

Tubular shaped composites made from polythiophene covalently linked to Prato functionalized N-doped carbon nanotubes

Manoko S. Maubane^{a,b}, Messai A. Mamo^{a,b}, Edward N. Nxumalo^{a,b,c}, Willem A.L. van Otterlo^{b,d,*}, Neil J. Coville^{a,b,**}

^a DST/NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, P.O. Wits 2050, South Africa

^b Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, P.O. Wits 2050, South Africa

^c Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, South Africa

^d Department of Chemistry and Polymer Sciences, Stellenbosch University, Stellenbosch 7600, Western Cape, South Africa

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ABSTRACT

A simple methodology to produce tubular nitrogen-doped carbon nanotube/polythiophene covalently linked composites is described. Nitrogen doped carbon nanotubes (N-CNTs) were made by the floating catalyst CVD method using toluene, ferrocene and tetramethylethylenediamine (TMEDA) as reagents. Functionalization of the N-CNTs was achieved using 3-thiophenecarboxaldehyde and *N*-methylglycine in 1,2-dichlorobenzene (*Prato* reaction). Elemental analysis showed nitrogen incorporation of N into the N-CNTs (1.8%) and also the *N*-methylglycine functionalized N-CNTs (f-N-CNTs; 6.2%). A series of f-N-CNT/thiophene monomer mixtures (weight ratios 1:3, 1:10 and 1:20) were used to make f-N-CNT/polythiophene tubular composites. As the amount of thiophene monomer was increased, the overall diameter of the polymer layer attached onto the N-CNTs increased. Polymer thickness also varied with reaction time (1 h, 12 h and 24 h). The combination of acid functionalization and N-doping gives the best coverage of the CNTs by polythiophene, in which the polythiophene preferentially binds to the f-N-CNTs to give tubular structures.

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1. Introduction

Since the report by Iijima describing the synthesis of carbon nanotubes (CNTs) in 1991 [1], and because of their unique structures, outstanding electrical and mechanical properties, structural properties and potential applications, CNTs have attracted considerable interest over the past two decades [2–4]. They are extremely promising materials for applications in materials science and medicinal chemistry [5]. The intentional introduction of impurities (dopants) into CNTs via the substitution of carbon atoms with boron or nitrogen atoms has been shown to modify the chemical, electrical and structural properties of the CNTs. Among all the doped CNTs, the N-doped CNTs are of special interest in both fundamental and application studies [6]. The additional electrons contributed by nitrogen atoms to the CNTs provide

electron carriers for the conduction band [7]; N-doped CNTs are thus found to be metallic and possess narrow energy gaps [8,9], offering the possibility of greater electrical conductivity as compared to pure CNTs. The introduction of nitrogen atoms into a CNT also impacts on the chemistry of CNTs as this can make CNTs more susceptible to chemical modification [10]. One characteristic commonly observed after nitrogen incorporation into the CNT lattice is the bamboo-shaped structures that are observed in the inner tube. This permits the easy identification of the presence of nitrogen atoms in CNTs that are made using Fe as catalyst [10].

Nitrogen-doping of carbon nanostructured materials can be achieved by various procedures [11]. These include (i) doping directly during the synthesis of carbon nanostructured materials, which is called “in situ” doping and (ii) post-treatment of pre-synthesized carbon nanostructure materials with a nitrogen-containing precursor (N₂, NH₃, etc.), i.e., post-doping.

CNTs have been used to make composites with polymers, typically using two different routes; by physically mixing the CNT and the polymer or by chemically linking the CNT to the polymer by “grafting to” or “grafting from” procedures [12]. CNTs functionalized with monomers that can form part of a polymer have been found to give a good dispersion of CNTs in polymer matrices [13].

* Corresponding author at: Department of Chemistry and Polymer Sciences, Stellenbosch University, Stellenbosch 7600, Western Cape, South Africa
Tel.: +27 21 808 3344; fax: +27 21 808 3360.

** Corresponding author at: DST/NRF Centre of Excellence in Strong Materials and the Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, P.O. Wits, 2050, South Africa. Tel.: +27 11 717 6738; fax: +27 11 717 6749.

E-mail addresses: wvo@sun.ac.za (W.A.L. van Otterlo), neil.coville@wits.ac.za (N.J. Coville).

The embedding of CNTs into conducting polymeric matrices has been reported [14,15] with research fuelled by the hope of delivering the properties of CNTs to the composites, in particular conducting polymers. Among the various conducting polymers, polythiophene (PTh) has high stability in its doped and undoped electronic states, can be easily modified and has controllable electrochemical behaviour [16]. PTh is generated by the polymerization of thiophene and can become conducting when electrons are added or removed from the conjugated π -orbitals via doping. The most notable property of a conductive polymer, electrical conductivity, results from delocalization of electrons along the polymer backbone [16]. Due to the polymer's versatility, PTh polymers have therefore been used in electrical conductors, recording materials, sensors, batteries, imaging materials, solar cells, etc.

