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Optically active substituted polyacetylene@carbon nanotube hybrids: Preparation, characterization and infrared emissivity property study

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ABSTRACT

Optically active substituted polyacetylene@multiwalled carbon nanotubes (SPA@MWCNTs) nanohybrids were fabricated by wrapping helical SPA copolymers onto the surface of modified nanotubes through ester bonding linkage. SPA copolymer based on chiral phenylalanine and serine was pre-polymerized by a rhodium zwitterion catalyst in THF, and evidently proved to possess strong optical activity and adopt a predominately one-handed helical conformation. Various characterizations including Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and transmission electron microscopy (TEM) demonstrated that the SPA had been covalently grafted onto the nanotubes without destroying their original graphite structure. The wrapped SPA was found to exhibit an enhancement in thermal stability and still maintained considerable optical activity after grafting. The infrared emissivity property of the nanohybrids at 8–14 μm was investigated in addition. The results indicated that the SPA@MWCNTs hybrid matrix could possess a much lower infrared emissivity value (ε=0.707) than raw MWCNTs, which might be due to synergistic effect of the unique helical conformation of optically active SPA and strengthened interfacial interaction between the organic polymers and inorganic nanoparticles.

1. Introduction

In recent years, an intense attention has been arisen to investigations dealing with materials with low infrared emissivity in both civil and military applications such as optical filtration, energy conservation and camouflage of weapons or vehicles [1–3]. Extensive works on the development of new materials in this field have been reported, such as metallic thin films [4], rare earth compounds [5], conductive polymers [6], and multi-component composites [7–9]. Among them, of particular interest should be the organic/inorganic nanocomposites which commonly consist of organic functional polymers and inorganic nanoparticles [10,11]. Physical and chemical interactions synergistically intertwine the soft and hard components at nanometric scale which may provide superior properties that not possessed by the individual component.

Carbon nanotubes (CNTs) are considered as rolled-up graphite sheets, the structures of which are nearly one-dimensional according to their large aspect ratio. Since the discovery in 1991 by Iijima, CNTs and related materials have been very active candidates for potential applications like molecular electronic device [12], catalyst [13], micro-sensor [14] and electromagnetic wave absorber [15]. However, due to their miniscule size, the excellent flexibility, mechanical strength, and electrical-related properties of CNTs can only be exploited when they are homogeneously embedded into light-weight matrices as those offered by a series of organic polymers [16,17]. Despite several strategies have been established to yield polymer/CNTs nanocomposites in the past decades, there still exist some disadvantages need to alleviate: (1) the insolubility of the CNTs in any solvents decreases the overall yield of useful products; (2) aggregation of nanotubes has been found to dramatically interfere the desired properties of resultant composites; (3) CNTs are normally curled and twisted, and therefore individual CNTs embedded in a polymer only exhibit a fraction of their potential. In order to enhance the chemical affinity of CNTs to polymer matrices, "grafting to" strategy has been proved quite successful where strong covalent bonding between nanotubes and polymers are established [18,19]. This approach involves presynthesis of an organic polymer with controlled molecular weight and reactive end groups, and subsequent attachment of organics onto the surface of CNTs through covalent bonds. So far, there have been many papers dedicated to processing and resulting properties of polymer/CNTs composites in this way. For example, Sun and co-workers [20] fabricated polystyrene/CNTs composites through the esterification reaction of the nanotube-bound carboxylic acids and the solubility of the products in common organic solvents allowed further film casting. Cheng and coworkers [21] presented a

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new strategy to chemically graft cost-effective and soluble polyetherimide onto CNTs and the tensile strength and modulus of the composite films were significantly improved. Moreover, doping CNTs in polymer matrices not only elevates mechanical or electrical properties of materials but also provides large amount of interfaces between CNTs and polymer chains [22,23]. The creation of more dangling bonds lain on the sidewall and ends of CNTs cause energy transformation, which may offer intriguing possibilities of controlling the infrared radiation of composites [24]. Therefore, it remains a challenging research objective to develop novel polymer/CNTs composites for controllable infrared emissivity applications.

Polyacetylene is a simple linear conjugated macromolecule and is representative of conducting polymers. The rigid π-stacked chains and strong interchain interaction make the polymer infusible and insoluble in any kind of solvent. However, substituted polyacetylenes (SPAs) not only possess similar characteristics like common polymers including low density, tractability, and anti-corrosion, but also exhibit numerous other interesting features [25,26]. By linking appropriate substitutes, the interplays of pendant and backbone (for instance, perturbation in the main-chain conjugation and side-chain alignment, etc.) tune into harmony and synergy and thus can provide novel functionalities such as liquid crystallinity, photoconductivity, chain helicity, and optical nonlinearity [27,28]. Especially, introduction of amino acid-derived moieties into side-chains will dominate the SPA chain to take a dynamic one-handed helical conformation like most naturally occurring macromolecules, thus providing huge potential in developing smart and intelligent macromolecules [29–31]. Proper structural design can endow them with attractive properties such as inherent optical activity, biologic compatibility and diverse functional groups for further modification. However, the oxygen-sensitivity, thermal instability, and poor mechanical strength of SPAs are disadvantageous to technical applications so that further modification of molecular or hybridization with inorganic materials is required. Many research groups have worked on the fabrication of SPAs/metal oxide nanocomposites [32–34], but for SPAs/CNTs composites, few reports can be found. Tang and co-workers [35,36] made breakthroughs in the hybridization of SPAs and CNTs by donor–acceptor interaction with the goals to improve the dispensability of CNTs and develop suitable SPA matrices for fabricating functional devices. Nevertheless, take into consideration of the complicated molecular design, simple, convenient and efficient approaches to obtain SPA/CNTs composites are indeed of great significance.

