Electrochemical performance of nanofibrous highly flexible electrodes enhanced by different structural configurations

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ABSTRACT: Due to their unique physicomelchanical properties, one dimensional (1D) nanostructured conductive materials offer remarkable potential as a flexible electroactive medium for developing miniaturized electronic devices such as supercapacitors, sensors and actuators. In this work, thin films composed of nanocomposite nanofibers with two different architectures, i.e. whiskered nanofibers (WNFs) and hierarchical-structured nanofibers (H-SNFs), were fabricated and their capability to serve as flexible and bendable electrodes were evaluated. The main difference of these two architectures is how the distributions of the nano-fillers (carboxylated multiwalled carbon nanotubes, CMWNTs) through the nanofibers, i.e. the isotropic and anisotropic arrangements, lead to WNFs and H-SNFs, respectively. The percolation threshold of conduction for the H-SNFs (composed of 0.5 wt% CMWCNTs) and the WNFs (composed of 5 wt% CMWCNTs) were 0.13 S cm$^{-1}$ and 0.07 S cm$^{-1}$, respectively. Moreover, according to the electrochemical characterizations, although the WNFs had ten orders of magnitude higher nanotube content, the electroactivity and electron transfer rate of H-SNFs was considerably higher than those of WNFs, so that the cyclic voltammetric peak currents of H-SNFs was approximately 1.6 times higher than that of WNFs. As a proof-of-concept, our results indicate that the structural configuration is a major determinative factor,
which can largely dictate the final electrical and electrochemical properties of the nanocomposite nanofibers. The bending durability results showed good electrochemical performance even upon 100 bending cycles with ±120° bending angles (retained 93.4% and 83.3% of the initial peak currents for H-SNFs and WNFs, respectively). These two flexible nanocomposite nanofibrous structures could be promising materials for the development of flexible electrodes for biosensing to energy storage applications.

**KEYWORDS:** nanocomposite nanofibers, flexible electrodes, whiskered nanofibers, hierarchical architectures, electrospinning.

**1. INTRODUCTION**

Flexible electrodes with adjustable physicochemical properties are extremely advantageous for various electrical and electrochemical applications ranging from portable electronic devices, flexible batteries, wearable sensors and biosensors [1, 2]. The essential requirements are superb reversibility and long lifetime, *i.e.* minimal variation in electrical conductivity after many bending cycles. In this regard, thin films composed of polymeric fibrous materials are promising structures [3]. The highly inter-connected porosities of fibrous materials are particularly useful in electrochemical energy storage and biosensing applications, due to their very high solid-liquid interface in aqueous media. Use of intrinsically conducting polymers (CPs) and polymeric nanocomposites consisting of conductive nano-fillers are two principal strategies to fabricate conductive polymeric fibrous materials. Although CPs (especially polyaniline (PANi)) have fairly good thermal and environmental stability, as well as interesting redox behavior, they are highly vulnerable to chemical and biological reactions, and their electrical conductivity is not comparable with the outstanding electrical conductivity of carbon-based materials [1, 4]. Moreover, the flexibility of CPs is not comparable with the favorable
flexibility of carbon-based materials, which are known as excellent materials for soft and flexible electrodes [1, 5]. Conductive nano-fillers not only can provide the electrical conductivity in the polymeric nanocomposite materials, but also influence their conventional physicochemical and mechanical characteristics [6].

Over the past two decades, nanostructuring has been emerged as a viable alternative. One-dimensional (1D) nanostructured materials (nanofibers) offer specific advantages, such as very high surface-to-volume ratio, high porosity, low barrier to diffusion of materials, enhancement in the mass activity and excellent structural mechanical properties [7, 8]. Nanofibers have been utilized in the fabrication of miniaturized electronic devices such as supercapacitors, sensors, and actuators, since scaling down the fibrous structures to the nanoscale range can lead to very high surface areas for electrochemical reactions [9]. Electrospinning is an effective approach to fabricate continuous and uniform nanofibers from polymeric and ceramic materials. The electrical, mechanical or physicochemical restrictions of nanofibers could be addressed by adopting the surprisingly simple technique of nano-filler dispersion (e.g. carbon nanotubes, CNTs) within the electrospinning solution [10].

Formation of a continuous network of interconnected CNTs within the nanofibers and along their longitudinal direction is crucial to have conductive nanofibers, therefore a key aspect to take into account is how the nanotubes are distributed inside the nanocomposite [11]. A homogeneous dispersion of CNTs through the electrospinning solution can lead to the fabrication of isotropic nanocomposite nanofibers [12]. Since the redox reactions in electrochemical measurements are localized to the thin surface layer of nanofibers, fabrication of conductive nanocomposite nanofibrous structures “whiskered” with CNTs would be an ideal way to improve the efficiency of electrochemical reactions [4, 13].

On the other hand, once the CNTs are inclined to adsorb to the surface of nanofibers in a way that a densely-interconnected network of nanotubes is decorated on the surface nanofibers, a
specific anisotropic nanofiber structure will be formed, called as “hierarchical-structured nanofibers” (H-SNFs). H-SNFs have been synthesized by three different approaches: electrostatic [14, 15], ultrasonication induced [16, 17], and covalent adsorption [18, 19]. Although H-SNFs can be considered as very attractive materials for various applications, only a few studies have been reported on these materials [20].

