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# Independently double-crosslinked carbon nanotubes/polyaniline composite films as flexible and robust free-standing electrodes for high-performance supercapacitors

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Flexible free-standing materials make the electrode fabrication process simple in comparison with the conventional binder-enriched electrodes, especially for those with desirable mechanical strength. In the present work, the crosslinked multi-walled carbon nanotubes (C-CNTs) films with tensile strength of >1.75 MPa, were prepared by facile filtering the dispersion of the micrometer-scaled 3-D framework of crosslinked carbon nanotubes with common water pump, and used as high-strength conductive skeleton for polyaniline (PANI). The preparing conditions were optimized for the best electrochemical property of the flexible C-CNTs/PANI composite films. As free-standing electrodes for supercapacitors, the highest specific capacitance of 507 F/g or 314 F/g, energy density of 70.4 or 43.6 Wh/kg and power density of 0.44 or 0.43 kW/kg were achieved with the *in-situ* chemical oxidative polymerization or solution coating technique, respectively. Then the independently double-crosslinked carbon nanotubes/polyaniline (C-CNTs/TC-PANI) composite films were obtained by thermal crosslinking (TC) the PANI coatings in the C-CNTs/PANI films. Their specific capacitance, energy density, and power density increased to 531 F/g and 455 F/g, 73.8 and 63.2 Wh/kg, 0.49 and 0.47 kW/kg with the *in-situ* chemical oxidative polymerization or solution coating technique respectively, and their electrochemical cyclic stability was also enhanced distinctly.

## 1. Introduction

Energy has become one of the biggest challenges due to the almost running out of fossil fuels and the increasing environmental pollution. New clean energy systems such as solar and wind energies have attracted considerable attention for electric power generation all over the world [1]. Owing to their distributed generation model, the storage of the excess power is desired to make such new energy sources completely reliable as primary ones [2].

Among numerous electrochemical energy storage devices, supercapacitors (also named electrochemical capacitors or ultracapacitors), have been intensively studied as an important class of promising clean and sustainable ones, due to their high power density and cycle efficiency, and long cycle life [3]. Based on their charge-storage mechanism, they are broadly classified into two categories: electrochemical double-layer capacitors (EDLCs) storing and releasing energy by nanoscopic charge separation at the interface of carbon electrode/electrolyte and pseudocapacitors with certain electrodes (such as metal oxides or conducting polymers) associated with electrosorption and surface redox processes [3]. In general, EDLCs possess excellent cycle life but lower specific capacitance, while pseudocapacitors present much higher specific capacitance but poor cyclic stability [4]. Therefore, the conducting polymers have been crosslinked [5,6] or supported onto various inorganic nanomaterials (carbons [7–9], metal oxides [10,11] and others [12,13]) in order to improve their cyclic stability.

The electrochemical property of the nanocarbon/polyaniline composite electrodes has been obviously improved, owing to the synergistic effect between polyaniline (PANI) and the carbon nanomaterials [14,15]. However, the processability of conductive polymers is poor and the inorganic nanomaterials are easy to aggregate, as well as their composites. Furthermore, these nanocomposites are brittle, also limiting their application [16]. These shortcomings make the electrode fabrication process complicated,

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in which both support and binder are usually needed. As a result, it is difficult to control the microstructure of the resultant electrodes, so their electrical and electrochemical properties would be weakened [16,17]. To solve this matter, self-standing conductive polymer-based nanocomposite films have been fabricated as binder-free electrodes with enhanced pseudocapacitive performance, by depositing PANI onto free-standing carbon-based current collectors (such as carbon nanotubes (CNTs) paper [18], carbon nanofiber film [19], graphene hydrogel [20] or carbon monolith [21]), or layer-by-layer assembly [22,23], filtration [24], and solution casting [25] methods.

Unfortunately, most of them are brittle and easy to crack and/or collapse when they are being bended without supporter, due to their intrinsic porous structure and non-covalent interconnection. Developing flexible electrodes with reliable mechanical property is the key technical bottleneck which limits their practical application in supercapacitors [26], although lots of flexible electrodes with excellent electrochemical properties have been developed [27–32]. Graphene is easy to restack into graphite-like structured carbon-based thin film due to its atom-thick 2D carbon nanostructure owing to the strong $\pi$-$\pi$ interactions [33], so some excellent properties of graphene such as high specific surface area will be lost. Furthermore, the graphite-like structure is bad to its capacitance, because of the lack of electrically porous channel and insufficient Faradaic reaction. To achieve porous graphene-based film, templates have been usually added in the precursors and then removed to introduce the porous structure [34]. In comparison, it is easier to form porous films with CNTs as raw materials. By now, only few flexible electrodes with reliable mechanical property have been reported, with ultra-long CNTs [26] or nonwoven CNT fabric [35]. It is still a challenge to develop flexible electrodes with excellent mechanical and electrochemical performance via facile method with common CNTs to translate such potentials into reality.