In this paper, we demonstrate a novel category of optically active nanocomposites consisting of an inorganic core (composed of MWCNT) and an organic wrapped shell (composed of amino acid-derived SPA) by simply grafting reactions in a common organic solvent. The SPA@MWCNTs organic/inorganic nanohybrids are expected to combine the advantages of both helical SPA and CNTs, for instance, excellent thermal stability, good processability, and abundant interfacial interactions. The SPA@MWCNTs nanohybrids are further characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) to record the grafting process. Besides, the strengthened interfacial synergistic interaction between the surface of CNTs and helical SPA macromolecules are also investigated to study the substantial improvement in decreasing the infrared emissivity values of the SPA@MWCNTs composites.

2. Material and methods

2.1. Materials

Propargylamine, *N-tert*-butoxycarbonyl-L-phenylalanine, *N-tert*-butoxycarbonyl-L-serine, and bicyclo[2.2.1]hepta-2,5-diene-rhodium (I) chloride dimer ($[(nbd)RhCl]_2$) were purchased from Aladdin. $(nbd)Rh^+B^-(C_6H_5)_4$ was prepared by the reaction of $[(nbd)RhCl]_2$ with $NaB(C_6H_5)_4$ in CH_2Cl_2. MWCNTs (length 5–15 μm, diameter 40–60 nm, purity > 98%) were purchased from Shenzhen Nanotech Port Co., Ltd. Tetrahydrofuran (THF) used for polymerization was distilled over CaH_2 prior to use. Deionized water was used for all the experiments. All other chemicals were used as received without further purification.

2.2. Measurements

FT-IR spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets. The spectra were obtained at a 4 cm^{-1} resolution and recorded in the region of 4000–400 cm^{-1}. UV–vis spectra were measured on a Shimadzu UV-3600 spectrometer at room temperature. CD spectra were determined with a Jasco J-810 spectropolarimeter. Specific rotations ($[\alpha]_D$) were measured in a WZZ-2S (2SS) digital automatic polarimeter at room temperature. ^1H and ^{13}C NMR spectra measurements were recorded on a Bruker AVANCE 300 NMR spectrometer. Chemical shifts were reported in ppm. The molecular weights and molecular weight polydispersities were determined by gel permeation chromatography (Shodex KF-850 column) calibrated by using polystyrenes with THF as the eluent. XPS data of the samples were obtained on a Shimadzu (Amicus, Japan) instrument. Thermal analysis experiments were performed using a TGA apparatus operated in the conventional TGA mode (TA Q-600, TA Instruments) at a heating rate of 10 K min^{-1} under nitrogen atmosphere, and the sample size was about 5 mg. TEM images were performed on a JEM-2100 microscope operating at an accelerating voltage of 100 kV. The samples were prepared by dropping the solution onto carbon coated copper grids with excess solvent evaporated. SEM images were obtained on the LEO-1530VP microscope. XRD measurements of the samples were recorded using a Rigaku D/MAX-R with a copper target at 40 kV and 30 mA. The powder samples were spread on a sample holder and the diffractograms were recorded in the range 5–70° at the speed of 4° min^{-1}. Infrared emissivity values of the samples were investigated on a silicon substrate by using an IRE-2 Infrared Emissometer of Shanghai Institute of Technology and Physics, China.

2.3. Surface oxidization of MWCNTs

The surface oxidization of MWCNTs is performed with a steaming procedure originally described by Zhao et al. [37]. In a typical experiment, MWCNTs (0.5 g) were loaded on the porous SiO_2 griddle of a glass funnel and placed into a 100 mL Teflon-vessel, at the bottom of which concentrated HNO_3 (2.5 mL, 65 wt %) was added previously. Then the Teflon-vessel was sealed in the autoclave and reacted at 160 °C for 5 h. After the steaming treatment, the product was subsequently washed with distilled water and ethanol and dried at 80 °C for 24 h.

2.4. Preparation of acyl chloride-activated MWCNTs (MWCNTs-COCl)

Dry oxidized-MWCNTs (0.1 g) was suspended in $SOCl_2$ (25 mL) and stirred at 65 °C for 24 h. The resultant mixture was then diluted with anhydrous THF and filtered through 0.45 μm millipore polypropylene membranes. The filtered solid was washed with THF repeatedly and dried under vacuum at 30 °C for further use.

2.5. Synthesis of SPA copolymer

N-propargylamide monomers derived from L-phenylalanine (LP) and L-serine (LS) were synthesized according to previous papers [31,38]. Polymerization was carried out in a Y-shaped glass