



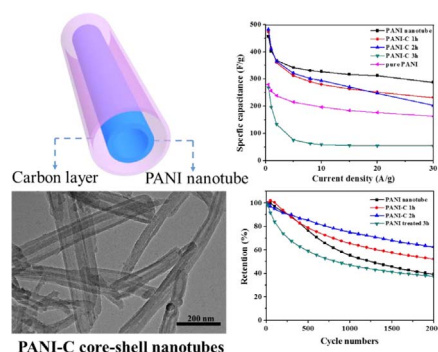
# Fabrication of hierarchical carbon layer encapsulated polyaniline core-shell structure nanotubes and application in supercapacitors



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## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel polyaniline (PANI) nanotube structure was prepared according to a facile in-situ polymerization process using  $\text{MnO}_2$  nanotubes as the reactive template. The obtained PANI nanotubes possess an excellent specific capacitance of 455.7 F/g at 0.5 A/g, exhibit good rate capability of 63.2% even up to 30 A/g, however PANI nanotubes reveal low cycle stability due to the swelling and shrinking during intercalating/deintercalating process. Thus, carbon layer was introduced via a facile hydrothermal method to fabricate core-shell structure of carbon layer encapsulated PANI (PANI-C) nanotubes, which is supposed to alleviate the swelling and shrinking of PANI and improve the cycle stability. The PANI-C nanotubes prepared with 2 h hydrothermal reaction exhibit well-controlled core-shell structure, possess an excellent specific capacitance of 410.5 F/g at 1 A/g and reveal optimal cycle stability as well, (63% of its original value up to 2000 cycles), which shows significant improvement with the pristine PANI nanotubes (maintaining 39% of its original value). Furthermore, symmetric supercapacitors (SCs) were assembled based on PANI-C 2 h, the symmetric SCs exhibit high energy density of 42.32 Wh/kg and power density of 16.44 kW/kg, which also deliver good cycle stability. Additionally, the tandem SCs can light up a red LED. Above all, the carbon layer encapsulated core-shell structure materials offer a feasible strategy to fabricate high cycle stability material for promising applications in high performance supercapacitors.

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## 1. Introduction

Sustainable and renewable energy techniques are indispensable for the development of our human society, and the energy storage plays an important role in building the sustainable energy systems [1–3]. Meanwhile, supercapacitors (SCs, also called electrochemical capacitors) are widely explored for energy storage application, which are also recognized as one kind of new generation clean energy-storage devices because of their fast charge-discharge rate, higher power density, long-term cycling life, wide thermal operating range, and lower maintenance cost [4–7]. Moreover, SCs have exhibited promising applications in many fields, such as utilization in supplement to batteries, backup power sources and stand-by power systems [8–11].

SCs are generally classified into electrical double layer supercapacitors (EDLCs) and pseudo-supercapacitors based on two different charge storage mechanisms [2,12]. In EDLC, the charges can be stored in electrical double layer, which is formed at the interface between electrode and electrolyte, the capacitance of EDLC strongly depends on the specific surface area of the active electrode materials. By contrast, the pseudo-capacitors can possess a greater amount of capacitance than the EDLC, owing to the fast and reversible redox reactions or Faradic charge transfer at the surface of electroactive sites, and the pseudo-capacitors are always achieved through transition metal oxides or conducting polymers [13–19]. Among wide variety of pseudo-capacitive materials, the polyaniline (PANI) material is considered as the most promising choice for electrode material in supercapacitors due to obvious advantages, such as low cost, facile synthetic method, high theoretical capacity, high conductivity, environmental stability and interesting electroactivity [19–23]. Numerous efforts have been devoted to design hollow structured materials in order to improve the capacitance of PANI. For instance, hollow spheres and nanotubes of PANI can be fabricated by facile emulsion polymerization and template polymerization method [20,22,24]. The unique hollow structure materials exhibit particular advantages in supercapacitors due to the enhanced surface-to-volume ratio and reduced transport lengths for charge transport [22,25]. The PANI nanotubes prepared via an in-situ doping polymerization revealed potential application in supercapacitor, with the maximum specific capacitance of 422.5 F/g [24]. However, the swelling and shrinking during intercalating/deintercalating process can result in mechanical degradation of PANI electrode and even fade electrochemical performance and the cycling stability. The composites of PANI and other materials have been recognized as one type of promising methods to improve the cycling stability of the conductive polymers. For instance, the graphene wrapped PANI hollow sphere can enhance the cycling stability, and the capacitance can maintain 90% of its original value after 500 cycles at a current density of 1 A/g [22]. Three-dimension hollow balls of graphene and PANI hybrid composites were fabricated with the poly(methyl methacrylate) (PMMA) particles as the templates, which own an enhanced specific capacitance of 331 F/g at 1 A/g and excellent cycling stability with a 14% loss of the capacitance after 500 cycles [26]. It proves that the combination of PANI and various carbon materials is an important strategy to improve the performance of material with both the electrochemical performance and the cycling stability [22,27].

