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Analysis of sensing properties of thermoelectric vapor sensor made of carbon nanotubes/ethylene-octene copolymer composites

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ABSTRACT

We designed a novel self-powered thermoelectric vapor sensor, whose thermogenerated voltage was modulated by chemical vapors. The sensor was made of composites of oxidized multi-walled carbon nanotubes within ethylene-octene copolymer. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy of the multi-walled carbon nanotubes within ethylene-octene copolymer showed that the oxidation with HNO3 or KMnO4 enhanced its *p*-type electrical conductivity and that the thermoelectric power increase was proportional to the formation of new oxygen-containing functional groups on the surface of carbon nanotubes. When this composite was subjected to a saturated vapor of either heptane (aliphatic hydrocarbon), toluene (aromatic hydrocarbon) or ethanol (alcohol), its respective relative resistance increased in average by 3.6, 1.1 and 0.05. Consequently, the magnitude of voltage generated by the thermoelectric device containing the oxidized multi-walled carbon nanotubes within ethylene-octene copolymer determined the absence or presence of the aforementioned chemical vapors.

1. Introduction

Thermoelectric devices are capable to convert thermal energy into electricity when there is a different temperature between the hot and cold junctions of two dissimilar conductive or semiconductive materials. The heat supplied at the hot junction causes flow of an electric current and thus generation of voltage [1]. At the sub-atomic scale, the temperature difference causes charge carriers in the material of *p*-type to diffuse from the hot side to the cold side.

The classical thermoelectric materials used in devices are metals and metallic alloys, e.g., Al, Cu, Ni, Bi, Sb, chromel, alumel as well as semiconductors PbTe and Bi2Te3. Even though the common feature of these materials is a high thermoelectric efficiency, among the disadvantages is an expensive production and high weight. Consequently, the alternative thermoelectric materials are investigated including organic polymers with carbon nanotube fillers [2–9]. In spite of the thermoelectric efficiency of organic thermoelectrics is currently lower than of the inorganic ones, the thermoelectric figure of merit of the polymer composites is typically in the range 0.001–0.01 at room temperature, their mechanical flexibility, processibility, light weight and low manufacturing costs may be desirable in applications. The composites, containing pristine or doped carbon nanotubes and polymers like polyvinylidene fluoride (PVDF) [2,3], polyester [4], polyaniline [5], polyvinyl acetate [6,7], poly(3-hexylthiophene) [8] and ethylene-octene copolymer [9,10], show great promise as *p*-type as well as *n*-type thermoelectrics, where *n*-type samples are synthesized by polyethyleneimine and sodium borohydride (NaBH4) doping [12]. The composites with carbon nanotube entangled networks insulated by PVDF or polymethyl methacrylate, polyvinyl alcohol, polystyrene, polycarbonate, polystyrene sulfonic acid, polyethyleneimine and polyvinylpyrrolidone matrices, which hinder phonon transport through the nanotube network, show the thermoelectric power up to 50 μV/K [13]. Organic thermoelectric composites can be assembled into thermopiles containing many alternating *p*–*n* junctions to produce sufficient power when connected electrically in series and thermally in parallel [8,12,13].

Micro-thermoelectric gas sensors, operating on the basis of the thermoelectric detection of a combustion catalyst, is developed for monitoring of H2 [14,15], CO [16–19], and CH4 [20,21] in human breath. The sensors have promising gas responsivity and show a

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clear linear relationship to allow the detection of gases at the ppm level.

Particulate-filled carbon nanotube polymer composites are applied in several cases for detection of various chemical vapors. Multi-walled carbon nanotubes (MWCNTs)/polymethylethacrylate sensors are used to detect ethanol [22,23] and other organic vapors [24]. To increase sensor sensitivity and selectivity, an unique technique is developed to functionalize MWCNTs together with the detailed determination of the effect of nanotube concentration [22–24]. Porous MWCNT/polyvinyl alcohol composite is tested for detection of methanol, ethanol and isopropyl alcohol [25].

In the present paper, we develop a self-powered thermoelectric sensor for detection of organic vapors based on particulate-filled carbon nanotubes/ethylene-octene copolymer (EOC) composites as thermoelements. MWCNT/EOC composites have several interesting features suggesting their potential use as a strain sensor or membranes for vapor separation from air or for some gas separations involving mixtures of highly condensable and lighter species [9–11]. Investigation of MWCNT/EOC composite response to organic solvent vapors by means of electric resistance measurements carried out in this paper prepares its potential use as mentioned flexible thermoelectric sensor.

