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Spontaneous polymerization of 2-ethynylpyridine with acylated multi-walled carbon nanotubes in supercritical carbon dioxide and their optical and electrochemical performance

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ABSTRACT

A facile and green approach was proposed for the synthesis of multi-walled carbon nanotubes (MWCNTs) covalently functionalized with poly (2-ethynylpyridine) (MWCNT/P2EP) in supercritical carbon dioxide as a reaction medium. The oxidized MWCNTs were refluxed with thionyl chloride to yield —COCl terminated MWCNTs, which were subsequently used as an initiator for the spontaneous polymerization of 2-ethynylpyridine to produce the MWCNT/P2EP hybrid. Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and X-ray diffraction confirmed the formation of amorphous MWCNT/P2EP with a large surface area of 38 $m^2 g^{-1}$ and high nitrogen content (up to 8%). Microscopic results revealed that the MWCNTs were well embedded in the polymer matrix and the P2EP chains were wrapped around the carbon nanotube wall. The strong covalent coupling at the interface of the MWCNT/P2EP resulted in high electrical conductivity and enhanced thermal stability. Furthermore, the optical and electrochemical properties were investigated. The hybrid exhibited a photoluminescence peak at 510 nm corresponding to the photon energy of 2.44 eV.

1. Introduction

Conjugated polymers (CPs) such as polyaniline, polypyrrole, polythiophene, are considered to be a novel class of functional materials due to their excellent electronic, optical and electrochemical properties [1]. These outstanding properties make them as a versatile material promising for various practical applications, including transparent conducting films [2], high performance composites [3], sensors and actuators [4], nanoelectronics [5] and energy storage devices [6]. Among various CPs, polyacetylene (PA) represents a class of technological importance owing to its high conductivity, high mechanical flexibility and excellent electrochemical property [7]. However, synthesis and applications of pristine PA are still challenging because of its low environmental stability and poor solubility, which arose from the strong π–π interaction of the conjugated backbone. To circumvent these problems, a number of mono- and di-substituted polyacetylene derivatives have been prepared by simple linear polymerization of the corresponding acetylene monomers through various catalyst systems [8]. The resulting polymers have a conjugated backbone, high electrical conductivity, high solubility and excellent stability in air for a long period of time. As a unique member of polyactylene derivatives, poly (2-ethynylpyridine) (P2EP) has been widely studied due to its unique properties [9,10]. It has been previously reported that quaternization of pyridine nitrogen in 2-ethynylpyridine (2-EPy) using alkyl halides in polar solvents led to the spontaneous polymerization of the monomer, resulting in P2EP salts of high molecular weight [11]. Based on this idea, Gal et al. have demonstrated the linear polymerization of 2-EPy by using various alkyl halides as initiators [12–14]. However, the electrical conductivity of most conjugated polymers is still far from the requirements, which further limits their practical applications.

Incorporation of carbon nanomaterials into polymers is an effective strategy to enhance the electrical conductivity and mechanical property of polymer matrices. Among various carbon nanostructures, carbon nanotubes are probably one of the most ideal candidates owing to its high aspect ratio, excellent electrical and unprecedented mechanical properties [15]. Nevertheless, the poor dispersibility of carbon nanotubes in water and organic solvents results in great difficulty for achieving high-performance

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hybrids. To this end, covalent and non-covalent functionalization approaches have been proposed to improve the dispersibility, in which carbon nanotubes are functionalized with small molecules or polymers via covalent or π–π interaction [16,17]. In particular, covalent functionalization using strong acids create numerous functional groups such as —COOH and —OH which are further used as coupling sites to graft polymers or molecules, and the resulting hybrid show very high dispersion stability in various solvents.

Green chemistry research using supercritical fluids has attracted tremendous attention for wide applications in food/drug industries [18], biomedical [19], catalysis [20], and microelectronic devices [21]. As an environmentally benign medium, supercritical carbon dioxide ($scCO_2$) has been widely considered as a premier green alternative for volatile organic solvents. It has several advantages including gas-like viscosity, liquid-like density, zero surface tension and can be easily removed without leaving any residues in the composite materials [22]. In our previous studies, the green synthesis of semi-conducting polymers/composites and a series of block copolymers were reported by using $scCO_2$ as a feasible reaction medium [23–25].

Herein we report a facile and green approach toward the synthesis of P2EP covalently functionalized multi-walled carbon nanotubes (MWCNT/P2EP) in $scCO_2$ as a reaction medium. The prime objective of this work is to investigate the spontaneous polymerization of 2-EPy by using acylated MWCNTs (a-MWCNTs) as an initiator. The linear polymerization of 2-EPy is also studied in the presence of purified MWCNTs (p-MWCNTs) and oxidized MWCNTs (o-MWCNTs). The structural and morphological measurements indicate the —COCl groups play a pivotal role for the formation of covalently bonded MWCNT/P2EP hybrid. Furthermore, the textural, conducting, optical and electrochemical properties of the resulting hybrid are studied in detail.