In this study, we synthesized carboxylated multiwalled carbon nanotubes (CMWCNTs) whiskered nanofibers (WNFs) through a new facile method of removing the sacrificial polymer phase from nanofibrous thin films after the electrospinning process. In this way, polystyrene (PS) was utilized to form the nanofiber polymer matrix and PEG served to fulfill two purposes: to improve the dispersibility of CMWCNTs, and to whiskerize the surface of nanofibers by dissolving the microdomains of PEG in water. Furthermore, we demonstrated the preparation of CMWCNTs/PS H-SNFs via a novel, controllable hybrid approach, in a way that the electrostatic adsorption of the highly negatively charged CMWCNTs could be accelerated onto the oppositely charged nanofiber surfaces under the ultrasonication induction. A schematic view of the two mechanisms is shown in Fig. 1. The morphology, electrical and electrochemical properties of both nanofibrous structures were evaluated and their potential applicability in flexible electronic devices, e.g. supercapacitors, sensors and actuators was assessed by a bending durability test.
Fig. 1. Schematic view of the electrospinning and the fabrication mechanisms of CMWCNTs/PS nanofibers with two different configurations; (a) WNFs, and (b) H-SNFs. (A short sector of the nanofibers and their cross-sections are plotted to show more details).

2. EXPERIMENTAL

2.1. Materials

Carboxylated multiwalled carbon nanotubes (CMWCNTs - extent of labeling: >8% carboxylic acid functionalized, average diameter × length: 9.5 nm × 1.5 µm), Polystyrene (PS, Mw=190 kDa), Sodium dodecylbenzenesulfonate (NaDDBS), cetyltrimethylammonium bromide (CTAB), Polyethylene glycol (PEG, Mw= 4 kDa) and N,N,-Dimethylformamide (DMF) were all purchased from Sigma-Aldrich (USA). Phosphate buffer saline (PBS) (10 mM, pH 7.4) was prepared by dissolving PBS tablets (pH 7.4 ) in 200 mL of Milli-Q water.

2.2. Fabrication of CMWCNTs whiskered nanocomposite nanofibers

CMWCNTs-whiskered conductive nanofibers were produced by electrospinning. CMWCNTs (50 mg L\(^{-1}\)) were dispersed in DMF solvent with different PS/PEG ratios (PS:PEG ratio of 15:0, 10:0, 5:0, 5:3, 5:5 and 0:5 wt%) in a bath-type sonicator (Elmasonic SH075EL, 37 k Hz) with different sonication time, to achieve a homogeneous and stable precursor of electrospinning solution at 15±5 °C. The size of CMWCNT bundles were measured and optimized using a ZS90 Zetasizer (Malvern Instruments Ltd., Worcestershire, UK). The optimized electrospinning solutions with different concentrations of CMWCNTs were loaded into a 1 ml syringe supplied with a laser cut needle with a blunt end (gage 22). The syringe was placed in an injection pump in a horizontal position and the metallic needle was connected to a high voltage supply. A grounded aluminum was used for collecting the electrospun nanofibers. The parameters for the electrospinning process were: applied voltage 14 kV, injection rate 0.3 ml h\(^{-1}\) and needle-collector distance 16 cm under room humidity and temperature conditions.

2.3. Fabrication of hierarchical-structured CMWCNs nanofibers (H-SNFs)
A hybrid approach consisting of ultrasonication induced and electrostatic adsorptions was utilized to fabricate the H-SNFs (see supplementary Information (SI), Note A1). Briefly, PS nanofibers with uniform structure and the lowest possible diameter were fabricated by controlling the solution and electrospinning variables. The mat of nanofibers was immersed in a supersaturated solution of CTAB with moderate stirring for 10 minutes. The CTAB/PS nanofibers obtained were adopted as templates for coating by highly negatively charged CMWCNTs. For this purpose, CMWCNTs were dispersed in water with anionic surfactant (NaDDBS, 0.2 wt%), by ultrasonication for different times, to gain a suspension with disaggregated CMWCNTs and higher electrical surface charge. The particle size, zeta potential (ζ, surface charge) and degree of dispersion of the CMWCNTs in solutions were evaluated using the Zetasizer. CTAB/PS nanofibrous mats were dipped in a glass bath containing CMWCNT suspensions at different concentrations (0.1, 0.3, 0.5, 0.7, 1 wt%) under sonication (Elmasonic S15H, power 35 watt, frequency 37 kHz) for 30 min. Afterwards, the samples were gently washed several times to remove the excess of weakly adsorbed nanotubes, and dried under ambient conditions for 1 h. The characterization procedures are described in detail in the SI (Note A2).

2.4. Conductivity measurements

The electrical conductivity of the nanofibrous samples was measured using a four-point probe DC conductivity analyzer (Keithley 4200 Semiconductor Characterization System, Keithley Instruments, Inc., Cleveland, OH, USA). In this method, the electrical conductivity can be calculated indirectly based on the electrical resistivity of layer, as shown in Equation (1):

$$\sigma \left( \frac{s}{cm} \right) = \frac{1}{\rho \left( \Omega m \right)} = \frac{1}{R \left( \Omega \right)} \frac{L(cm)}{T(cm)W(cm)}$$

(1)

Where σ is electrical conductivity, ρ is electrical resistivity, R is electrical resistance, L is the distance between each probe and its neighbor, W is the width of the specimen and T is thickness of the sample. The thickness profile of the nanofibrous samples were determined using a Dektak
6M Profilometer (Veeco Instruments Inc., USA) at scanning rates of 50 mm/s and applying a stylus force of 1 mg.

2.5. Design of flexible electrodes

In order to study the electrochemical performance of the nanofibrous structures during cyclic bending tests, a flexible supporting electrode yielding stable and repeatable electrochemical results during experiments was fabricated on a polyethylene terephthalate (PET) sheet. A rectangle 2.5×0.5 cm² was laser cut in paper and utilized as shadow mask on the surface of PET sheet. The electrode was fabricated by means of gold-sputtering for 100 s on the surface of PET sheet covered by shadow mask.

