

Conductive polyaniline composite films from aqueous dispersion: Performance enhancement by multi-walled carbon nanotube



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ABSTRACT

The intractable multi-walled carbon nanotube (MWNT) was dispersed in aqueous solutions of conductive polyaniline (cPANI) by externally doping of MWNT/polyaniline (PANI) employing an organic polymeric phosphate acid as the dopant. Free-standing composite films were obtained from the MWNT/cPANI aqueous dispersion after drying. In comparison with the cPANI, the conductivity of MWNT/cPANI composites showed a 2 order of magnitude increase with the maximum value 1.2 S cm^{-1} , at the MWNT loading of 1.0 wt% because of the doping effect of MWNT on PANI. Under the strong π - π interactions between PANI and MWNT which were discussed by FT-IR and UV-vis analysis, the redox performance of the MWNT/cPANI composites was significantly modified compared with the pure cPANI. In addition, the capacitive behaviors of the MWNT/cPANI films varied with the difference of the MWNT loading due to the morphology variation resulted from the established interactions. The enhanced specific capacitance with the highest value of 371 F g^{-1} at a current loading of 0.5 A g^{-1} was obtained for the MWNT/cPANI films containing MWNT content of 1.0 wt%, as well as the better cyclability.

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1. Introduction

Among numerous conductive polymers, polyaniline (PANI) is considerably attractive because of easy synthesis, environmental stability and high controllable conductivity, which has been widely used in light weight battery electrodes [1], energy storage devices [2,3], light-emitting diodes [4] and anticorrosion coatings [5]. To further enhance electrical and mechanical properties over pure conducting PANI (cPANI), introduction of carbon nanotube (CNT) showing high conductivity into cPANI matrix has recently attracted much attention [6,7]. Because of the strong molecular adhesion among them, the main challenge is to obtain processable CNT/PANI in the emeraldine salt form, which is considerably required for the fabrication of flexible electrochemical devices.

Soluble conducting polyanilines can actually be obtained by incorporation of functional groups on the backbone and doping of PANI by soluble polymeric acid [8,9]. Once cPANI becomes soluble, the intractable CNTs can be dissolved into the formed solutions stabilized by the solubilized cPANI chains [10]. By using of the anionic surfactant as a common stabilizer as well as an additional

dopant, the composite of cPANI/single-walled carbon nanotube (SWNT) prepared by interfacial polymerization was successfully extracted from the aqueous phase to the organic xylene phase, forming a processable organic dispersion [11]. With the increasingly environmental concerns, synthesis of water-soluble conductive polyaniline/CNT composites from environment-benign processes becomes inevitable. Whereas micelle-CNT hybrid template directed synthesis method is a feasible route to aqueous dispersion of CNT/cPANI composites [12], post elimination of the surfactant from the system is generally needed during practical applications. Therefore, the chemical modification method by hydrophilization of cPANI has been a favorably used route to prepare the water-borne CNT/cPANI composites, where the tedious removal of insulating surfactants is not required. In Haddon group, by covalent attachment of poly(m-aminobenzene sulfonic acid) to single-walled carbon nanotube, the nanotube-sulfonic cPANI compound without the presence of surfactant was made water-soluble [13], which showed a conductivity of $5.6 \times 10^{-3} \text{ S cm}^{-1}$. In addition, via noncovalent functionalization of multi-walled carbon nanotube (MWNT) by sulfonic cPANI, the nanotube/cPANI composite also showed good water-soluble behaviors [14]. However, the conductivity of these nanotube/sulfonated cPANI composites was difficult to be further increased because of the presence of the electron-withdrawing sulfonic group on the

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aromatic rings of PANI. In fact, cPANI can also be well dispersed in water by externally doping PANI with a suitable polymeric acid, aside from the style of synthesizing water-soluble self-doped cPANI. Employing acidic phosphate diester carrying long hydrophilic tail as the dopant, stable aqueous solution of cPANI was successfully prepared by Wang et al. [15–17]. However, the conductivity of the free-standing films obtained was less than 0.1 S cm^{-1} , due to the presence of high concentrations of insulating polymeric components in the system. For the electrochemical performance enhancement, addition of some compounds showing high conductivity such as CNTs into the cPANI matrix is a facile approach.

We report here a water-dispersible conducting MWNT/cPANI composite with enhanced electrochemical performance than pure cPANI. The conducting MWNT/PANI composite was prepared based on the in-situ polymerization of aniline and MWNTs followed by doping with acidic phosphate diester carrying long hydrophilic tail in water, as shown in Fig. 1. By using a solution casting method, the free-standing flexible MWNT/cPANI composite films were available. On the other hand, CNTs and conducting polymers are considered as the main materials for the supercapacitor electrode aside from metal oxides [18,19]. Therefore, combination of MWNT and cPANI may endow the composites surprisingly high capacitance, thus opening many new possibilities for their prospective technological applications.

