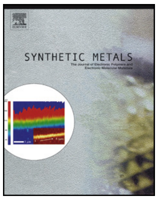
Synthetic Metals 176 (2013) 55–64

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Synthesis and characterization of single wall carbon nanotube-grafted poly(3-hexylthiophene) and their nanocomposites with gold nanoparticles

Jilian N. de Freitas[a], Manoko S. Maubane[b,c], George Bepete[b,c], Willem A.L. van Otterlo[c,d], Neil J. Coville[b,c], Ana F. Nogueira[a,*]

[a] Laboratory of Nanotechnology and Solar Energy, P.O. Box 6154, Chemistry Institute, University of Campinas (UNICAMP), 13083-970, Campinas, SP, Brazil
[b] DST/NRF Centre of Excellence in Strong Materials University of the Witwatersrand, PO Wits, 2050, Johannesburg, South Africa
[c] Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, PO Wits, 2050, Johannesburg, South Africa
[d] Department of Chemistry and Polymer Sciences, Stellenbosch University, Stellenbosch, 7600, Western Cape, South Africa

ARTICLE INFO

Article history:
Received 20 February 2013
Received in revised form 6 May 2013
Accepted 21 May 2013
Available online 21 June 2013

Keywords:
Poly(3-hexylthiophene)
Gold nanoparticles
Carbon nanotubes
Nanocomposites

ABSTRACT

Single-wall carbon nanotubes (SWCNTs) were functionalized *via* the Prato reaction, by using a combination of *N*-methylglycine and 2-thiophenecarboxaldehyde (2T) or 3-thiophenecarboxaldehyde (3T). Pristine SWCNTs or functionalized SWCNTs were then reacted with 3-hexylthiophene (3HT) in the presence of $FeCl_3$ to produce a composite (P3HT/SWCNT) or copolymers (P3HT-2T-SWCNT and P3HT-3T-SWCNT), containing 3-hexylthiophene units as the main chain and carbon nanotubes as side groups. After that, gold nanoparticles (AuNPs) were synthesized using a two-phase, one-pot reaction involving the reduction of $HAuCl_4$ by $NaBH_4$, in the presence of P3HT, P3HT/SWCNT, P3HT-2T-SWCNT or P3HT-3T-SWCNT. This approach generated nanocomposites where AuNPs were stabilized directly with P3HT- or P3HT-containing SWCNTs. The characteristics of the ternary nanocomposites were investigated using UV–vis and fluorescence spectroscopy, thermogravimetric analysis, X-ray diffraction and high-resolution transmission electron microscopy.

1. Introduction

Carbon nanotubes have been used in numerous applications due to their unique mechanical properties, thermal stability, high electrical conductivity and ultrahigh dimensional aspect ratios. The 1D characteristic of carbon nanotubes is perhaps the most promising feature for their application in electronic devices, because the charges have high mobility and show ballistic transport characteristics along their main axis. For example, many groups have introduced single-wall carbon nanotubes (SWCNTs) into organic solar cells to act both as an exciton dissociation center and an electron acceptor [1–5]. In these applications, the nanotubes are combined with regioregular poly(3-hexylthiophene) (P3HT), because of the high hole mobility ($\sim$0.1 $cm^2 V^{-1} s^{-1}$), low band gap ($\sim$1.9 eV) and solution processability of this polymer [6,7].

Advantage can be taken of the hybridization of conjugated polymers with carbon nanotubes as it can enhance the attributes of each component in the nanocomposite. However, the dispersion of carbon nanotubes in polymeric matrixes is poor. The van der Waals interactions between the tubes tend to generate undesired aggregates, thus decreasing their solubility in most solvents. Also, the presence of impurities in the sample, such as graphite, amorphous carbon or metal nanoparticles (residues of catalysts used in the synthesis), can alter the physical and chemical properties of nanotubes.

Generally, dispersion can be improved through chemical functionalization of carbon nanotubes [8–11]. Another elegant approach is to use grafting methods to provide chemical bonds between the components [12–16]. It is reasonable to expect that composites containing carbon nanotube-grafted polymers will behave differently from carbon nantoubes/polymer physical mixtures in which no covalent bonds exist.