2.6. Cyclic bending test

A symmetric cyclic bending test was designed in which the length of bending can be attributed to the degree of buckling. Hence, by controlling the bending length, different buckling angles can be formed. In this study, three buckling angle (±60, ±90 and ±120°) in three different consecutive bending cycles (10, 50 and 100 cycles) were studied.

2.7. Electrochemical measurements

Electrochemical measurements were carried out using an IVIUM potentiostat in combination with IviumSoft program version 2.645 (Ivium Technologies, Eindhoven, The Netherlands). The electrochemical cell was a conventional three-electrode system with an Ag/AgCl electrode as reference electrode, a platinum wire as counter electrode and the designed gold-sputtered electrode (GSE) as working electrode. Cyclic voltammetric (CV) experiments were carried out in a static electrochemical cell (10 mL) with a solution of PBS containing 5 mM [Fe(CN)₆]³⁻/⁴⁻ at a scan rate 50 mVs⁻¹ from −0.4 to 0.8 V. The [Fe(CN)₆]³⁻/⁴⁻ redox probe was used as a marker to study the electrochemical variations of nanofibrous mats after each cyclic bending test.

3. Results and discussion

3.1. Whiskerization of CMWCNT/PS nanocomposite nanofibers
PEG as an amphiphilic and nonionic polymer was employed to improve the stability and dispersibility of the CMWCNTs. The average size of the CMWCNTs in suspension, after ultrasonication for 3 h in a water bath maintained at 15 ± 5 °C, were measured with the Zetasizer as shown in Fig. 2a. The measured average size of CMWCNTs declined with decreasing the concentration of PS up to 5 wt%, whereas this trend did not continue on further decreasing the concentration. The dispersion of CMWCNTs was further improved by addition of PEG as an auxiliary polymer. The experiments showed that PEG concentrations of more than 5% can adversely affect the homogeneity of final electrospinning solution. The effect of sonication time on the size distribution of the CMWCNTs is presented in Fig. 2b. It is clear that the average size of nanotube bundles and their diameter distributions decreased with increasing the ultrasonication time up to 6 h, while on further increasing the sonication time, these terms remained almost constant. Overall, the lowest average size of CMWCNT bundles in suspension was produced under the optimized conditions: 6 h sonication in a solution of 5 wt% PS and 5 wt% PEG. Similar results have been reported with other solvents and dispersing agents [21, 22]. The electrospinning solutions were prepared by adding the adequate amount of PS (so that the final PS concentration was 15 wt%) to the suspensions prepared under the optimized condition. The effects of CMWCNTs concentration on the morphology and diameter distribution of electrospun nanofibers are shown in Fig. A1 of SI.

![Graph](image)

**Fig. 2.** Average size and size distribution results for a solution of 50 mg/L CMWCNTs with (a) different PS/PEG concentrations and ultrasonication time of 3 h, and (b) different ultrasonication times of a solution with PS/PEG concentrations of 5/5 wt%.
The distribution of the CMWCNTs within the nanofibrous structures was studied by TEM (Fig. 3). The polymer matrix regions which are not impregnated with CNTs have a neat and homogeneous appearance, while the CNT-impregnated regions have a mottled, hazy and heterogeneous appearance. For nanofibers with 1 wt% CMWCNT (Fig. 3a) no significant aggregation of nanotubes in the nanofibers structure was observed. Moreover, the organization of the CMWCNTs within the nanofibers was fairly aligned with the direction of nanofiber axis, which might be due to the jet stretching and drawing forces during the electrospinning process [23]. Fig. 3a-c show that increasing the volume fraction of CMWCNTs inside the electrospinning solution, clearly results in the formation of a network of CMWCNTs bundles. The circles mark the CNT-impregnated regions within the nanocomposite structure. Fig. 3c (nanofibers with 5 wt% CMWCNTs) obviously shows that an interconnected CMWCNT network formed a suitable percolating pathway for electrical conductivity. It can be also seen that the nanotube network is extended out to the surface of the nanofiber structure, as marked with arrows, which allows electrical communication between adjacent nanofibers.

Fig. 3. TEM images of PS/CMWNT nanocomposite nanofibers: (a) 1 wt% CMWCNT, (b) 3 wt% CMWCNTs, and (c) 5 wt% CMWCNTs. The CNTs regions are marked with circles and arrows.

Since PS and PEG are partially miscible polymers, phase separation can occur during the electrospinning process due to the solvent evaporation [14, 24]. The excess PEG auxiliary polymer will result in the formation of PEG micro-domains within the nanofibers. After the
electrospinning process, the nanofiber mat was immersed in water (which acts as a solvent for PEG) for 1 h to remove the accessible PEG micro-domains. Fig. 4a and b show the SEM images of nanofibers before and after their immersion in water, respectively, illustrating the increased surface roughness and more accessible CMWCNT on the surface of the nanofibers. Additional images of the WNFs are provided in Fig. A2 of SI. The surface hydrophobicity of the resulting WNFs having different CMWCNT contents is shown in Fig. 4b. WNFs displayed lower static contact angles than those of neat PS nanofibers, and a decrease in measured contact angle was observed with increasing CMWCNT content. The increase in surface wettability might be attributed to the presence of the carboxylic acid groups of CMWCNTs and increasing the surface roughness by exposing the CMWCNT domains on the surface.