2. Experimental

2.1. Materials

MWCNTs (ca. 95% purity) with a diameter range of 10–30 nm were obtained from Iljin Nanotech. 2-EPy (97%, Aldrich) was vacuum distilled over CaH_2 (85 °C/12 mmHg) and stored in a refrigerator prior to use. All other reagents were purchased from Junsei Chemical and used as received without further purification. The analytical grade solvents were dried with an appropriate drying agent and distilled.

2.2. Purification of MWCNTs

Pristine MWCNTs have a mixture of byproducts such as an unreacted catalyst, metal nanoparticles, amorphous carbon, and other carbon species. Therefore, the as-produced MWCNTs were purified by thermal and acid treatment according to the following typical procedure. 1.0 g of pristine MWCNTs were heated in air at 650 °C for 2 h, and then cooled and refluxed with 100 mL of conc. HCl for 24 h. The mixture was filtered and washed repeatedly with deionized (DI) water until the filtrate became neutral. The obtained product was dried in a vacuum oven for 12 h at 40 °C.

2.3. Preparation of a-MWCNTs

0.2 g of p-MWCNTs was suspended in 60 mL of conc. H_2SO_4/HNO_3 (3/1, v/v), and ultrasonicated for 8 h. The above dispersion was diluted with 300 mL of DI water and filtered through 0.1 μm polytetrafluoroethylene filter membrane. The product (o-MWCNTs) was washed with DI water and dried under vacuum. Then, 0.1 g of o-MWCNTs was refluxed with an excess of $SOCl_2$ containing a catalytic amount of N,N-dimethylformamide under Ar atmosphere for 24 h. After the reaction, the mixture was cooled down to 0 °C and volatile compounds were removed under vacuum. The solid product (a-MWCNTs) was washed with anhydrous THF and subsequently used for the following reaction.

2.4. Synthesis of MWCNT/P2EP hybrid in $scCO_2$

The MWCNT/P2EP hybrid was prepared in a 5 mL high-pressure view cell reactor equipped with sapphire window, which permits the visual observation of the reaction mixture. Typically, 0.15 g of a-MWCNTs and 0.3 g of 2-EPy were transferred into the reactor. The reactor was then sealed, and liquid CO_2 was added to occupy approximately one half of the cell volume. The temperature was then gradually increased to 60 °C. As the reaction vessel was heated, the remaining CO_2 was added to the system until a desired pressure was reached. The black color reaction mixture turned into reddish brown within a few minutes indicating the spontaneous polymerization of 2-EPy. After polymerization, the reactor was cooled in an ice water bath, and unreacted 2-EPy was extracted with liquid CO_2 at the flow rate of 20 mL/min. The remaining CO_2 was slowly vented out from the reactor. The resulting hybrid was collected, washed several times with ether and dried under vacuum at 60 °C for 24 h (yield 95%). For comparison, the polymerization of 2-EPy was also monitored in the presence of p-MWCNTs and o-MWCNTs. As expected, no significant color change was observed even after prolonged time.

2.5. Characterization

Fourier transform infrared spectra (FTIR) were recorded on a Perkin-Elmer spectrometer in the range 4000–400 cm^{-1}. The samples were dispersed into KBr powder by a mortar and compressed into pellets. X-ray Photoelectron Spectroscopy (XPS) analysis was carried out on an ESCA 2000 XPS (Thermo VG Scientific) using a monochromatic (Mg KR = 1253.6 eV) source. The Brunauer–Emmert–Teller (BET) surface area of the composites was measured by nitrogen adsorption/desorption isotherms. High-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM-2000EX electron microscope operated at 200 kV. The HRTEM specimens were prepared by dispersing a small amount of sample in ethanol and dropping a suspension on a carbon-coated copper grid. Field-emission scanning electron microscopy (FESEM) images were acquired with a Hitachi S-4800 FESEM operated at 20 keV. Thermal gravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris 7 TGA analyzer with a heating rate of 10 °C/min in N_2 atmosphere. X-ray diffraction (XRD) measurement was performed on a Rigaku X-ray diffractometer, over the range of $2\theta = 5–80°$. The electrical conductivity of the compressed pellets of P2EP and the hybrid was measured with four-probe measurements using a Keithley 6221/2182A Delta Mode System. The absorption spectrum of the hybrid was obtained with a Perkin Elmer Lambda 40 ultra-violet (UV–Vis) spectrometer. Photoluminescence spectrum was recorded on an F-4500 spectrofluorometer (Hitachi, Japan). The electrochemical property of the hybrid was studied by cyclic voltammetry (CV) performed in a three-electrode electrochemical cell with 1 M tetraethylammonium tetrafluoroborate in acetonitrile solution ($TEABF_4$/AN) as the electrolyte. A platinum plate and saturated calomel electrode were used as counter and reference electrodes, respectively. All electrochemical analyses were performed on electrochemical workstation, CHI 605B at ambient conditions.

3. Results and discussion

Fig. 1 shows the schematic illustration for the synthesis of the MWCNT/P2EP hybrid in $scCO_2$. The possible reaction mechanism