



# Flexible solid-state supercapacitors based on freestanding electrodes of electrospun polyacrylonitrile@polyaniline core-shell nanofibers



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## ABSTRACT

Three-dimensional porous polyacrylonitrile/polyaniline core-shell (PAN@PANI) nanofibers are fabricated by electrospinning technique combining in situ chemical polymerization of aniline monomers. The obtained PAN@PANI nanofibers possess unique continuous and homogeneous core-shell nanostructures and high mass loading of PANI (~60 wt%) as active materials, which have greatly improved the electrochemical performance with a specific capacitance up to 577 F/g at a scan rate of 5 mV/s. Moreover, the porous networks of randomly arrayed PAN@PANI nanofibers provide binder-free and freestanding electrodes for flexible solid-state supercapacitors. The obtained devices based on PAN@PANI networks present excellent electrochemical properties with an energy density of 12.6 Wh/kg at a power density of 2.3 kW/kg and good cycling stability with retaining more than 98% of the initial capacitance after 1000 charge/discharge cycles, showing the possibility for practical applications in flexible electronics.

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## 1. Introduction

Wearable electronics provide a platform for biofeedback and tracking of physiological function to support people in various situations and activities, such as monitoring of surrounding conditions and physiological signals in sports, healthcare, rehabilitation, and high-risk environments [1–3]. The large market pushes to develop high-performance, flexible, lightweight and safe energy storage sectors [4,5]. Flexible solid-state supercapacitors, with many advantages such as high flexibility, lightweight, high safety and environmentally benign nature, represent a new class of energy storage devices that can provide high specific/volumetric energy and power densities for next-generation wearable electronics [6–10]. The realization of high-performance flexible solid-state supercapacitors strongly depends on developing freestanding binder-free electrodes with high conductivity, large capacitance, good flexibility and also light weight [10–15]. Conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh), with advantages of good electrical conductivity and multiple intrinsic redox states leading to large theoretical specific capacitance, are better candidates and have attracted growing interests [11,16–18].

Among these conducting polymers, PANI with a specific capacitance up to 775 F/g has attracted much attentions as the electrode materials for supercapacitors [19]. However, pure PANI is fragile due to its cross-linked structure and unstable for long term charge/discharge cycling. It is not suitable to be directly used as freestanding flexible electrodes for solid-state supercapacitors. In order to solve these drawbacks, choosing a suitable freestanding flexible support for PANI might be an effective approach including conductive carbon materials and nonconductive polymer supports.

Several examples of PANI based freestanding hybrid electrodes have been reported. He et al. synthesized of needle-like PANI nanowires on graphite nanofibers with a specific capacitance of 976.5 F/g at a current density of 0.4 A/g based on active materials (45.5%) [11]. Zhou et al. reported a high specific capacitance of 503 F/g based on electrospun carbon nanofibers surface-grown with carbon nanotubes and PANI at a current density of 0.3 A/g [20]. It should be pointed out that these works were based on conductive electrospun carbon nanofibers as the supports, which were fabricated by high carbonization temperature with multistep synthesis resulting in high production costs and time waste. By contrast, the nonconductive polymer-based supports with unique advantages of excellent flexibility, mechanical strength, low cost and large-scale fabrication have attracted numerous attentions, recently [21,22]. Wang et al. synthesized cloth-supported single-walled carbon nanotubes and PANI nanowire array ternary electrodes with a specific capacitance of 410 F/g at a current density of 0.5 A/g [23]. While this nonwoven cloth with low surface areas would limit the mass loading of active

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materials and decrease the active contact surface areas of active materials with electrolyte. Notably, Chaudhari et al. successfully synthesized PANI nanofibers web by using electrospinning technique directly, exhibiting a specific capacitance of 267 F/g at a current density of 0.35 A/g [24]. This directly blending PANI with nonconductive PEO for electrospinning resulted in very large contact resistance between PANI nanoparticles, which might limit the rapid electron transport and greatly affect the electrochemical performance. Similar work by Zhang et al. synthesized PANI/PAN/multi-walled carbon nanotubes composite nanofibers also through directly electrospinning, which exhibited enhanced conductivity while have not been used as electrodes for supercapacitors [25]. Moreover, several other groups also synthesized PANI nanotubes through electrospinning technique by using polymer (PAN or PAA) nanofibers as sacrificial templates [26,27]. However, the as-synthesized PANI nanotubes without polymer nanofibers as supports, although achieving high specific capacitance, were very brittle which were not suitable as freestanding electrodes for solid-state supercapacitors.