Composites incorporating noble metal nanoparticles are also attractive materials as they combine the unique optical and catalytic properties of metal nanoparticles with the high surface area of organic materials [17]. For example, the incorporation of metal nanoparticles into solar cells has been investigated [18–21]. The addition of 5 wt% of gold nanoparticles (AuNPs) into solar cells composed of mixtures of a polymer/fullerene derivative increased the efficiency due to a combination of enhanced light absorption (light scattering of AuNPs) and improved charge transfer (lower series resistance) [21].

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[*] Corresponding author. Tel.: +55 19 35213029; fax: +55 19 35213023.
E-mail address: anaflavia@iqm.unicamp.br (A.F. Nogueira).

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http://dx.doi.org/10.1016/j.synthmet.2013.05.026

Here, our interest is to explore the characteristics of three-component nanocomposites based on a conjugated polymer, carbon nanotubes and metal nanoparticles. We present a simple route to synthesize copolymers containing P3HT units as main chain, chemically bonded to SWCNTs (side groups) and ternary nanocomposites comprising mixtures of these copolymers with AuNPs. These new types of nanocomposites could provide advantages over two-component systems (P3HT/SWCNTs, P3HT/AuNPs or SWCNTs/AuNPs), as they are expected to combine the unique electrical and mechanical properties of carbon nanotubes with the optical and catalytic features of AuNPs, as well as the solution processability of P3HT.

2. Experimental

2.1. Functionalization of SWCNTs

SWCNTs were purchased from Aldrich and used as received. The functionalization of this material was achieved by adapting a procedure developed by Prato and co-workers [22]. SWCNTs (30 mg) were dispersed in 1,2-dichlorobenzene (25 mL) by sonicating for 10 min at rt. The mixture was heated to 150 °C, followed by the addition of 2-thiophenecarboxaldehyde (2 T) (300 mg, 2.7 mmol) or 3-thiophenecarboxaldehyde (3 T) (300 mg, 2.7 mmol). *N*-Methylglycine (360 mg, 4.0 mmol) was then added to the reaction mixture in small portions over 5 days (about 72 mg per 24 h) whilst keeping at 150 °C. At the end of the reaction, the resulting solid was filtered using a PTFE membrane (1.0 μm, Millipore) and washed with DMF (100 mL), MeOH (500 mL) and a mixture of acetone:water (1:1 v:v, 500 mL). After drying under vacuum for 48 h, the products 2T-SWCNT (functionalized with 2-thiophenecarboxaldehyde) and 3T-SWCNT (functionalized with 3-thiophenecarboxaldehyde) were isolated as black solids. Fig. S1 and Fig. S2 (Supplementary Information) show the TGA and HRTEM characterization data for the functionalized SWCNTs.

2.2. Synthesis of P3HT

The synthesis of P3HT was achieved by a simple route, using $FeCl_3$ as catalyst [23]. $FeCl_3$ (2.0 g, 12.3 mmol) was added to dry $CHCl_3$ (~12 mL) and stirred for 10 min at rt. 3-Hexylthiophene (3HT) (0.50 g, 3.0 mmol) in dry $CHCl_3$ (~12 mL) was then added drop-wise to the $FeCl_3$ solution and the reaction mixture was stirred overnight under Ar at rt. The polymerization reaction was then terminated by pouring the reaction mixture into excess MeOH (~50 mL). The crude polymer precipitate was filtered using a PTFE membrane filter (1 μm, Millipore) and washed with ethanol (100 mL), a distilled water:acetone mixture (1:1 v:v, 500 mL) and finally with acetone (500 mL). The dark brown solid product obtained was dried under vacuum for 48 h to afford P3HT (0.45 g, 90%).