![Fig. 4. SEM images of (a) PS/CMWCNTs/PEG nanocomposite nanofibers and (b) formation of whiskerized structures on the surface of nanofibers, and (c) measurement of water contact angles on the WNFs mat with different nanotube contents.](image)

3.2. Hierarchical-structured nanofibers

A facile and controllable approach was developed by merging the ultrasonication induced adsorption along with electrostatic adsorption of CMWCNTs onto the surface of oppositely charged nanofibers to over-coat the PS nanofiber with CMWCNTs and fabricate the H-SNFs. The ultrasonication induced method takes advantage of high frequency ultrasonic waves which can generate localized cavitation involving the formation, growth, and implosive collapse of bubbles in liquid. In accordance with the proposed mechanism for this approach, micro-jets and shock waves will concurrently form close to the nanofiber surface with the collapse of the
bubbles, in a way that the interfacial collisions and sintering of CMWCNTs to the PS nanofibers occurs at very high speeds. Using the proposed approach, adsorption of charged species onto the oppositely charged nanofiber surface could be accelerated under the synergistic effect of the ultrasonication induction. For this purpose, the PS nanofibers were modified so that the negatively charged CMWCNTs have considerable electrostatic affinity to their surfaces.

Firstly, supporting PS nanofibers containing the anionic surfactant NaDDBS with an average diameter of 168±26 nm and uniform morphology were fabricated by the optimized electrospinning parameters. Our results showed that the morphology, surface tension and average diameter of nanofibers could be substantially affected by adding the NaDDBS to the electrospinning solution. Since during the electrospinning the surface of the Tailor cone is positively charged, the negatively charged heads of surfactants in the solution will preferentially tend to segregate to the surface of cone [25]. Moreover, from a polarity point of view, PS is a hydrophobic polymer without any polar functional groups, thus during the solvent evaporation, the hydrophilic head of surfactant will tend to stand out the surface of jet. Ergo, an array of hydrophilic heads of surfactants will form on the nanofibers surface. Fig. A3a of SI shows the water contact angles (WCA) measured from the supporting PS nanofibers for different modification steps. The measured water contact angle decreased by adding 0.3 wt% NaDDBS surfactant, which is consistent with the availability of the hydrophilic heads of surfactants on the surface of nanofibers. Overall, it could be concluded that the surface of PS-NaDDBS nanofibers are composed of both hydrophobic and hydrophilic regions so that the hydrophilic regions will be negatively charged in aqueous media, owing to the presence of sulfonate ions (R-SO$_3^-$).

The nanofibers surface modification was followed by adding a positively charged CTAB to form positively charged PS/NaDDBS/CTAB supporting nanofibers. The WCA results (Fig. A3a of SI) depict that the surface wettability of the nanofibrous mat is strongly affected by the
adsorption of CTAB molecules onto the surface of nanofibers (WCA decline from 131° to 27°). Fig. A3b and A3c of SI show the EDX spectra of PS-NaDBBS nanofibers before and after wrapping the positively charged CTAB molecules round the surface of nanofibers, and their inset images depict the corresponding SEM micrographs. The appearance of a nitrogen peak confirm the attachment of CTAB molecules onto the nanofibers surface. The adsorption of CTAB molecules onto the surface of nanofibers can be ascribed to the van der Waals attractive forces between the long linear chain of CTAB molecules and the hydrophobic regions of the nanofibers, and the electrostatic interactions between sulfonate ions on the surface of the nanofibers and the quaternary ammonium cations ([Me₃NR]⁺) of the CTAB molecules [26]. Overall, it can be concluded that the surface of PS nanofibers were decorated by positively charged ions which can to be used as a template to electrostatically adsorb negatively charged CMWCNTs.

After obtaining the positively charged PS/NaDBBS/CTAB supporting nanofiber, highly negatively charged CMWNTs were introduced to create a conductive H-SNFs mat. For this purpose, the CMWCNTs were dispersed in water with NaDBBS, as dispersing agents, to accommodate the more negative charges on the surface of nanotubes. The effect of different ultrasonication times on the average size of the nanotube bundles was examined (Fig. 5a) and 3 h was chosen as the optimum sonication time. The zeta potential values of the CMWCNTs suspended in water-NaDBBS solutions as a function of pH after 3 h sonication are shown in Fig. 5b. The negative value of the zeta potential increased up to roughly −64.3±6.9 mV with increasing pH over the range of 3–7, while further increases in the pH reversed this upward trend. Therefore, pH 7 was chosen as the optimum working pH to achieve a nanotube suspension with a zeta potential as low as -64.3 mV. The detailed information and arguments about the effect of pH on the measured zeta potentials are provided in the Note A3.
Fig. 5. (a) Average size of CMWCNT dispersions with different sonication time, and (b) Zeta potential results of CMWCNT dispersions at different pH values.

Fig. 6 shows the pristine PS nanofibers and different surface morphologies of CMWCNTs-adsorbed nanofibers via SEM. Once the surface of nanofibers is not covered by CTAB molecules (Fig. 6b), there are just scattered nanotubes stuck to the nanofibers surface due to collision and physical entanglements arising from ultrasonication. Fig. 6c clearly shows that the supporting nanofibers decorated with CTAB could significantly enhance the CMWCNT’s adsorption efficiency as indicated by a relatively higher surface coverage of CMWCNTs. The surface coverage of the CMWCNTs could be further improved by increasing the initial concentration of CMWCNTs from 0.3 to 0.5 wt% (Fig. 6c and d). The high-resolution inset picture shows that the CMWCNTs almost covered the entire surface of the supporting PS nanofiber.

Fig. 6. SEM images of (a) pristine PS/NaDDBS nanofibers, nanofibers immersed in: 0.3 wt% CMWCNT dispersion without (b) and with (c) surface modification, and 0.5 wt% CMWCNT dispersion with surface modification.