Based on the above discussion, it is worth noting that the electrospinning technique can provide a simple and effective way to obtain these freestanding binder-free supports. Specially, the electrospun polymer nanofibers with extremely long length and large surface areas is thought as ideal to optimize both the mass loading of PANI as active materials and the interfacial contact between active materials and electrolyte. To the best of our knowledge, no reports are available on PANI depositing on electrospun polymer nanofibers directly severing as freestanding electrodes for solid-state supercapacitors. It has been well established that proper nanostructures may obviously enhance their electrochemical performance. Taking this into account, physical and chemical stable electrospun PAN nanofibers were selected as supports in our work. Because cyano group of PAN was a kind of strong electron-attracting group, while aniline monomer was electron-repulsing. The aniline monomers could be absorbed onto the surface of PAN nanofibers through the strong electrostatic attraction during the polymerization. As a result, the PAN@PANI nanofibers with unique continuous and homogeneous core-shell nanostructures were synthesized by in situ chemical polymerization of aniline monomers and possessed very high-loading PANI as active materials on PAN nanofibers. This unique conductive core-shell nanostructure instead of needle-like PANI on the substrate can significantly improve the electrochemical performance. Meanwhile, their porous structure enables effective electrolyte transport into the inner region to increase active-site accessibility with electrolyte. The obtained PAN@PANI nanofibers used as electrodes demonstrated high specific capacitance of 517 F/g (based on PANI; 310 F/g based on the total mass) at the current density of 1.0 A/g. This fabrication process is very simple and fabricated in scalability. Notably, the obtained freestanding porous networks of PAN@PANI nanofibers were also with good flexibility, excellent conductivity and mechanical strength characteristics, two pieces of which could be binder freely processed into solid-state supercapacitors. The fabricated devices presented good flexibility and prominent electrochemical properties, i.e., an energy density of 12.6 Wh/kg at a power density of 2.3 kW/kg and retaining 98% of its initial capacitance after 1000 cycles under the best optimal conditions. A demonstration of a practical device was also presented, showing significant applications of the PAN@PANI nanofibers as flexible electrode materials for the high performance energy storage devices for the wearable electronics.

## 2. Experiment section

### 2.1. Preparation of PAN@PANI core-shell nanofibers

Preparation of electrospun PAN nanofibers could be found elsewhere [28]. For PAN@PANI nanofibers, 4.5 mmol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

and 6 mmol (0.2 M) concentrated HCl were put into 30 ml distilled water stirring for 20 minutes. And then electrospun PAN nanofibers were immersed in it and 4.5 mmol (0.4 ml) aniline monomers added with slowly stirring for 12 hours at room temperature. The obtained products were sequentially washed with distilled water and absolute ethanol several times to remove residual impurities and then the products were dried at fume cupboard for 6 hours. Powdery PANI with the same doping level, suspending in the solution, could also be synthesized during the process of polymerization and purified by the same way. PANI nanotubes can be obtained by immersing PAN@PANI nanofibers into DMF solution and then PAN nanofibers dissolved. Moreover, series of different HCl doping level samples were obtained by adjusting the concentration of HCl with 0.01, 0.1, 0.4 and 1.0 M to investigate the influence of acid doping level on their electrochemical performance. By the same way, series of different PANI loading samples were obtained by adjusting the concentration of aniline monomers with 0.1, 0.2, 0.8 and 1.6 ml to investigate the effect of mass loading of active materials on their electrochemical properties.

### 2.2. General characterization

The morphologies of all samples were characterized by a field emission scanning electron microscopy (FESEM, FEI Quanta 250 FEG). High-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL JEM-2100 (acceleration voltage: 200 kV). X-ray diffraction (XRD) patterns were recorded on a Rigaku, D/MAX-2500 X-ray diffractometer. Fourier transform infrared (FT-IR) spectra were obtained on Magna 560 FT-IR spectrometer with a resolution of  $1 \text{ cm}^{-1}$ . Thermogravimetric analysis (TGA) was used to analyze thermostability of the samples. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB LK II instrument with a Mg  $K\alpha$ -ADES ( $h\nu=1253.6 \text{ eV}$ ) source at a residual gas pressure of below  $10^{-8} \text{ Pa}$ . Photoluminescence (PL) spectra were detected with a Jobin Yvon HR800 micro-Raman spectrometer using a 325 nm line from a He-Cd laser.

### 2.3. Electrochemical characterization

Electrochemical measurements were carried out in both two- and three-electrode configurations using Model 660D electrochemical workstation (CH instruments). For three-electrode configuration, PAN@PANI nanofibers ( $1 \times 1 \text{ cm}^2$ ) was used as working electrode, Hg/Hg<sub>2</sub>SO<sub>4</sub> as reference electrode and Pt mesh as counter electrode. The EIS curves were performed in the frequency range from 100 kHz to 10 mHz at open circuit voltage by applying a 5 mV signal. All three-electrode measurements were performed in 1 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte at room temperature.

### 2.4. Preparation of flexible solid-state supercapacitors

First, polyvinyl alcohol (PVA)/H<sub>2</sub>SO<sub>4</sub> gel electrolyte was simple made as follows: in a typical process, 6 g H<sub>2</sub>SO<sub>4</sub> was mixed with 60 ml distilled water and then 6 g PVA powder was added. The whole mixture was heating up steadily to  $\sim 85^\circ \text{C}$  under vigorous stirring until the solution became clear. Second, two pieces of PAN@PANI nanofibers ( $2 \times 3 \text{ cm}^2$ , same rectangle shape with stainless steel wire as collector, they were pressed together under a pressure of 1 Mpa) were immersed in the above PVA/H<sub>2</sub>SO<sub>4</sub> solution for 10 minutes and picked out. After that, the electrodes with a thin solution layer coating were left in the fume hood at room temperature for 6 hours to vaporize the excess water. Then the two electrodes were pressed together under a pressure of  $\sim 1 \text{ Mpa}$  for 10 minutes.

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