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Thin and flexible all-solid supercapacitor prepared from novel single wall carbon nanotubes/polyaniline thin films obtained in liquid–liquid interfaces

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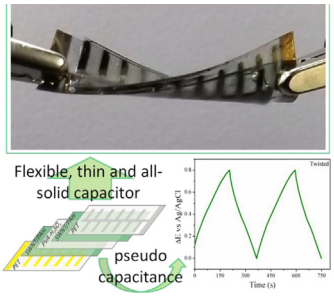
HIGHLIGHTS

- Flexible, transparent, ITO-free and all solid supercapacitor.
- Excellent performance and improved stability under bending.
- Active layer based on thin films (approximately 120 nm) prepared in an innovative way.
- Complex material for electrochemical energy systems prepared in liquid–liquid interfaces.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work describes for the first time the synthesis and characterization of single wall carbon nanotubes/polyaniline (SWNTs/PAni) nanocomposite thin films in a liquid–liquid interface, as well as the subsequent construction of a flexible all-solid supercapacitor. Different SWNTs/PAni nanocomposites were prepared by varying the ratio of SWNT to aniline, and the samples were characterized by scanning and transmission electron microscopy, Raman and UV–Vis spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The pseudo-capacitive behavior of the nanocomposites was evaluated by charge/discharge galvanostatic measurements. The presence of the SWNTs affected the electronic and vibrational properties of the polyaniline and also improved the pseudo-capacitive behavior of the conducting polymer. A very thin and flexible all-solid device was manufactured using two electrodes (polyethylene terephthalate-PET covered with the SWNT/PAni nanocomposite separated by a H_2SO_4-PVA gel electrolyte). The pseudo-capacitive behavior was characterized by a volumetric specific capacitance of approximately 76.7 F cm^{-3}, even under mechanical deformation, indicating that this nanocomposite has considerable potential for application in new-generation energy storage devices.

1. Introduction

In recent years, the development of energy storage technology has become very important as clean energy generation from flexible, thin and lightweight devices has been developed. Supercapacitors are highly promising candidates to fulfill these energy

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storage requirements, as these devices combine the high storage capacity of batteries along with the fast and efficient energy release of capacitors [1]. Supercapacitors can be divided in two types: the double-layer capacitor and the pseudo-capacitor, which differ strictly in their charge storage mode. In the double-layer capacitor, the capacitance results from the separation of charges, being purely electrostatic. Meanwhile, in the pseudo-capacitor, the capacitance results from a Faradaic process, meaning that the storage occurs in response to a redox reaction [1,2].

Carbon-based materials, conducting polymers and metal oxides are broadly applied singly or as composites in the development of supercapacitors. As carbonaceous materials, single wall carbon nanotubes (SWNTs), which generally present double-layer capacitive behavior, are powerful materials that are applied as electrodes for supercapacitors due to their desirable properties such as high surface area, porosity and electrical conductivity [3,4]. Polyaniline (PAni), a conducting polymer with capacitive properties from a Faradaic process, is another material widely applied as a supercapacitor due to its unique properties such as environmental stability, facile preparation, high doping level and fairly high conductivity [2,5,6]. The charge is stored from the redox process of the polyaniline into its different forms (e.g., the transition from the leucoemeraldine to the emeraldine form), which is accompanied by the intercalation and depletion of the counter ions. Besides the conducting polymers as polyaniline, several metal oxides present pseudocapacitive behavior from Faradaic process, being the RuO_2 the most promissory material due to the high specific capacitance and good electronic conductivity [7]. Meanwhile, compared to the metal oxides, the conducting polymers are advantageous due to easiness in synthesis and flexibility [8].

The combination of carbon nanomaterials (such as CNTs) with electroactive materials (conducting polymers/metal oxides) is widely studied. The addition of RuO_2 in a CNTs matrix provided a significant increase in the specific capacitance [7]. CNTs/PAni nanocomposites obtained by chemical [9,10] and electrochemical [11] methods of aniline polymerization has proven very successful in achieving high values of capacitance. The reasons for such performances of CNTs/PAni nanocomposites are the increase of the polyaniline stability due to the presence of the CNTs, the formation of a porous network that provides electrolyte permeation through the entire sample and the enhancement in the conductivity and charge-transfer behavior of the conducting polymer [11,12].