In this study, we have prepared a novel PANI nanotube structure according to a facile in-situ polymerization process using the  $\text{MnO}_2$  nanotubes as reactive template. The PANI nanotubes possess an excellent specific capacitance of 455.7 F/g at 0.5 A/g, exhibit good rate capability 63.2% even up to 30 A/g. The core-shell structure of carbon layer encapsulated PANI (PANI-C) nanotubes were fabricated by introducing carbon layer using a facile hydrothermal method to improve cycle stability of PANI nanotubes, and the thickness of the carbon layer was controlled by different hydrothermal reaction time. The PANI-C nanotubes prepared with 2 h hydrothermal reaction exhibit obvious core-shell structure and reveal optimal cycle stability, the value can keep 63% of its original value up to 2 000 cycles, much higher than that

of the PANI nanotubes maintaining 39% of its original value. Furthermore, the PANI-C 2 h was used as electrode material to assemble symmetric SCs, which exhibited high energy density and power density, and delivered good cycle stability as well. In addition, in order to explore the potential application, the SCs was connected in series, and the tandem SCs can light up a red LED in series.

## 2. Experimental section

### 2.1. Materials

Aniline was used after purified with distillation. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and concentrated hydrochloric acid (HCl) were received from Baiyin Liangyou Chemical Reagent Co., Ltd. Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ ), potassium permanganate ( $\text{KMnO}_4$ ) and ammonium persulfate (APS) were purchased from Guangfu chemical reagent Co., used as received without further treatment.

### 2.2. Preparation of the PANI nanotubes

PANI nanotubes were prepared according to an in-situ polymerization process. Firstly,  $\text{MnO}_2$  nanotubes were prepared by a facile hydrothermal method [28,29], 0.658 g of  $\text{KMnO}_4$  was dissolved in 75 mL of DI water, and then 1.5 mL of concentrated HCl was dropwise added into the solution. After stirred for 15 min, the  $\text{KMnO}_4$  solution was transferred to 100 mL Teflon-lined stainless autoclave, the autoclave was kept at 150 °C for 12 h. The final brown precipitate was filtrated and washed with deionized water and ethanol, then dried at 60 °C in oven. The PANI nanotubes were fabricated using  $\text{MnO}_2$  nanotube as reactive template, 0.2 g of  $\text{MnO}_2$  nanotube was dispersed in 1 M HCl solution (50 mL) under sonication. After stirring 30 min in ice bath, 220  $\mu\text{L}$  of aniline was added to this suspension solution, and the polymerization was carried out for 12 h in ice bath. The dark blue precipitate was collected by centrifugation and washed with DI water and ethanol several times. After dried at 60 °C, the PANI nanotube was fabricated.

The comparison sample of pure PANI was synthesized using redox polymerization reaction: 0.22 mL of aniline was dissolved in 50 mL of HCl solution (1 M) in ice-bath, then 5 mL of precooled APS solution (0.18 g of APS dissolved in 1 M HCl solution) was dropped into the mixture solution to initiate the polymerization reaction, after stirred for 12 h in ice-bath, the formed PANI was filtrated and washed with DI water and ethanol. Pure PANI was obtained after dried in oven.

### 2.3. Preparation of carbon layer encapsulated PANI nanotube core-shell structure (PANI-C nanotubes)

PANI nanotubes were dispersed in 30 mL of DI-water under sonication, then 0.3659 g of glucose was added to the suspension solution, after stirred for 30 min, the mixture suspension was transferred to 50 mL Teflon-lined stainless autoclave, the autoclave was kept at 160 °C for a set time. The reaction time was 1 h, 2 h, and 3 h, respectively [30]. The suspension was centrifuged and washed with DI water, and then dried at oven.

### 2.4. Characterization

The morphologies of  $\text{MnO}_2$  nanotube, PANI nanotube and PANI-C core-shell structure were characterized by transmission electron microscopy (TEM, JEM-1200 EX/S) and scanning electron microscopy (SEM, Hitachi S-4800, Japan). The crystallographic structures were identified by X-ray powder diffraction (XRD; Shimadzu XRD-6000 X-ray diffractometer) from 5° to 80°. The Raman spectrums of PANI nanotube and PANI-C core-shell structure were investigated from 3200 to 100  $\text{cm}^{-1}$  on the Thermo Scientific DXR Raman Microscope using a wavelength of 633 nm as the laser source. The elementary composition

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