



The effect of 3-amino benzoic acid linker and the reversal of donor–acceptor pairs on the electrochemical performance and stability of covalently bonded poly(pyrrole) nanotubes



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ABSTRACT

The multiwall carbon nanotubes–polypyrrole (MWCNTs–PPy) composite is a well-known hybrid material suitable for energy storage applications such as capacitors. Since the electrochemical activity, and long-term stability of carbon–PPy systems are critical for their application, we examined the effect of grafting PPy via a 3-ABA linker with MWCNTs with respect to the preference of the donor–acceptor pairs, and furthermore, the durability. X-ray photoelectron spectroscopy studies of C 1s and O 1s signals reveal the electronic interaction between carbon and polymer (π – π^* stacking), as well as a binding energy shift for C 1s and O 1s carbonyl signals due to the chemical bonding via the electron donating linker and grafted polymer. Cyclic voltammetry and galvanostatic charge–discharge studies of the capacitor electrode reveal the effect of the reversal doping of the polymer with chloride, as well as the synergy of double layer capacitance (MWCNTs) and pseudo-capacitance of the poly(pyrrole). Impedance spectroscopy studies confirm the improved electrochemical stability for the composite (stable until 1.2 V) in comparison to the bare polymer (degradation at 0.58 V).

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1. Introduction

The need for developing long-life, affordable and non-toxic energy storage materials is a driving motivation for current research in the area of energy reposition. With respect to this, one of the most promising materials is the carbon–polymer composite. The understanding of carbon–macromolecule interactions requires knowledge in the fields of colloidal science and polymer physics. Collectively, these disciplines allow the possibility to explore complex systems, which regardless the unique morphology, are expected to generate many synergistic effects affecting the optical, electrical, mechanical and thermal properties of the composite in question [1]. Although there have been a plethora of carbon–polymer combinations studied, some behaviors of carbon

nanotube (CNT)–polymer systems, and the origin of the synergies, are not yet fully understood. The interfacial modification of CNTs by polymers can be approached in two ways. In the first, the macromolecule provides the specific surface functionalities (inherent additive) [2,3]. In the second, the polymer interacts with CNTs via either strong covalent [4,5], electrostatic [6], π – π^* stacking [7], or hydrogen bonding interactions [8]. These interactions generate strong coupling between the components, resulting in CNTs with completely new surface properties, new carbon–solvent balance, or alteration of CNT internal diameter [9]. The range and strength of the interaction can be controlled by the molecular weight, physical size, and density of the polymer film [10]. Although there is plenty of freedom in modifying carbon with macromolecule of various chemical compositions, shapes, thickness, and type of intermolecular invasion, the challenge is to modify carbon without affecting its intrinsic properties, especially in the case of CNTs. For instance, a strong coupling has been reported for electronically conducting polymers–CNTs composites [4]. These types of conducting polymers

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are quasi-infinite conjugated π -systems, extending over a large number of repeating monomer units, and result in a band-like electronic structure. The conduction mechanism relies on the transfer of charged defects within the conjugated framework, and strongly depends on the level of doping [11]. Regarding the composites and taking MWCNTs-(poly)-L-tyrosine as an example, the electronic structure of conducting polymer is modified by the presence of CNTs, indicating a strong coupling between the MWCNTs and polymer π - π systems [12]. The CNTs can also promote the solution-protonation of the polymer, resulting in modification of the polymers electrical properties [5]. Another critical aspect in the synthesis of an ultra-efficient composite is the molecular-scale particle design and the geometry control. For example, in CNT-polymer systems it can be the helical wrapping of the tubes in an ultra-thin polymer film [14]. Polymer-reinforced CNTs form long-lived stable dispersions in different media [13], with improved mechanical and electrical properties in comparison to their individual components [13].

In this work we study a model system composed of MWCNTs and poly(pyrrole) to emphasize the effect of grafting on electrochemical properties. We utilize a metal-free Friedel–Crafts derivatization of multi-walled carbon nanotubes using poly(phosphoric acid), phosphorus pentoxide, and 3-amino benzoic acid [4]. This generates a covalent linker between the carbon fraction and a pyrrole that is introduced *via* an oxidative/radical polymerization with ammonium persulfate in hydrochloric acid [15,16]. The composite is able to be analyzed by conventional methods ($^1\text{H}/^{13}\text{C}$ NMR, FTIR and FT Raman for the phase identification) and TEM to validate the morphology. The X-ray photoelectron spectroscopy (XPS) is employed to study the binding character and the interaction between molecular components (CNTs-grafted-PPy and the 3-amino-benzoic acid (3-ABA) linker). Furthermore, the electrochemical response of the combined composite system is investigated by cyclic voltammetry accompanied by galvanostatic charge–discharge long-term cycling. The electrochemical impedance spectroscopy will validate the long-term electrochemical stability of the composite, revealing its potential for practical applications.

