

# Conducting polymer/carbon nanotube composite films made by in situ electropolymerization using an ionic surfactant as the supporting electrolyte

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## Abstract

We have demonstrated a simple and general strategy, namely in situ electropolymerization by using an ionic surfactant as the electrolyte, for alignment of disordered CNTs within conducting polymer/carbon nanotube composite films. The single- or multi-walled CNTs were first dispersed in an aqueous solution containing SDS (sodium dodecyl sulfate), then electroactive monomer pyrrole or *N*-methylpyrrole was added into the above mixture, finally electrochemical reaction was proceeded at the surface of the Au electrode and correspondingly a series of conducting polymer/carbon nanotube composite films with the orientation of carbon nanotubes were obtained.

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**Keywords:** Carbon nanotubes; Electrochemical treatment; Electron microscopy

## 1. Introduction

Carbon nanotubes (CNTs) possess exceptional mechanical properties, superior thermal and electrical properties [1,2], hence nanotubes can be ideal additives for structural and functional composites. For example, epoxy resin loaded with 1% single-walled carbon nanotubes (SWNTs) showed a 70% increase in thermal conductivity at 40 K, increasing to 125% at room temperature [3]. The presence of SWNTs in poly(*m*-phenylene vinylene-co-2,5-dioctoxy-*p*-phenylene) (PmPV) composites shifts the radiative recombination region in the double-emitting organic light-emitting diodes (DE-

OLEDs) without changing the PmPV emission energy [4]. Addition of only 1% multi-walled carbon nanotubes (MWNTs) to polystyrene results in a significant increase in the mechanical properties of the polymer because the external load can be effectively transferred to the nanotubes [5] and the introduction of MWNTs to polyaniline composites enhances the electrical properties by facilitating charge-transfer processes between the two components [6]. Carbon nanotubes have been aligned through different techniques such as template-directed fabrication, template-free chemical vapor deposition, self-assembly, mechanical stretching and electrophoresis, etc. [7–11]. However, when introduced into a polymeric matrix, CNTs disperse randomly, losing their orientations. Because of the unique one-dimensional structure of nanotubes, a high anisotropy is expected for nanotube-polymer composites. Hence, fabrication of high-performance nanotube-based composites should take into consideration the alignment of CNTs in a certain direction. Melt [12] or electrical [13] spinning of a

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composite through a narrow hole leads to nanotube alignment, but the method provides only fibers. The use of perpendicularly aligned carbon nanotubes for making composite materials with polymers should offer additional advantages to many applications with great ease [14]. Magnetic field assisted alignment of carbon nanotubes in a polymeric matrix is another very powerful strategy [15,16]. The reorientation of carbon nanotubes in a polymeric medium occurs due to the cooperative effect of the magnetic torque exerted by the magnetic field directly on the nanotubes and by the hydrodynamic torque and viscous shear exerted on the nanotubes by the polymer chains.

Herein, we describe a simple strategy for alignment of disordered carbon nanotubes within the conducting polymer matrix by in situ electropolymerization using an ionic surfactant as the supporting electrolyte. The CNTs were first dispersed in an aqueous solution containing an ionic surfactant similar to the procedure reported by Islam et al. [17], then electroactive monomer was added into the above mixture and finally electrochemical reaction was proceeded at the surface of the Au electrode.

## 2. Experimental

Pyrrole and *N*-methyl pyrrole were distilled under reduced pressure. Multi-walled carbon nanotubes used in this work were synthesized by ethylene CVD using  $\text{Al}_2\text{O}_3$  supported Fe catalysts as described elsewhere [18]. Typical multi-walled carbon nanotubes were uniform with diameters in the range of 8–25 nm and lengths up to several hundreds of nanometers. Their hollow cores and multi-layer walls could be clearly seen by TEM observation [19,20]. Single-walled carbon nanotubes were synthesized by pyrolysis of methane over MgO supported Fe catalyst, the preparation of which was mentioned elsewhere [21]. All carbon nanotubes were first treated with concentrated HCl for getting rid of the catalyst, then calcined for removal of amorphous carbon, and finally treated with concentrated HCl again before use. The as-made nanotubes were uniform with diameters of several nanometers and lengths up to several hundreds of nanometers. The single walls and hollow cores of the nanotubes could be clearly seen by high-resolution TEM images [22]. Other reagents were used without further purification.