It is realized that the robust scaffold and strong interaction between the current collector and electroactive materials are propitious to the mechanical properties of the electrodes [26]. Based on this principle, the independently double-crosslinked carbon nanotubes/polyaniline (C-CNTs/TC-PANI) composite films with crosslinked carbon nanotubes (C-CNTs) films as the high-strength conductive skeleton and thermal crosslinked polyaniline (TC-PANI) as skin, were designed for the first time as free-standing electrodes with good mechanical strength for high-performance supercapacitor by depositing PANI onto the as-prepared crosslinked carbon nanotubes (C-CNTs) films via *in-situ* chemical oxidative polymerization or solution coating technique, followed by thermal crosslinking the PANI coatings by simple thermal treatment (Fig. 1). The preparing conditions were optimized for the best electrochemical property in detail. The results indicated the independently double-crosslinked C-CNTs/TC-PANI composite films excellent candidate flexible free-standing electrodes for high-performance supercapacitors, with excellent comprehensive performance, including specific capacitance, electrochemical cyclic stability and mechanical properties.

## 2. Experimental

### 2.1. Materials and reagents

Multi-walled carbon nanotubes (L.MWCTs-60100 with diameter of 60–100 nm, length of 5–15 μm, and purity ≥95%) were obtained from Shenzhen Nanotech Port Co. Ltd. The filtering membranes (pore size: 0.45 μm; diameter: 50 mm) were purchased from Shanghai Mili Membrane Separation Technology Co., Ltd.

Aniline was purchased from Tianjin Chemical Reagent Co. Ltd. (Tianjin, China), and freshly distilled under reduced pressure prior to use. Other reagents were analytical reagent grade, and used directly. Doubly deionized water was used throughout.

### 2.2. C-CNTs films

The micrometer-scaled 3-D framework of crosslinked carbon nanotubes were prepared according to the previous work, via coupling the diazotized CNTs with 1,4-benzoquinone [36]. The crosslinked carbon nanotubes (C-CNTs) films were then prepared by facile filtering the dispersion of the micrometer-scaled 3-D framework of crosslinked carbon nanotubes with a common water pump: 6.0 mg/mL ethanol dispersion of the micrometer-scaled 3-D framework (10, 20, 30, or 40 mL) was filtered through filtering membrane, respectively. The corresponding film with initial volume of 10, 20, 30 or 40 mL of the dispersion was denoted as C-CNTs$_1$, C-CNTs$_2$, C-CNTs$_3$, or C-CNTs$_4$, respectively.

For comparing the mechanical strength, the CNTs film was also prepared with the same procedure with pristine CNTs (10 mL, 6.0 mg/mL in ethanol).

### 2.3. Free-standing C-CNTs/PANI composite films

The free-standing C-CNTs/PANI composite films were prepared by the *in-situ* chemical oxidative polymerization or solution coating technique, The PANI contents in the resultant C-CNTs/PANI composite films were measured with the gravimetric method, by weighing the products before and after polymerization or coating, respectively.

#### 2.3.1. In-situ polymerization

Aniline was firstly dissolved in 25 mL 1.0 M HCl solution in a three-neck flask. Then the C-CNTs films with the length of 10.0 mm and width of 5.0 mm were submerged into the mixture solution for 2 h. After cooling to 0 °C, 25 mL ammonium persulfate (APS, molar ratio of 1:1 to aniline) solution in 1.0 M HCl was added in the above solution drop by drop over 20 min. The reaction was conducted in ice-water bath for 24 h. The product was washed with excess water and then rinsed with ethanol for 12 h to completely remove any oligomers, and dried at 45 °C in vacuum overnight. The composite films were denoted as C-CNTs/PANI$_1$-1, C-CNTs/PANI$_2$-1, C-CNTs/PANI$_3$-1, and C-CNTs/PANI$_4$-1 with the increasing the feeding amount of aniline respectively (Table 1).

#### 2.3.2. Solution coating

Polyaniline (PANI) was synthesized via the chemical oxidative polymerization: aniline (0.36 mL) was dissolved into 25 mL 1.0 M HCl aqueous solution and stirred for 5 min. Another 25 mL 1.0 M HCl solution containing APS (0.857 g, molar ratio of 1:1 to aniline) was added into the mixture drop by drop over 20 min. After stirring in ice-water bath for 6 h, the product was filtered, washed with excess distilled water and ethanol, and finally dried at 45 °C in vacuum overnight.

After dedoping with 0.5 M ammonia, the dedoped PANI was dissolved into 10 mL tetrahydrofuran (THF). Then the C-CNTs films with the length of 10.0 mm and width of 5.0 mm were immersed into the solution for 24 h. The products, denoted as C-CNTs/PANI$_1$-2, C-CNTs/PANI$_2$-2, and C-CNTs/PANI$_3$-2 with the increasing amount of PANI respectively (Table 1), were washed with distilled water and redoped in 1.0 M $H_2SO_4$ solution for 8 h, finally dried at 45 °C in vacuum overnight.

### 2.4. Thermal crosslinking

After heating at 140 °C for 1.0 h in muffle furnace [6], the independently double-crosslinked C-CNTs/TC-PANI composite