Synthesis of P3HT-2T-SWCNT and P3HT-3T-SWCNT copolymers and a P3HT/SWCNT composite

The syntheses and purification of SWCNT-grafted P3HT were performed using a similar procedure as described in section 2.2. In this case, 3-hexylthiophene (200 mg, 1.2 mmol) plus 2T-SWCNT or 3T-SWCNT (20 mg) were added to the $FeCl_3$ reaction medium.

The synthesis of the non-covalently bonded P3HT/SWCNT composite was obtained by adding 3-hexylthiophene (200 mg, 1.2 mmol) and unfunctionalized SWCNTs (20 mg) into the $FeCl_3$ reaction medium.

The monomer:carbon nanotube ratio was kept at 10:1 wt% in all cases. At the end of the purification procedure, ~180 mg of a black solid was obtained in each case. The synthesized materials are listed in Table 1.

2.3. Synthesis of P3HT-capped gold nanoparticles

Synthesis of P3HT-capped AuNPs was carried out using the procedure reported by Zhai and McCullough [24]. Tetraoctylammonium bromide (0.27 g, 0.5 mmol) was added to toluene (8 mL) in a 25 mL round bottom flask and the solution was stirred until all the material had dissolved. An aqueous solution of HAuCl4 (3 mL, 0.1 mmol) was added and the two phase mixture was stirred vigorously until all the HAuCl4 was transferred into the organic layer. This was determined by observing a color change from yellow to colorless in the aqueous phase. P3HT (15 mg) was dissolved in toluene (3 mL) and added to the mixture. The mixture was then stirred for 3 h at rt. A freshly prepared aqueous solution of NaBH4 (2.5 mL, 10 mmol) was next slowly added to the mixture with vigorous stirring. During this time, dark purple polymer-gold nanoparticles were formed and the mixture was stirred overnight at rt, before being quenched in MeOH (30 mL). Purification was performed by filtering the resulting mixture through a PTFE membrane filter (0.45 μm, Millipore) and washing with MeOH and water, followed by drying under vacuum at rt for 24 h.

2.4. Synthesis of P3HT, SWCNT and AuNP-based nanocomposites

Ternary nanocomposites were prepared according to the procedure described in section 2.4, with the exception that P3HT was replaced with P3HT/SWCNT composite, or P3HT-2T-SWCNT or P3HT-3T-SWCNT copolymers. AuNPs were also synthesized in the presence of pristine P3HT and pristine SWCNTs. All the materials that were synthesized are listed in Table 1.

2.5. Characterization

The optical characteristics of toluene solutions (1 mg mL^{-1}) of the synthesized materials were determined. UV–vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer and fluorescence spectra were measured with a ISS PC1TM Photon Counting Spectrofluorometer, operating at room temperature (excitation = 430 nm). Powder X-ray diffraction (XRD) data were obtained from a Shimadzu XRD 7000 diffractometer with CuKα, 40 kV, 30 mA and 2° min^{-1} scanning rate, over the range 2–80°. Thermogravimetric analysis (TGA) was performed using a Thermogravimetric Analyser 2950 from TA Instruments. All measurements were done under a continuous argon flow of 100 mL min^{-1}, and heating from rt to 900 °C at a rate of 10 °C min^{-1}. High-resolution transmission electron microscopy (HRTEM) images were acquired in a HRTEM-JEM 3010 URP operating at 300 kV with resolution of 0.17 nm. The samples were prepared by casting one drop of a dispersion of the material in $CHCl_3$ onto a copper grid (300 mesh) pre-covered with a thin holey carbon layer.

3. Results and discussion

3.1. Synthesis of polymer, copolymers and nanocomposites

The functionalization of SWCNTs and the synthesis of P3HT, copolymers and a composite based on P3HT and SWCNTs were performed according to Scheme 1.

In the first step, the Prato reaction was used to functionalize SWCNTs with 2-thiophenecarboxyaldehyde (2T) or 3-thiophenecarboxyaldehyde (3T), to give 2T-SWCNT and 3T-SWCNT, respectively. After purification, it was observed that functionalized SWCNT samples appeared to be cleaner, with less tube aggregation, when compared to a pristine sample, as seen by HRTEM images (Fig. S2).