The deposition of conducting polymer/carbon nanotube composite films was carried out at room temperature in a one-compartment cell by the use of CHI660A electrochemical workstation. The working and counter electrodes were gold (Au) plate and platinum (Pt) wire, respectively. All potentials were referred to a saturated calomel electrode (SCE). Scan rate was fixed at  $50 \text{ mV s}^{-1}$  and scan potential range was between  $-0.2$

and  $+0.8 \text{ V}$ . The typical electrolyte was an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS (sodium dodecyl sulfate),  $25 \text{ mmol L}^{-1}$  monomers and  $0.17 \text{ g L}^{-1}$  carbon nanotubes.

Infrared spectra were recorded with a Magna-IR 750 system. Raman spectra were recorded with a Renishaw system 1000 using a 50 mW He–Ne laser operating at 632.8 nm with a CCD detector. The final spectrum presented is an average of 10 spectra recorded at different regions over the entire range of the sample. SEM was conducted at 10 kV using XL30S-FEG field-emission instrument.

## 3. Results and discussion

Fig. 1 shows the cyclic voltammograms during the deposition of polypyrrole/CNT composite films. No obvious anodic current was seen by repeat cyclic voltammetric scanning in the potential scale of  $-0.2$  to  $+0.8 \text{ V}$  (vs SCE) in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS (sodium dodecyl sulfate) and  $0.17 \text{ g L}^{-1}$  CNTs (curve 4 in Fig. 1), which indicated both SDS and CNTs were stable in the experimental condition. No substances were deposited at the surface of the Au electrode by SEM observation, which was consistent with the electrochemical results. However, irreversible anodic current was seen in the presence of pyrrole and by keeping other experimental parameters constant (curves 1, 2 and 3 in Fig. 1). The onset of anodic current was at  $\approx 0.6 \text{ V}$ , and the value of anodic current at the maximal scanning potential ( $+0.8 \text{ V}$ ) was decreased with the increase of scanning cycles. These indicated that pyrrole was electropolymerized at the surface of the electrode [23]. It is well-known that, in order to get uniform dispersion of carbon nanotubes in aqueous solution,

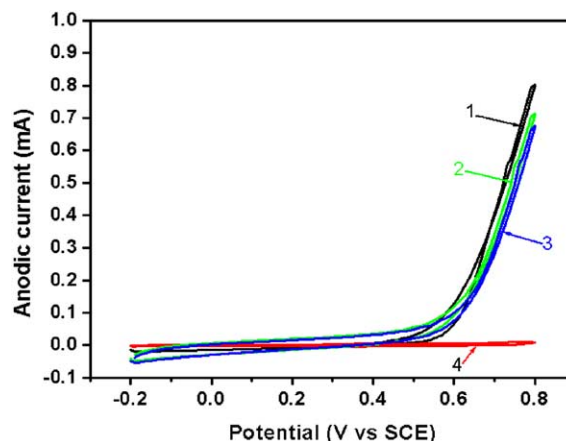


Fig. 1. Cyclic voltammograms of bare Au electrodes in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS,  $25 \text{ mmol L}^{-1}$  pyrrole and  $0.17 \text{ g L}^{-1}$  carbon nanotubes at different cycles: (1) first cycle, (2) fifth cycle, (3) tenth cycle and (4) first cycle in the absence of pyrrole monomer.

various surfactants were used [17,24,25]. Here, we used SDS to disperse CNTs. For purposes of getting such dispersion stable, we have avoided introducing other conventional supporting electrolytes. Chen et al. [26] has reported ionized CNTs as electrolytes, however, due to the absence of charges at the surfaces of CNTs, they could not serve as an electrolytes in this study. Hence the fact that the pyrrole has successfully electropolymerized at the surface of the electrode demonstrated that SDS has acted as the supporting electrolyte.