3.3. Electrical and electrochemical characterizations flexible electrodes

The electrical conductivities of the CMWCNT/PS nanofibers with the two different structural architectures, *i.e.* WNFs and H-SNFs, are plotted in Fig. 7a and b, respectively. In the case of
WNFs, in order to obtain a conductive CMWCNT/PS composite nanofibrous mat, the density and distribution of the CMWCNTs inside the nanofibers is critical such that a continuous network of interconnected CMWCNTs can form a percolating pathway for electron transfer, which is known as the percolation threshold of electrical conductivity [27, 28]. Our results showed that the conductivity of the WNFs dramatically increased as the concentration of the CMWCNTs content increased from 3 wt% to 5 wt%. This indicated the continued growth and formation of the interconnected CMWCNT network structure that enhances the electrical conductivity [29, 30]. In the case of H-SNFs, the measured electrical conductivity dramatically increased with increasing the concentration of CMWCNTs suspension up to 0.5 wt%, whereas for higher concentrations the variations in electrical conductivity is insignificant. This result suggests that the dense interconnected CMWCNT network on the surface of the H-SNFs is sufficient to produce a highly conductive nanofiber mat. Moreover, the use of less CMWCNTs for the H-SNFs is a more environmentally friendly and green approach for the fabrication of flexible nanofiber-based electrodes. The electrical conductivity of nanofibrous thin films based on WNFs (5 wt%; the concentration of nanotubes in electrospinning solution) and H-SNFs (0.5 wt%; the concentration of nanotubes in immersion solution) were found to be approximately 0.07 and 0.13 S cm⁻¹, respectively. Although the nanotubes concentration in electrospinning solution utilized to fabricate WNFs is ten times higher than that in the immersion solution utilized to fabricate H-SNFs, its electrical conductivity is approximately two orders of magnitude lower than that of H-SNFs. The relatively low electrical conductivity of WNFs seems to be due to the fact that only a few percent of the dispersed nanotubes are in the desired locations to construct a continuous channel, resulting in inefficient electrical conduction [31]. Whereas in the case of H-SNFs, almost all of the CMWCNTs formed a dense network on the surface of the nanofibers to facilitate effective electron conduction [32]. Summarizing the results, it can be stated that the electrical conductivity of nanocomposite nanofibers could be
influenced not only by the degree of nanotube dispersion and nanotube concentration, but also
by the configuration of the nanotubes within the nanocomposite nanofibers.

**Fig. 7.** Electrical conductivity dependence of the WNFs (a) and H-SNFs (b) to the nanotube concentrations (dashed-line circles represent the percolation threshold). Cyclic voltammograms of bare GSE and electrodes covered with WNFs (c) and H-SNFs (d).

The electrochemical properties of the WNFs and H-SNFs were characterized by cyclic voltammetry using a $[\text{Fe(CN)}_6]^{3/-4}$ redox probe, and shown in Fig. 7 c and d, respectively. A clear pair of redox peaks for the $[\text{Fe(CN)}_6]^{3/-4}$ probe were observed for both nanotextured electrodes, which unambiguously confirms the electroactivity and electrical conductivity of the electrode surfaces. As can be seen, the absolute values of the anodic and cathodic peak currents for H-SNFs are considerably higher than those of WNFs. Moreover, it is clear that the peak-to-peak separation value ($\Delta E_p$) is increased more for the WNFs in comparison with H-SNFs. These observations may relate to the differences in the fabrication process, and different configurations of nanotubes within the two nanostructured materials [32]. The intensity of the anodic and cathodic peak currents are directly related to the number of electron exchanged in the electrochemical reactions, which highly depends on the accessibility of the redox probes to the nanotubes on the surface of nanofibers. In the case of WNFs, the lower electrochemical current can be attributed to two possible reasons: (1) the coverage of the major part of interconnected nanotube network with non-conductive polymer matrix, which can hinder the electron exchanges; and (2) the high elongation of the jet during electrospinning might lead to formation of zones having lower nanotube density inside the nanocomposite nanofibers, which
can confine the electron transfer [6]. In contrast, in the case of H-SNFs, the whole nanotube network is freely accessible which can cause enhanced electron exchanges in electrochemical reactions. The low relative standard deviation (RSD %) for bare and two other nanostructured electrodes by performing 5 successive cyclic voltammograms implies excellent stability and repeatability of the nanostructured platforms making them suitable for electrochemical applications (as shown in Fig. A4 of SI).

3.4. Evaluation the bending durability of the flexible electrodes

To demonstrate the flexibility and bending durability of the nanostructured electrodes, the electrodes were subjected to different bending angles and bending cycles as illustrated schematically in Fig. 8.

Fig. 8. Schematic diagrams of the fabrication of GSE (a), directly electrospun and synthesizing the WNFs and H-SNFs on the electrode surface (b), bending test with different bending angles (BAs) (c) and the electrochemical measurement cell (d).

The voltammograms of WNFs and H-SNFs at the bending angle of ±120˚ and different bending cycles are shown in Fig. 9a and b, respectively (other bending angles are not shown for the sake of brevity). The relative changes of anodic and cathodic peak currents at different bending angles and bending cycles are summarized in Fig. 9c and d. The electrochemical responses reflect the structural stability of the CNTs within the WNFs and H-SNFs. The low fluctuation in currents for the two nanostructured electrodes up to 100 bending cycles demonstrates the
desired long-term electrochemical durability and good reversibility of the systems, especially at low bending angles (i.e. ±60° and ±90°).

For both of the electrodes, it was found that as the bending cycles were increased, the absolute values of anodic and cathodic peak currents were slightly decreased. This downward trend accelerated once the bending angle was increased. Furthermore, although the ΔE_p values for both nanostructured electrodes increased, this trend for H-SNF electrodes was smoother. Generally, the higher ΔE_p can be attributed to a reduced electron transfer rate for the redox probe with the electrode surface [33]. A conductive nanofibrous mat with sufficiently high packing density and fiber-fiber connections would be more desirable for electron transfer [31]. Therefore, the decreasing trend in the peak currents could be ascribed to the slight loss the packing density and fiber-fiber intersections, owing to stretching and compression arising from bending cycles.

