



# Preparation of carbon nanotube-activated carbon hybrid electrodes by electrophoretic deposition for supercapacitor applications

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## ABSTRACT

This study examines the possibility of preparing activated carbon (AC) and carbon nanotubes (CNT) based electrodes for supercapacitors by a facile electrophoretic deposition (EPD) method. The EPD method is able to deposit AC and CNTs on a stainless steel substrate, fabricating a three dimensional porous structure. The weight proportions of CNT to AC in the as-prepared electrodes are estimated by thermogravimetric analysis. The amount of CNTs in the electrodes can be easily controlled by tuning the solution bath composition before the EPD process. The effects of the presence of CNTs in the AC electrode on supercapacitor performance are also examined in this work. The addition of CNTs not only increases the specific capacitance but also enhances the rate capability of the AC electrodes. After a cyclic stability test for 11,000 cycles, the as-prepared AC/CNT electrode shows capacitance retention of 85%, clearly demonstrating the commercial applicability of the electrodes fabricated by EPD process.

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## 1. Introduction

As a result of the continuing drive to the development of renewable energy sources, developing electric vehicles, hybrid electric vehicles and power saving devices is the priority now. In order to back-up the development, more effective energy storage devices like batteries and supercapacitors are expected to become more efficient [1]. With their high energy and power density and long cycle life, supercapacitors have the potential to bridge the gap between traditional batteries and dielectric capacitors [2–4]. Basically, there are two kinds of supercapacitors: (i) electrochemical double layer capacitors (EDLC) and (ii) pseudo-capacitors [5]. EDLCs mainly consist of porous carbon materials and offer better power density and longer cyclic stability, but suffer from low energy density [6]. On the other hand, pseudo-capacitors are metal oxides or conducting polymer based, characterized by high energy density, but show low cyclic stability and poor power density [7].

Activated carbon (AC) has been in use as an EDLC electrode material for a long time because of its high capacitance, low cost and long cycle life [8–12]. In AC, an electrical double layer of charges are formed at the AC/electrolyte interface; there is no significant faradaic reaction. However, AC has drawbacks of poor rate capability because of its microporous structure and low conductivity [13]. To alleviate this problem, some groups have developed electrodes consisting of AC mixed with a small amount of carbon nanotubes (CNTs) [14]. Recently, CNTs have

been extensively used as an electrode material for supercapacitors because of their high conductivity, stability, low density and narrow pore size distribution [15–21]. However, CNTs show a poor specific capacitance mostly due to their low specific surface area [8,13].

Unlike previous reports, this study adopts an electrophoretic deposition (EPD) method to fabricate AC/CNT electrodes. In an EPD process, the electrode current collector is immersed in colloidal solution of the nano-materials. The charged nano-materials are deposited continuously on the current collector as a voltage difference is applied across it. The EPD method has some major advantages over other coating techniques, making it a very attractive synthesis method for preparing supercapacitor electrodes in recent years. Firstly, it is a very simple process requiring just a DC current source and one solution bath container; secondly, the EPD process takes place at ambient temperature; thirdly, the process is cheap and scalable to industrial production [22–23]. Another advantage of EPD processes is that it allows dispersing different nano-materials very uniformly on the electrode, whereas other methods like slurry coating and spin coating show poor dispersion resulting from poor dispersibility of nano-sized materials in slurry composing of solvent, nano-materials, polymer binders and conducting agents [24–25]. Lastly, having no binding material in the EPD made electrode not only reduces the cost but also ensures no unwanted blockage in the microporous materials.

In this research, we report the fabrication of AC-based electrode by EPD method for the first time. The effects of adding CNTs in the AC structure in EPD process have also been discussed. This study will open the pathway for EPD to fabricate AC/CNT-based electrode for high-performance supercapacitors.

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## 2. Experimental section

The commercial AC powder used here was purchased from the First Chemical Group (Taiwan). Multi-walled CNTs were procured from Taiwan Maxwave Co. Ltd. All other chemicals such as magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ), nitric acid ( $\text{HNO}_3$ ), and ethanol were reagent grades and used as received.

Herein AC powder and CNTs were pretreated according to the following procedure: first, 500 mg of carbon samples (*i.e.*, AC or CNTs) were stirred in 1000 ml of 1 M  $\text{HNO}_3$  at 95 °C for 2 h. Then, the suspension was vacuum filtered with a filter paper and the obtained slurry was washed with deionized water until the pH becomes 7. Lastly, the carbon powders were dried in a vacuum oven overnight. The solution bath for the EPD contained 12 mg of AC and CNTs with varying proportions, 14 mg of  $\text{Mg}(\text{NO}_3)_2$  and 50 ml of ethanol. Herein  $\text{Mg}(\text{NO}_3)_2$  served as a charging agent. Prior to the EPD process, the solution bath underwent 1 h of sonication treatment. In the present work, 2 cm by 2 cm of stainless steel foils (SS) were used as current collectors for the electrodes. The SS foils were also given a sonication treatment in acetone for 1 h so as to remove any oil from the surface. EPD was carried out by applying a voltage of 100 V, using the SS current collector as the negative electrode and another SS foil of the equal size as the positive electrode. Deposition time was set to 5 min for making each electrode. After the EPD process, the electrodes were dried in an oven and then given a heat treatment at 300 °C in nitrogen environment for 1 h. For identification, electrodes prepared from solution baths containing 50% and 25% CNTs content are designated as AC-CNT-1 and AC-CNT-2, respectively. In order to calculate the specific capacitance of AC in AC/CNT electrodes, an electrode containing solely CNTs was also prepared by the same method. To find out whether EPD method can retain the capacitance of the active material, one AC electrode was made by dropping ethanol containing AC particles on a carbon paper. This electrode had a weight loading of 1.5 mg  $\text{cm}^{-2}$  and had no binder material. The electrode is designated as AC-D.