Figs. 2a and b show the SEM images of conducting polypyrrole/single-walled carbon nanotube composite films obtained by repeat cyclic voltammetric scanning in the potential scale of  $-0.2$  to  $+0.8$  V in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS,  $25 \text{ mmol L}^{-1}$  pyrrole and  $0.17 \text{ g L}^{-1}$  single-walled carbon nanotubes (SWNTs). It was clearly seen that a uniform film was deposited at the surface of the Au electrode. There were so many one-dimensional nanostructures that stood almost vertically on the deposited films. Such nanostructures were of roughly uniform size with diameters in the range of several hundreds of nanometers and height of up to several micrometers. The rough distances among these nanostructures were in the range of several micrometers. However, these one-dimensional nanostructures could not be seen in the absence of carbon nanotubes and by keeping other experimental parameters constant, which indicated that the growth of these nanostructures at the surface of the Au electrode has something to do with CNTs. Comparing the size of these nanostructures with that of nanotube bundles (the diameters of these nano-

structures were much larger than that of nanotube bundles), we could deduce that these nanostructures were not nanotube bundles themselves, but nanotubes or their small bundles enwrapped with the deposited substance.

Fig. 3 shows the vibrational spectra of films obtained by repeat cyclic voltammetric scanning in the potential scale of  $-0.2$  to  $+0.8$  V in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS,  $25 \text{ mmol L}^{-1}$  pyrrole and  $0.17 \text{ g L}^{-1}$  single-walled carbon nanotubes. For IR spectrum, strong peaks at  $1549$  and  $1469 \text{ cm}^{-1}$  were due to the antisymmetric and symmetric ring-stretching modes of the PPy, respectively [27]. The peak at  $1176 \text{ cm}^{-1}$  indicated the doping state of polypyrrole, and the peaks at  $1045 \text{ cm}^{-1}$  and  $1315 \text{ cm}^{-1}$  were attributed to C–H deformation vibrations and C–N stretching vibrations of the PPy, respectively [28,29]. The two very strong peaks around  $2914 \text{ cm}^{-1}$  and  $2846 \text{ cm}^{-1}$  were attributed to the stretching vibration mode of methylene, indicating that surfactant SDS had been doped into the chains of PPy [30]. For Raman spectrum, the strong peak at  $1583 \text{ cm}^{-1}$  represents the backbone stretching mode of C=C bonds, and the peaks at  $\approx 1377$  and  $1083 \text{ cm}^{-1}$  belong to the ring stretching and the N–H in-plane deformation of the oxidized (doped) species of the PPy, respectively. The corresponding band of the neutral species at  $1048 \text{ cm}^{-1}$  is relatively weak [31]. These indicated that the doping level of the PPy was relatively high. The characteristic peaks of carbon nanotubes could not be seen in the vibrational spectra of as-made pyrrole/CNT composite films, which indicated that carbon

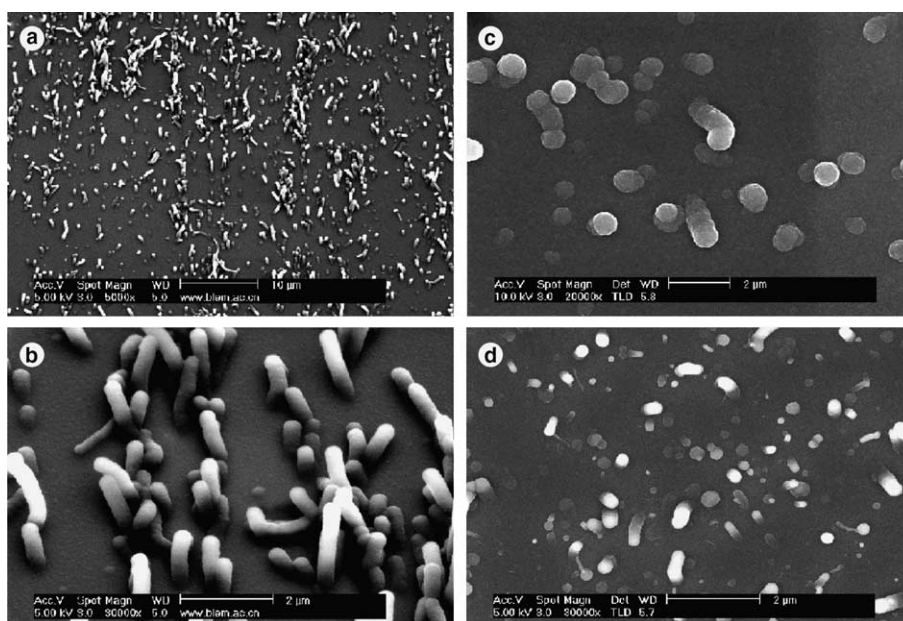


Fig. 2. (a) SEM image of polypyrrole/SWNT composite films obtained by repeat cyclic voltammetric scanning in the potential scale of  $-0.2$  to  $+0.8$  V in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS,  $25 \text{ mmol L}^{-1}$  pyrrole and  $0.17 \text{ g L}^{-1}$  SWNTs; (b) SEM image of (a) with  $30^\circ$  rotation; (c) SEM image of polypyrrole/MWNT composite films with the condition same to (a); (d) SEM image of poly(*N*-methylpyrrole)/SWNT composite films with the condition same to (a).

