S-Twin operated at 200 keV, Holland) and by field emission scanning electron microscope (Quanta-FEG 250, FEI Company, Holland) equipped with Energy-dispersive X-ray analysis (EDX). The crystal structure of the samples was characterized using X-ray diffractometer (Philips PW3050/60) with a  $\text{Cu-K}\alpha$  X-ray source. Infrared transmission spectra were taken by FT-IR spectrometer (Vertex 70–Bruker, Germany). Raman spectra of the obtained samples were recorded by using (SENTERRA – Bruker, Germany) with laser source (Nd:YAG) at wavelength 532 nm. The weight loss of the samples was collected by TGA thermal analyzer (STD-Q600, USA).  $\text{N}_2$  sorption isotherms were measured for all samples at 77.35 K on NOVA 2000e (Quantachrome, USA). The specific surface area of the samples were calculated by using Brunauer-Emmett-Teller (BET) method and the pore-size distribution curves were obtained from Nitrogen desorption isotherm by using Barrett-Joyner-Halenda (BJH) method.

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