Fig. 9. Cyclic voltammograms of GSE covered by WNFs (a) and H-SNFs (b) after ±120° bending for 10, 50 and 100 bending cycles. The relationship of the bending angle and the bending cycles to the measured anodic and cathodic peak currents for WNFs (c) and H-SNFs (d).

Since the CMWCNTs are adsorbed on the surface of the nanofibers in H-SNFs, the cavities between the nanofibers are partially filled with nanotubes, which can lead to a higher packing density in comparison with WNFs. Moreover, in the fiber-fiber intersections of H-SNFs, there are some nanotubes protruded from one nanofiber, connecting to the other fibers [17]. This can help to preserve the nanofibrous mat packing density and the fiber-fiber connections during the
tensions associated with the bending cycles and therefore explain the relatively better electrochemical performance of the H-SNFs. Whereas in the case of WNFs, the packing density and fiber-fiber intersections could be more adversely influence by the bending cycles. The strong conductive network of nanotubes coating on the surface of nanofibers in H-SNFs even upon 100 bending cycles with ±120˚ bending angles, confirm that this configuration can be considered as a superbly bendable material for various applications that require severe bending.

4. Conclusion

In summary, thin films composed of conductive nanocomposite nanofibers with two different configurations, i.e. WNFs and H-SNFs, and their capability to serve as flexible and bendable electrodes were evaluated. The surface morphology, interior structure, electrical conductivity, electrochemical and bending durability characteristics of both nanostructured materials were evaluated. Our results showed that although the concentration of CMWCNTs in the immersion solution used to fabricate H-SNFs is several times lower than that in the electrospinning solution used to fabricate WNFs, their electrical conductivity was approximately two times higher than that for WNFs. Moreover, H-SNFs showed significantly better electrochemical performance after being subjected to different bending angles and bending cycles. By and large, it can be stated that besides the nano-filler concentration and its quality of dispersion, the configuration of the nano-filler is a major determinative factor, which can largely dictate the final electrical and electrochemical properties of the nanocomposite nanofibers.

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References


Supplementary information

Electrochemical performance of nanofibrous electrodes enhanced by different structural configurations

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Experimental Section
Hierarchical-structured CMWCNs nanofibres (H-SNFs)

PS nanofibres with uniform structure and lowest possible diameter were fabricated by controlling the solution and electrospinning variables. The polymer of PS (15 wt%) was added to a solution of 0.3 wt% NaDDBS surfactant in DMF solvent during moderate magnetic stirring, and the stirring was continued at room temperature for another 6 hours. Electrospinning was conducted at 17.6 kV applied voltage, 15.9 cm needle-collector distance, 0.3 ml/h feeding rate and the rotational speed of collector was set to be 20 RPM as optimal conditions. In the following, two methods were applied to fabricate the H-SNFs with desired structural and electrical properties.

The first approach was based on the adsorption of nanotubes to the surface of nanofibres by means of ultrasonication induction method. For this purpose, the CMWCNTs were dispersed in water with 0.2 wt% NaDDBS under sonication treatment (Elmasonic S60H, power 150 watt, frequency 37 kHz) for 3 hr. Thereupon, the mat of nanofibres was dipped in nanotubes suspension and the sonication process was followed for another 60 min. Eventually, The nanofibrous mat was pulled out from the solution and incubate for 10 min at room temperature and wet condition, in a way that the adsorbed nanotubes on the surface of nanofibres have enough time to become relaxed from the tensions caused by ultrasonication. The samples were gently washed out several times to remove the excess of weakly adsorbed nanotubes, and dried at ambient conditions for 1 h. The ultrasound generates localised cavitation phenomena involving the formation, growth, and implosive collapse of bubbles in liquid. The accepted mechanism to explain the adsorption of nanotubes to the surface of PS nanofibres is related to the microjets and shock waves created near solid surfaces after the collapse of the bubbles, which push the nanotubes toward the PS nanofibres surfaces at very high speeds[1].

In the following a hybrid approach consist of ultrasonication induced and electrostatic adsorption was also evaluated to fabricate H-SNFs. For this purpose, the mat of nanofibres was immersed into a solution of cationic surfactant CTAB during the moderate stirring for 10 minutes. The concentration of CTAB was taken to be higher than CMC (Critical micelle concentration, ~ 1 mM at 25 °C) and the solution was heated until 40 °C to attain a super-saturated solution of surfactant. During the immersing process, the solution was left to cool at room temperature, which means that with decreasing the temperature, extra molecules of CTAB will tend to move out of the aqueous media, which can lead to better coating of the nanofibrous mat with CTAB molecules. After 10 min, the nanofibrous mat was gently washed out several times with DW to remove the redundant CTAB molecules that were not properly attached.
to the nanofibre’s surface, and dried at room temperature. The obtained CTAB/PS nanofibres were adopted as templates for coating by highly carboxylated MWCNTs.

Characterisations

High-resolution scanning electron microscopy (SEM, LEO 1550 Gemini, Zeiss, Germany) coupled with energy-dispersive X-ray spectroscopy (EDX, oxford instrument) was utilised to study the surface morphology and elemental compositions of the samples. Image J Software (National Institute of Health, Bethesda, MD) was used to measure the average nanofibre diameter and nanofibres diameter distribution from SEM photomicrographs by 100 measurements of random fibres. Transmission electron microscopy (FEI Tecnai G2 TF20 UT HR-TEM with a field emission gun operated at 200 kV) was applied to study the interior structure of the nanocomposite nanofibres. The nanofibres were directly electrospun onto TEM carbon lacey grids. Water contact angle (WCA) measurements were performed with fresh Milli Q water (18.2 MΩ) by means of a CAM200 Optical Contact Angle Meter (KVS Instrument, Finland) based on static sessile drop method to study the variations in wettability of the nanofibrous mats in different steps of preparation. The electrical conductivity of the nanofibrous samples were measured using a four-point probe DC conductivity analyzer (Keithley 4200 Semiconductor Characterization System, Keithley Instruments, Inc., Cleveland, OH, USA). In this method, the electrical conductivity can be calculated indirectly based on the electrical resistivity of layer, as shown in Equation (1):