2. Experimental

All materials, if not otherwise stated, were used as received without further purification. Multi-walled carbon nanotubes (carbon content, >95% trace metal basis), phosphorous pentoxide (Reagent Plus 99%), ammonium persulfate (ACS reagent, $\geq 98\%$), polyphosphoric acid ($\geq 83\%$ phosphate as P_2O_5 basis), and poly(vinylidene fluoride, $M_w \sim 180,000$) were purchased from Sigma Aldrich, Germany. Pyrrole (Merck KGaA, Darmstadt, Germany) was distilled over calcium chloride (Carl Roth GmbH + Co. KG, Karlsruhe, Germany, $\geq 94\%$, drained) and stored under dry nitrogen. Potassium chloride (for analysis Empure) and 2-propanol (EMPLURA) were purchased from Merck KGaA, Darmstadt, Germany. Methanol (GPR RECTAPUR) and hydrochloric acid (37%) were purchased from VWR International GmbH. Carbon black (Super P Conductive, 99%, metal basis) was purchased from Alfa Aesar, UK. Ultra-pure water 18 M Ω was used for all aqueous solutions.

TEM imaging was carried out using a FEI Technai G2 20 cryo-transmission electron microscope operating at 120 kV.

XPS measurements were performed using a EA200 ESCA system (SPECS GmbH) with Mg K α radiation (1.253 eV). All data were calibrated with respect to the C 1s excitation (284.6 eV) to account for charging effects by the electron beam. Narrow scans for C 1s and O 1s were carried out with 0.2 eV step size, revealing information of the chemical state of each sample. The spectra were deconvoluted with a mixed Gaussian function.

Raman spectra were recorded using a micro-Raman setup (HR

LabRam inverse system, Jobin Yvon Horiba). Raman scattering was excited by a frequency-doubled Nd/YAG laser at 532 nm using a laser power of 4 mW, and focused on polymer samples using Olympus 50 \times microscope objective. The dispersive spectrometer has an entrance slit of 100 μm and is equipped with a grating of 300 lines mm^{-1} (spectral resolution $\sim 1 \text{ cm}^{-1}$). The Raman scattered light was detected by a charge-coupled device camera operating at 220 K. The acquisition time per spectrum was 30 s.

Electrochemical experiments were carried out using a Princeton Applied Research VersaSTAT MC potentiostat and an electrochemical cell containing a platinum wire counter electrode (CE), a Ag/AgCl reference electrode (RE), and PPy-g-MWCNTs ink cast onto glassy carbon as a working electrode (WE). All potentials are quoted vs. Ag/AgCl (+197 mV vs a standard hydrogen electrode). All electrochemical measurements were carried out in 1 M KCl purged with N_2 for 30 min prior to experiments (N_2 gas blank was kept during measurement). A glassy carbon working electrode disk of 0.5 cm diameter (PINE Instrument Company, U.S.A.) was mechanically polished with 0.05 μm Al_2O_3 slurry (Cypress Systems, Inc., U.S.A.), rinsed in deionized water, sonicated in ultrapure water for 5 min, and finally rinsed in ultrapure isopropanol followed by acetone. Ink was prepared by dissolving PVDF (2 mg) in isopropanol (2 mL) sonicated for 0.5 h together with carbon black (2 mg) and 17 mg of an active material PPy-g-MWCNT. The resulting ink (10 μL) was cast onto the polished glassy carbon working electrode and dried for 10 min in air. Cyclic voltammetry (CV) was carried out in the potential range from -0.5 to 0.5 V vs Ag/AgCl reference electrode at a scan rate of 50 mV s^{-1} . Electrochemical impedance spectroscopy measurements were conducted in the frequency range from 10 kHz to 10 mHz with a 10 mV potential amplitude and at OCP potential for a fresh and degraded material. The electrochemical degradation studies were carried out chronoamperometrically by holding the potential at 0.7, 0.8, 0.9, 1.2 and 1.5 V for 5 min. EIS spectra were recorded after each degradation test at the same conditions as for the fresh electrode. Before EIS measurement 10 CV scans were applied to ensure relaxation of the polymer component (and to maintain comparable conditions to a fresh sample). ZView software (Scribner Associates Inc. USA) was applied for the fitting of EIS spectra.

3. Synthesis of MWCNTs-PPy nanocomposite

Fig. 1 represents reaction steps during the synthesis of grafted nanocomposite (an auto accelerating loop) [4]. The covalently bonded nanocomposite consists of multi-walled carbon nanotubes (MWCNTs, also considered as a core fraction) linked to a polypyrrole (PPy, shell or coating) through the 3-amino-benzoic acid (3-ABA) linker. This synthesis begins from the activation of the polyphosphoric acid (PPA) and 3-ABA in the presence of phosphorous pentoxide (P_2O_5), resulting in the formation of a carbonyl anchor that participates in functionalization of MWCNTs [4]. The polyphosphoric acid is both a solvent and a protonating agent of the carbonyl groups of 3-ABA. Simultaneously, deprotonated PPA is recovered during the reaction with the phosphonate center of the P_2O_5 [4]. Furthermore, the common Friedel–Crafts type reaction takes place between 3-aminobenzylidene oxonium mote (generated through α -elimination of water from the protonated 3-ABA's carboxyl group) and MWCNTs, resulting in functionalized carbon nanotubes. According to literature [4,17] the stability of the acylium ion produced affects the primary protonation of carboxyl group. An important point to be observed is that the phosphorous pentoxide and poly(phosphoric acid) do not participate in protonation amino groups, and therefore do not affect the progress of the Friedel–Crafts reaction at the conditions applied in this synthesis procedure. Additionally, the alkalinity of amino-group is strongly

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