In addition to the synthesis of thin and easily handled nanocomposites for applications in capacitors, the modern market demand is driving the production of flexible, lightweight and all-solid devices capable of retaining pseudo-capacitive behavior even under mechanical deformation. The construction of a flexible, simple and safe device is possible using an all-solid capacitor when the liquid electrolyte generally used in conventional devices is replaced with a gel electrolyte. Recently, many efforts have been made in the development of all-solid devices from carbon nanotubes and polyaniline [13–16], in addition to other capacitors with different capacitive materials, gel electrolytes and device configuration [17–21]. Meanwhile, the fabrication of an all-solid pseudo-capacitor from a thin, flexible and freestanding CNT/PAni nanocomposite has not yet been reported.

Even though several reported composites present impressive values of specific capacitance, most of them display some type of limitation in their processability, requiring multiple steps for the conversion of the nanocomposites to films, the use of external matrices for the nanocomposite deposition during synthesis, as in the case of buckypaper-like devices [15], or a previous synthesis of CNT films for the electrochemical deposition of PAni [11]. Hence, the development of a completely new method to obtain a nanocomposite in a single step is extremely interesting. Our previous report showed, for the first time, the synthesis and characterization of multi-walled carbon nanotubes/polyaniline (MWNTs/PAni) nanocomposites as thin films from the interfacial method [22], and its utilization as transparent and flexible electrodes in a solar cell [23]. This method was further extended to graphene/polyaniline nanocomposites [24] and also enables the synthesis of nanocomposites using SWNTs, which have displayed superior features as capacitors compared with MWNTs, due to their desirable properties such as high surface area and electrical conductivity.

The present work reports three main goals: the synthesis of SWNTs/PAni nanocomposites as thin and freestanding films in a liquid–liquid interface; the deposition of these films over flexible substrates for the construction of all-solid capacitors; and the characterization of both the nanocomposites and the device.

2. Experimental section

The SWNTs (Unydim-HiPCO) with a diameter of 0.8–1.2 nm and a length of 100–1000 nm were used as received. Aniline (Acros) was distilled twice before use. Chloroform (Biotec), toluene (Carlo Erba), sulfuric acid (Carlo Erba) and ammonium persulfate (Acros) were used as received. All solutions were prepared in deionized water (Milli-Q Ultra-Pure-Water Purification System).

The SWNT/PAni nanocomposite films were synthesized by a liquid–liquid interfacial polymerization, adapted from our previous report [22]. All reagent amounts are summarized in Table 1. Firstly, a SWNT dispersion in chloroform (3.12 mg L^{-1}) was prepared using an ultrasonic probe system with 40% amplitude for 10 min (Cole-Palmer ultrasonic processor). The dispersion was maintained in an ice-bath to avoid solvent evaporation. The aniline was added to the dispersion, and subsequently, the resulting mixture was transferred to a round-bottom flask containing ammonium persulfate (APS) previously dissolved in 30 mL of a 1 mol L^{-1} H_2SO_4 aqueous solution. The resulting system was maintained under magnetic stirring (approximately 750 rpm) for 22 h at room temperature. Afterward, the magnetic stirring was stopped, and a thin and freestanding film was formed at the chloroform/water interface. The aqueous phase was removed and renewed several times with a H_2SO_4 (pH 3) aqueous solution until this pH was reached to remove excess of acid. The organic phase was also removed and renewed three times to remove any side products. Finally, the chloroform was changed by toluene to facilitate the removal of the interfacial film. The two-phase system containing the nanocomposite film was transferred to a beaker containing a substrate (the synthesis and film removal are presented in Fig. S1). The substrate was removed using tweezers, and the interfacial film was deposited over it. Neat SWNT and PAni (in the same ratio of aniline in the SWNTs/PAni 1:96 nanocomposite) films were also synthesized following the same procedure described above. The SWNTs/PAni 1:96 nanocomposites and raw PAni with 2 and 3 layers were prepared. Firstly, one layer of nanocomposite (or raw PAni) was deposited over the substrate, as

Table 1
Experimental data for the different samples synthesized.

Sample	Mass of CNT (mg)	Volume of aniline (μL)	Mass of APS (mg)
SWNT	0.1	–	–
SWNT/PAni 1:16	0.1	1.6	1.02
SWNT/PAni 1:96	0.1	9.6	6.12
SWNT/PAni 1:144	0.1	14.4	9.19
PAni	–	9.6	6.12
$MWNT_{commercial}$/PAni	0.1	9.6	6.12
MWNT-Fe/PAni	0.16[a]	9.6	6.12

[a] Considering 37.2% of Fe-species residue.