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\sigma \left( \frac{S}{cm} \right) = \frac{1}{\rho (\Omega m)} = \frac{1}{R(\Omega)} \frac{L(cm)}{T(cm)W(cm)} \quad \text{Eq. (1)}
\]

Where \( \sigma \) is electrical conductivity, \( \rho \) is electrical resistivity, \( R \) is electrical resistance, \( L \) is the distance between each probe and its neighbor, \( W \) is the width of the specimen and \( T \) is thickness of the sample. The thickness profile of the nanofibrous samples were determined using a Dektak 6M Profilometer (Veeco Instruments Inc., USA) at scanning rates of 50 mm/s and applying a stylus force of 1 mg.

Results and Discussion

3.1. Whiskerisation of CMWCNT/PS nanocomposite nanofibres

Electrospinning solutions were prepared by adding the adequate amount of PS (so that the final concentration of PS in solution was 15 wt%) to the suspensions containing different concentrations of CMWCNT dispersed under the optimized condition. Electrospinning process was performed under the previously explained conditions. It is clear from the results that for low concentrations of nanotubes (less than 2 wt%) with increasing the nanotube concentration, the average nanofibre diameter is decreased. This result could be understood by consideration of the effect of nanotubes on the electrical properties of electrospinning solution[2]. The presence of CNTs can considerably lead to increase the jet stretching and elongation in electrostatic field, owing to enhance the electrical conductivity and surface charge of the electrospinning solution. For nanotube concentrations of more than 2 wt%, however, the recognisable trend of average nanofibre diameter was on the increase. This could be explained by two different factors which are competitive and have opposite effects on the electrospun nanofibre diameter: (i) viscosity and (ii) electrical conductivity of electrospinning solution[3].
On one hand, it is generally accepted that the electrical conductivity and surface charge of solution increase with increasing the concentration of nanotubes, which have reductive effect on average nanofibres diameter. On the other hand, the viscosity of electrospinning solution growth due to physical entanglements between the nanotube-nanotube and nanotube-polymer chain, which has additive effect on average nanofibre diameter. The outcome of these two parameters for high concentration of nanotube is higher average nanofibre diameter. Moreover, by increasing the nanotube concentration, by and large, the diameter distribution became wider and nanofibre uniformity is reduced. A plausible explanation is that the number and size of bundles and aggregations of nanotubes in high concentrations of CNTs is higher, which can lead to decrease in the interface area between nanotubes and polymer matrix, more heterogeneity of electrospinning solution and formation of irregular bead-on-string structures.
3.2. Fabrication of H-SNFs

PS nanofibres with lowest possible diameter and controlled morphology were fabricated by tuning different solution and electrospinning parameters. It worth mentioning that bead-free nanofibres with smooth surfaces and uniform diameter (i.e. low variation in the morphology of nanofibrous mat) are crucial to have structures with appropriate reproducibility[4]. The SEM images of PS and PS-NaDDBS nanofibres at high and low magnifications and diameter distributions corresponding to these images are illustrated in Fig. 3 SI. The formation of bead-on-string structures in Fig. 3a-b SI. can be ascribed to low electrical conductivity of DMF, high surface tension of this solvent and the lack of any polar functional groups on the PS polymer chain. It is apparent from the results that the morphology, average nanofibres diameter and diameter distribution are drastically affected by adding the anionic surfactant to the electrospinning solution. The presence of NaDDBS enhanced the electrical conductivity and reduced the surface tension of electrospinning solution, due to formation of ions inside the solution and electrostatic repulsions between the heads of surfactants with the same charge, respectively. Therefore, with improving the electrospinnability of the solution and controlling the electrospinning parameters (which are not reported here for the sake of brevity), desirable PS nanofibres with average diameter of 168±26 nm were fabricated and utilised for the next steps of this experiment.
An ultrasonication induced adsorption approach, as a simple alternative method, was employed to decorate the surface of optimised nanofibres with CMWCNTs. In accordance with the proposed mechanism for this approach, high frequency ultrasonic waves can cause formation of micro-jets and shock waves near to the solid surface after the collapse of the bubbles, in a way that the interfacial collision and sintering of nanotubes to the surface will occur at very high speeds. Under a constant ultrasonication power, the energy imparted to the individual or CNTs bundles would be approximately the same. Thereby, it is generally known that nanotubes will accelerate toward the surface of nanofibres according to their size and surface drag. Contrary to expectation, our results showed that the nanotubes are loosely and randomly distributed on the PS nanofibre surface (Fig. 4a SI.), and the morphology of nanofibres is seriously affected by ultrasonication process. From fig. 8a, it can be found out that the nanofibres took on ribbon-like morphology and lost their cylindrical shape, they were packed to each other, and some physical linkages in the intersection points formed. This could be attributed to increase in the temperature of polymer nanofibre owing to ultrasonication power, which may cause the nanofibres to be softened or even partially melted. The high magnification SEM image (Fig. 4b SI.) reveals that the nanotubes with short length were even incorporated into the nanofibres, which can be ascribed to higher acceleration of these nanotubes when they knock the surface of nanofibres. Furthermore, losing the structural integrity of the nanofibrous layer and delamination from the substrate is another negative effect arises from sonication power. The reason that the above approach doesn't work well in our experiments is not completely clear; however, it might be related to the lower viscoelasticity and wettability of the PS vis-à-vis the polymers used by other researchers so far. Form the results, it can be concluded that there is a relation between the power and duration time of ultrasonication, and the structural morphology of product. Therefore, in the following a novel hybrid approach was proposed and implemented to achieve favorable H-SNFs with unperturbed structural morphology.
Fabrication of highly negatively charged CMWCNTs suspension

Since one of the principal strategies for fabrication of H-SNFs in this research was focused on electrostatic adsorption, i.e., attempting to produce suspensions in which the nanotubes were highly negatively charged inside the solution. For this purpose, anionic surfactants (SDS and NaDDBS) were studied as dispersing agents to accommodate more negative charge on the surface of nanotubes. It is worth mentioning that the carboxylic acid groups of CMWCNTs can also generate excessive negative charge on the surface of nanotubes in the suspension, which will have a profoundly positive effect on the efficiency.