A number of groups have disclosed the successful incorporation of CNTs into polymer matrices such as poly(3-hexylthiophene) (P3HT) [12,17–20]. For instance, Karim et al. [21] described the successful formation of single wall carbon nanotube/polythiophene (SWNT/PTh) composites by an in situ chemical oxidative polymerization method. They also reported on the structure and properties of these composites. On the other hand, Pokrop et al. investigated the electrochemical and Raman spectroelectrochemical properties of SWNT-PTh hybrid materials [22]. The incorporation of N-CNTs into polymer matrices has also been reported [23]. Fragneaud et al. [24] reported on the efficient coating of N-CNTs with polystyrene (PS) using aromatic transfer radical polymerization and found that all the tubes were uniformly coated with an amorphous layer of PS. The same group later reported on the electrical and mechanical behaviour of materials made by incorporating N-CNTs into PS [25,26]. To date, and to the best of our knowledge, no incorporation of N-doped CNTs into a PTh polymer has been published.

In this present work, the covalent functionalization of N-CNTs by the *Prato* reaction [27,28], followed by in situ chemical oxidative polymerization of the functionalized N-CNTs (f-N-CNTs) is reported. It is to be noted that while many reports have appeared in which the *Prato* reaction has been applied to SWCNTs [29–31], the *Prato* reaction has, to our knowledge, not been applied to N-CNTs. Thus, this study focuses on the synthetic strategy of applying the principle of making a composite in which covalent bonds link the two constituent materials together, one of which is a N-CNT material. To ensure that the new materials could readily be observed in TEM/SEM studies, a large excess of thiophene monomer (relative to the f-N-CNT) was used. Polymerization was thus performed in the presence of N-CNT:thiophene monomer ratios of 1:3, 1:10 and 1:20 by weight, and for varying polymerization times (1 h, 12 h, 24 h) to ensure that the new composites, in the shape of tubular structures, could readily be observed.

2. Experimental

2.1. Chemicals and materials

All chemicals used in this study were reagent grade quality and were used as supplied, unless otherwise stated. The thiophene monomer (99+%), anhydrous iron (III) chloride (97%), *N*-methylglycine (98%), TMEDA (99%), 3-thiophenecarboxaldehyde (98%) and other organic solvents were purchased from Sigma Aldrich. In the case of organic solvents, these were dried by distillation over calcium hydride or sodium wire and stored under argon gas prior to use. All the polymerization reactions were carried out under a continuous flow of argon, unless otherwise stated. Nitrogen-containing CNTs (N-CNTs) used in this study were synthesized in our laboratory using a CVD floating catalyst method (see below). Undoped functionalized CNTs made from toluene and ferrocene were synthesized by way of a literature procedure [32].

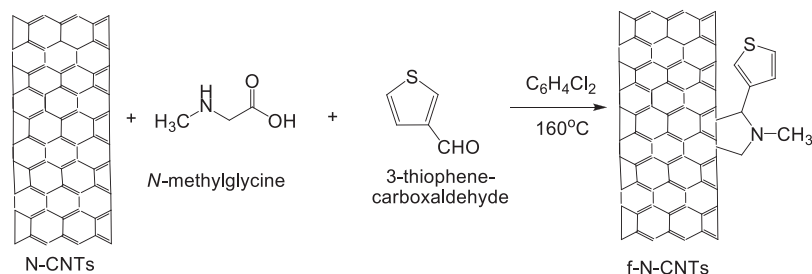
2.2. Synthesis of N-CNTs, f-N-CNTs, PTh and the composite materials

2.2.1. Synthesis of N-CNTs

The N-CNTs used in this study were synthesized by the floating catalyst CVD method [33]. In a typical run, a weighed empty boat was placed in a horizontal quartz tube (18 mm \times 22 mm) which was placed in a furnace. The furnace was heated to 900 °C and a continuous flow of 5% H₂ gas in Ar (AFROX) was passed through the quartz tube. A ferrocene (2.5%), toluene (90%) and TMEDA (tetramethylethylenediamine; 7.5%) mixture (by weight) was prepared and transferred into a 20 mL syringe driven by a SAGE pump. The solution was then injected into the quartz tube at 0.8 mL/min. The reactor system was then allowed to cool to rt under a flow of 5% H₂ in Ar. The boat was then removed from the quartz tube, the carbon deposit removed and weighed, and the material characterized. The synthesized N-CNTs were purified by heating at reflux in 32% HCl (48 h), followed by filtration (MN 615 110 mm filter paper) and subsequent drying (oven at 120 °C for 12 h and under vacuum for a further 12 h).

2.2.2. Functionalization of N-CNTs (*Prato* reaction)

The *Prato* reaction was performed to achieve functionalization of the N-CNTs (Scheme 1) [27]. In particular, purified N-CNTs (0.104 g) was dispersed in 1,2-dichlorobenzene (50 mL) and sonicated for \sim 30 min. To this mixture, under argon, was added 3-thiophenecarboxaldehyde (1.027 g; 20 mmol), followed by the addition of *N*-methylglycine (sarcosine, 1.24 g; 14 mmol), which was added in small portions (\sim 0.25 g per day) over 5 days. After the last addition of *N*-methylglycine, the reaction was allowed to proceed for a further 24 h. The reaction mixture was then cooled to



Scheme 1. Functionalization of N-CNTs (*Prato* reaction).

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