2. Experimental

2.1. Materials

All reagents and chemicals were used as received unless otherwise noted. MWNTs were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Science (>99% purity, length 10–20 μm). Poly(ethylene glycol monomethyl ether)-350 (PEGME-350, where 350 is the average molecular weight of the ether oligomer) were of analytical purity purchased from Acros Co. Aniline and POCl_3 were used after distillation (the POCl_3 solution is highly corrosive, and therefore extreme care had to be exercised during handling).

2.2. Synthesis of organic protonic dopant

The organic protonic dopant of acidic phosphate ester (APE) was synthesized from the reaction of POCl_3 (0.5 mol) and PEGME-350 (1.0 mol) under vigorous stirring at 65°C for 24 h under nitrogen [15]. The residual water was removed in vacuum at 70°C for 2 h, and the product was further dried over 4 \AA molecular sieves

for 2 d prior to use. The acidity value of APE determined by potentiometric titration was $1.75 \times 10^{-3} \text{ mol/ml}$.

2.3. Preparation of MWNT/PANI composite

The composite of PANI with MWNT was synthesized via in-situ chemical oxidation polymerization. In a typical synthesis experiment, various weight ratios of MWNTs were dissolved in 30 ml of 1.0 M HCl solutions and ultrasonicated for 1 h, then transferred into a 250 ml beaker. 0.4 ml of aniline monomer (4 mmol) was added to the above MWNTs suspension and ultrasonicated for 0.5 h. A 50 ml of 1.0 M HCl solution containing 5 mmol ammonium persulfate (APS) was slowly added dropwise into the suspension under vigorous agitation at a reaction temperature of $0\text{--}5^\circ\text{C}$ for 4 h. The resulting deep green suspension was filtered and rinsed several times with 1.0 M HCl solution, methanol and distilled water. After thoroughly undoped by 0.1 M ammonia, the obtained black powder of MWNT/PANI composite was then dried under a vacuum at 60°C overnight.

2.4. Doping of MWNT/PANI composite

Doping of MWNT/PANI composite was realized through protonation of the imine nitrogen sites on PANI by the protonic acid APE (H^+M^-) according to the acid-base chemistry. PANI was thus doped to be conducting. The formed counter ion (M^-) containing the long tail of PEG endowed the MWNT/PANI system good water solubility besides ensuring overall charge neutrality. The MWNT/PANI aqueous complex was formed by mixing 10 mg of MWNT/PANI and an appropriate amount of APE at room temperature under vigorous stirring for 1 h, where the molar ratio of H^+ in APE to phN- in PANI was 0.5. Followed by adding 4 ml of distilled water and then stirred at 50°C for 2 h, stable dispersions of MWNT/PANI caused by the counter-ion induced processability from APE were formed (Fig. 1). The free-standing MWNT/cPANI composite films showing good flexibility were then obtained by solution casting of MWNT/PANI aqueous solution on a plastic disk and dried at room temperature.

2.5. Cyclic voltammetry measurements

Cyclic voltammetry of MWNT/cPANI was performed using a commercial potentiostat (CH Instrument 660C). The electrochemical cell used was a conventional three-electrode cell with a commercial Ag/AgCl (3MKCl) electrode as the reference electrode and a platinum wire as the counter electrode, in 1.0 M sulfuric acid at a scan rate of 50 mV/s in a voltage range of -0.4 to 1.0 V .

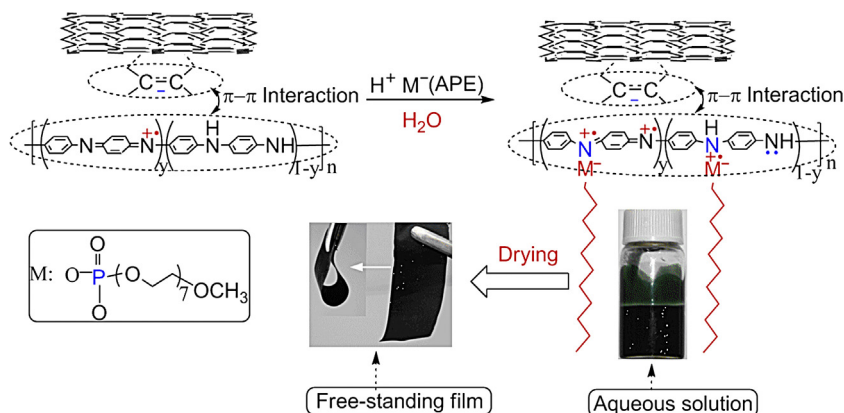


Fig. 1. Illustration of preparation of MWNT/cPANI composite films by doping and proposed composite interactions.

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