The ability of the anionic surfactants to facilitate the dispersion of nanotubes in aqueous media were evaluated by Zetasizer measurements. The average nanotube bundle sizes for suspensions containing 0.2 wt% of SDS and NaDDBS after 1 h ultrasonication were determined to be 294 nm and 164 nm, respectively. Since all the other parameters are taken to be same, the differences in measured average bundle sizes and diameter distributions can be attributed to chemical characteristics of the surfactants molecules. It is usually tacitly accepted that the interactions between the surfactant molecules and the nanotube surface are mainly hydrophobic in nature. Hence, the chemical and structural characteristics of hydrophobic tail of surfactants dictate their ability to disperse the nanotube agglomerates. NaDDBS consists a benzene ring moiety which can cause strong π–π interactions closed to the basal planes of nanotubes, whereas SDS with its long linear hydrophobic tail can be adsorbed on the basal planes just by the aid of van der Waals attractive forces. Therefore, with respect to the relatively better dispersion of nanotubes in the presence of NaDDBS, this surfactant was chosen as dispersing agent for the following experiments.

The effect of pH on zeta potential results of nanotube suspension

The isoelectric point (pH$_{iep}$, which is defined as pH point of zero charge) of pristine MWCNT was reported to be around 5, so that higher and lower than this point the nanotubes have negative and positive surface charges, respectively[5, 6]. Chemical and physical modifications of nanotube surfaces with different oxidants and anionic surfactants can shift the measured pH$_{iep}$ to the lower values[7, 8]. As in the case of the highly carboxylated nanotubes coated with NaDDBS utilised in these experiments, no pH$_{iep}$ was observed overall in the evaluated pH range. The negative value of zeta potential increased up to roughly $-64.3$ mV with increasing the pH in the range of 3–7, while with further increase in the pH, this upward trend was reversed. Since the dissociation constant of NaDDBS (which is consistent with
acid dissociation constant of dodecylbenzenesulfonic acid, i.e. pKa ~2.55) is lower than the evaluated pH range, the dissociated form of NaDDBS will be present over the whole of this pH range [9]. The lower magnitude of zeta potential obtained at low pH values (lower than pH 7) is consistent with the adsorption of hydrogen ions (H+) to (I) the negatively charged head of NaDDBS wrapped around the nanotubes, (II) surface of unsaturated carbon rings and (III) the functional carboxyl groups of nanotubes, in this pH range[10]. The increase in the magnitude of zeta potential with pH increasing from 3 to 7 can be explained by deprotonation of the functional carboxyl groups of nanotubes. Meanwhile the deprotonation of the functional carboxyl groups of the nanotubes with increase in pH, means that the electrostatic repulsions between similarly charged species on the surface of nanotubes also grow, which may lead to swelling and release of the surfactants from the surface of the nanotubes. The unwrapping of the surfactants at high pH values (higher than pH 7) could be associated with the decrease in the measured magnitude of the zeta potential (as observed in our results, fig. 8b). Similar results have been obtained by other researchers as well [11]. Moreover, our results showed that for pHs higher than 11, the surfactants wrapped around the nanotubes were not sufficient enough to form a stable suspension, and therefore coagulation and sedimentation of nanotubes occurred as time progressed.

**Electrochemical characterisation of the CMWCNT/PS nanofibre-based electrodes**

The structural uniformity and thickness homogeneity of the nanofibrous layer on the surface of GSE are crucial to have reliable and reproducible electrochemical results. In this context, the electrospinning time is one of the important parameters which should be considered owing to the dependence of the thickness and the collected nanofibre layers on the surface of electrode to this parameter. Once the thickness of nanofibre layer is high, the underlying layers would not be accessible enough for adsorption and attachment of nanotubes. Therefore, after some preliminary optimisation, 1 minute was chosen as optimum electrospinning time, since after times of lower than 1 minute the nanofibre layer was not visually uniformly distributed on the surface of GSE, and at times higher than 1 minute, the electrochemical result was extremely adversely affected. In the case of WNFs, since the surface of GSE was uniformly covered by nanofibres after 1 minute of electrospinning, this time was chosen to fabricate flexible electrodes based on WNFs too. In order to obtain an evenly distributed nanofibre layer, the electrode was rotated 180° on the collector to limit the effects of local electric field inhomogeneities and improve the structural uniformity of nanofibrous layer.

The repeatability of the electrochemical measurements for bare and two other nanostructured electrodes were evaluated by performing 5 successive cyclic voltammograms. The low computed values of coefficient of variation (CV%) for all of them implies excellent stability and repeatability of the designed electrode and nanostructured platforms for the electrochemical applications (as shown in Fig. SL5a, b and c).
Figure SI. 5: CVs of bare GSE (a), WNFs (b) and H-SNFs (c). The 5 consecutive cyclic voltammograms were conducted at 5 mM [Fe(CN)₆]³⁻/⁴⁻ in PBS solution (10 mM, pH 7.4). Scan rate was set to be 50 mV/s.

References