To estimate the individual weight loading of AC and CNTs in AC-CNT-1 electrodes after EPD, two separate solution baths, one containing solely AC (12 mg of AC/50 ml of ethanol) and another containing solely CNTs (12 mg of CNTs/50 ml of ethanol) were prepared. Then, AC and CNTs were deposited by EPD method on separate SS foils with different deposition times. The weights of the AC and CNT electrodes were taken with a scale (Mettler Toledo AX205, Switzerland) of high precision ( $\pm 0.1$  mg). Herein 5 samples of each type were prepared with different deposition times.

The weight proportions of CNTs in different electrodes were estimated with a thermogravimetric analyzer (TGA, Perkin Elmer TA7). The TGA samples were collected by mildly scratching the electrode. Prior to the experiment, the samples were washed in nitric acid so as to remove any Mg. The experiments were carried out under air atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$ . The crystalline structure of the as prepared AC/CNT electrode material was analyzed by X-ray diffraction (XRD) with  $\text{Cu-K}\alpha$  radiation, using an automated X-ray diffractometer (Shimadzu Labx XRD-6000). In order to remove interference from the SS current collector during XRD, the electrode materials were carefully scratched off the SS foil. Scanning electron microscopy (FE-SEM, JEOL 2010F) was used to examine the morphology and structure of the as prepared electrodes.

The electrochemical performance of the AC/CNT electrode was studied by a three-electrode system with 1 M  $\text{Li}_2\text{SO}_4$  electrolyte at ambient temperature, where a Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. Cyclic voltammetry (CV) was conducted within the voltage window of  $-0.2$  to 0.6 V at scan rates ranging from 5 to 100  $\text{mV s}^{-1}$ . The galvanostatic charge and discharge (GCD) cycle was also conducted at different current densities (*i.e.*, 100–2000  $\text{mA g}^{-1}$ ). The specific

capacitances of the electrodes were calculated from CD curves by using the following equation

$$C_s = \frac{i\Delta t}{m\Delta V} \quad (1)$$

where  $C_s$  is the specific capacitance,  $i$  is the current density in GCD test,  $\Delta t$  the discharge time,  $m$  the mass of carbon in the electrode and  $\Delta V$  the potential window. In order to examine the behavior of the electrode at different alternating current frequencies, electrochemical impedance spectroscopy (EIS) was carried out with an electrochemical impedance spectroscopy analyzer (CH Instrument, Inc., CHI 608) within the frequency range of 0.01 Hz to 100,000 Hz.

## 3. Results and discussion

### 3.1. Characterization of AC-CNT electrodes

Electrode material prepared by EPD of pure AC, pure CNTs and mixture of AC/CNTs (AC-CNT-1) were characterized by XRD. Fig. 1 shows the XRD patterns of the electrodes. Electrode material composing AC shows amorphous pattern, since AC has very limited crystallinity. On the other hand, AC-CNT-1 and pure CNT electrodes show the (002) diffraction peak of CNTs at  $2\theta = 26.2^\circ$ , corresponding to d-spacing distance of 0.34 nm. The (002) diffraction peak from AC-CNT-1 electrode is not only a little weaker, but also broader than that of pure CNTs, confirming a successful deposition of amorphous AC and crystalline CNTs on the SS foil.

Fig. 2 presents the FE-SEM images of the CNT, AC-CNT-1 and AC-CNT-2 and AC electrodes. Fig. 2(a) shows the CNTs deposited by EPD. The CNTs are 30–40 nm in diameter and several micrometers in length.

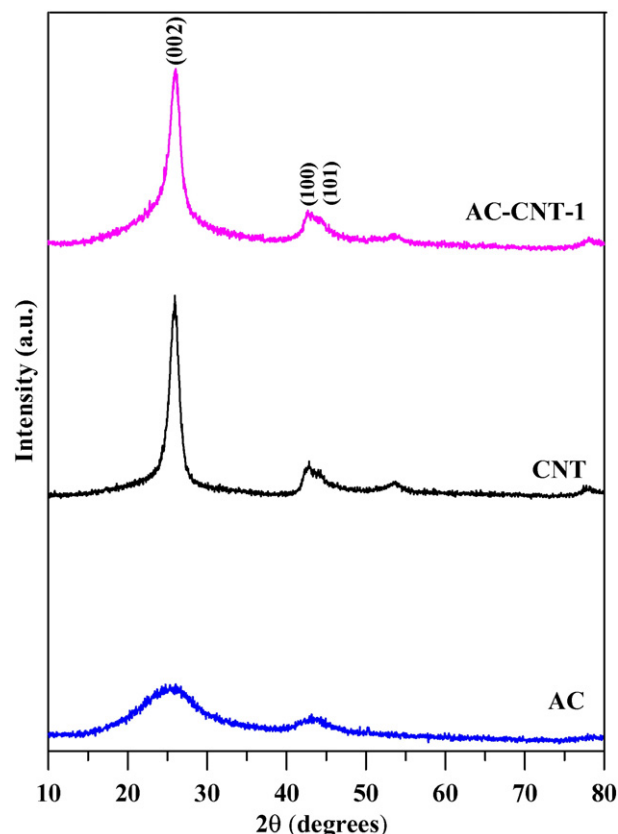


Fig. 1. XRD patterns of neat AC, neat CNT and AC-CNT-1 electrode materials.

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