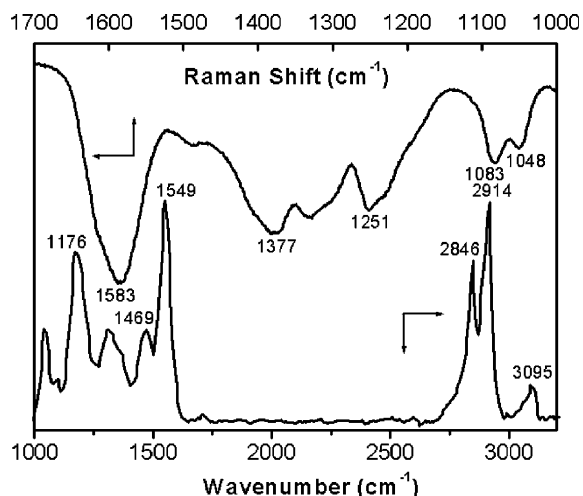


Fig. 3. IR (bottom) and Raman (top) spectra of polypyrrole/CNT composite films obtained by repeat cyclic voltammetric scanning in the potential scale of  $-0.2$  to  $+0.8$  V in an aqueous solution of  $0.1 \text{ mol L}^{-1}$  SDS,  $25 \text{ mmol L}^{-1}$  pyrrole and  $0.17 \text{ g L}^{-1}$  single-walled carbon nanotubes.

nanotubes were perfectly wrapped with the deposited PPy [19,20].

To determine the mechanism by which the composite films formed, we examined the role of specific reagents used in the above procedure. The surfactant was examined first by replacing the anionic surfactant SDS with a cationic surfactant dodecyltrimethyl ammonium bromide (DTAB). In this case, no polypyrrole/CNT composite films were observed, which indicated that both CNTs and the electroactive monomer were wrapped and dragged by the surfactant molecules with an electric field existing. Then either replacing SWNTs with multi-walled carbon nanotubes (MWNTs) or replacing pyrrole with *N*-methylpyrrole, both polymer/CNT composite films could be obtained with protrusive nanostructures, respectively (Fig. 2c,d). Moreover, SEM images of the resulting composite films with different deposited times (Fig. 4) showed the similar morphology, which indicated the well aligned and dispersed CNTs in the matrix of the polymer as a result that the latter deposited layers would cover the former deposited layers.

From these investigations, it was possible to put forward a mechanism for conducting polymer/CNT composite film formation (Fig. 5). It is well-known that micelle-encapsulated carbon nanotube composite nanostructures would form when using SDS to disperse carbon nanotubes in aqueous solution [17,24,25], and that pyrrole could enter the interiors of micelle-encapsulated carbon nanotubes and locate at the interfaces between surfactants and carbon nanotubes [19,20]. These micelle-encapsulated carbon nanotube composite nanostructures were with random orientation without an electric field existing (Fig. 5a). When exerting positive

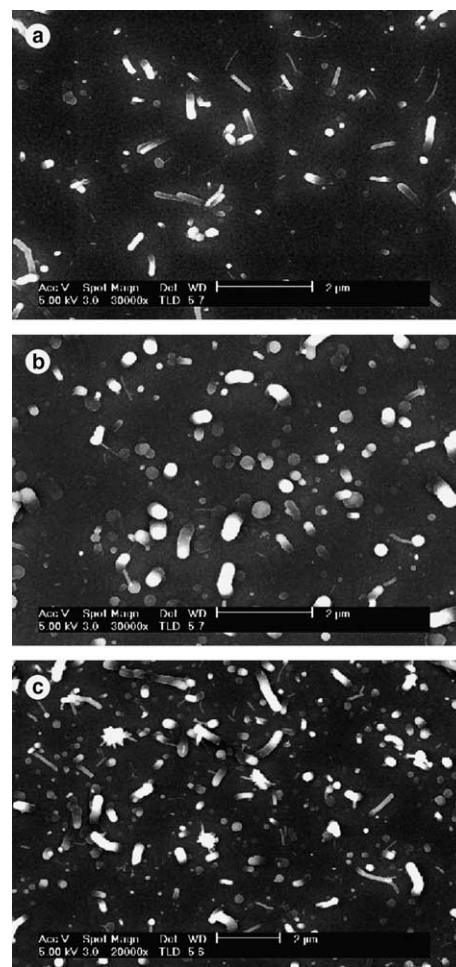


Fig. 4. SEM images of poly(*N*-methylpyrrole)/SWNT composite films obtained with the different electro-deposition time: (a) 40 s; (b) 240 s; (c) 400 s.

voltage to Au electrode, due to orientation of carbon nanotubes in the presence of an electric field [32,33], these micelle-encapsulated carbon nanotube composite nanostructures at the vicinities of the Au electrode would orient towards the surface of the Au electrode [34] (Fig. 5b). Meanwhile, due to the interaction between positive Au electrode and SDS negative ions, the micelle-encapsulated carbon nanotube composite nanostructures would move towards and as far as the surface of the Au electrode (Fig. 5c). Once micelle-encapsulated carbon nanotube composite nanostructures ran into the Au electrode, if potential high enough, pyrrole located at the interfaces between surfactants and carbon nanotubes would oxopolymerize at the surfaces of both the Au electrode and carbon nanotubes (Fig. 5d).

In summary, we have demonstrated a simple and general strategy, namely in situ electropolymerization by using the ionic surfactant as electrolyte, for alignment of disordered CNTs within conducting polymer/carbon nanotube composite films. Surfactant SDS has played

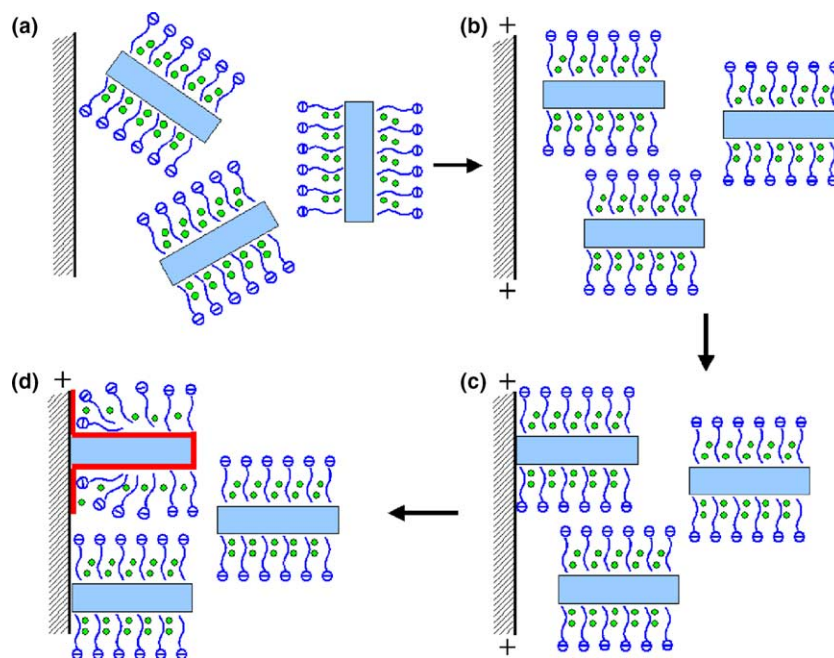


Fig. 5. Schematics of different stages in a typical electrochemical synthesis of conducting polymer/CNT composite films: (a) disordered micelle-encapsulated CNTs without electric field existing, within which electroactive monomer was filled; (b) orientation of micelle-encapsulated CNTs with electric field exerting; (c) migration of oriented micelle-encapsulated CNTs to the surface of the Au electrode in the presence of electric field; (d) filled electroactive monomer was polymerized at the surfaces of both Au electrode and CNTs when potential high enough.

a key role in the synthesis of conducting polymer/carbon nanotube composite films. It has not only served as electrolyte and dopant, but dispersed and stabilized carbon nanotubes in aqueous solution. It can be envisioned that conducting polymer/carbon nanotube composite films made by this simple approach would have great potentials in field emission devices and sensors. It also provides the appropriate materials for testing the physical properties of the individual conducting polymer/carbon nanotube coaxial nanowires.

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