2. Experimental

The purified multi-walled carbon nanotubes produced by acetylene chemical vapor deposition method were purchased from Sun Nanotech Co. Ltd., China with purity >90% and electrical resistivity 0.12 Ωcm. Further details on the nanotubes are obtained by means of the transmission electron microscopy analysis presented in Refs. [26–29]. From the corresponding micrographs the diameter of individual nanotubes is determined to be between 10 and 60 nm, their length from tens of micrometers up to 3 μm. The maximum aspect ratio of the nanotubes is about 300. The ethylene-octene copolymer (EOC) with 45 wt% of octene content (ENGAGE 8842) was purchased from Dow Chemicals. The density of EOC was 0.8595 gcm-3.

KMnO4 oxidation: Oxidized MWCNTs were prepared in a glass reactor with a reflux condenser filled with 250 ml of 0.5 M H2SO4, into which 5 g of potassium permanganate (KMnO4) as oxidizing agent and 2 g of MWCNTs were added. The dispersion was sonicated at 85 °C for 15 h using thermostatic ultrasonic bath (Bandelin Electronic DT 103H). The dispersion was filtered and then MWCNTs were washed with concentrated HCl to remove MnO2 and then washed with water until pH = 7. These oxidized nanotubes were denoted MWCNT(KMnO4).

HNO3 oxidation: 2 g of MWCNTs was added to 250 ml of HNO3 (concentrated) and heated at 140 °C for 2 h. After that the dispersion was cooled and filtered. The sediment was washed by deionized water and dried at 40 °C for 24 h. The oxidized nanotubes were denoted MWCNT(HNO3).

MWCNTs were analyzed via transmission electron microscopy (TEM) using microscope JEOL JEM 2010 at the accelerating voltage of 160 kV. The sample for TEM was fabricated on 300 mesh copper grid with a carbon film (SPI, USA) from MWCNT dispersion in acetone prepared by ultrasonication, which was deposited on the carbon grid and dried.

The structure of MWCNT networks and MWCNT/EOC composite was observed with the help of scanning electron microscope (SEM) NOVA NanoSEM 450 (FEI). MWCNT networks were deposited on carbon targets and covered with a thin Au/Pd layer. For the observations the regime of secondary electrons was chosen. MWCNT/EOC nanocomposite specimen was prepared from the composite plate. The plate was freeze for 2 min in liquid nitrogen and broken by bending. The fracture surface was hold for 30 s in toluene and dried at room temperature.

For the purpose of X-ray photoelectron spectroscopy, MWCNT networks were prepared either from pristine or oxidized nanotubes as thin entangled filtering cake on the non-woven polyurethane filtration membrane prepared by electrospinning [27]. At first, the nanotubes were mixed into aqueous paste using a mortar and pestle (100 mg MWCNT and 50 ml deionized water), and diluted with deionized water. Consequently, sodium dodecyl sulfate (SDS) and 1-pentanol were added, and pH was adjusted to the value of 10 using aqueous solution of NaOH. The final concentration of nanotubes in the suspension was 0.3 wt%, with concentrations of SDS and 1-pentanol 0.1 and 0.14 M, respectively. The dispersion was homogenized using UZ Sonopuls HD 2070 kit under the temperature of about 50 °C [9]. The homogenized dispersion of nanotubes was vacuum filtered through the non-woven polyurethane membrane. The disk-shaped filtration cake was washed several times by deionized water and methanol in situ and then peeled off the filtering membrane as a free-standing porous carbon paper (more details about the method and results can be find in Refs. [27,28]).

The X-ray photoelectron spectroscopy (XPS) signals were measured to get information on functional groups attached onto the nanotube surface. The XPS signals from MWCNT, MWCNT(KMnO4) and MWCNT(HNO3) network surfaces were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al K⟨ X-ray source (1486.6 eV). An X-ray beam of 400 μm size was used at 6 mA × 12 kV [29]. The spectra were acquired in the constant analyzer energy mode with pass energy of 200 eV for the survey. Narrow regions were collected using the snapshot acquisition mode (150 eV pass energy) enabling rapid collection of data (5 s per region). The narrow region data was post-processed using Jansson's algorithm to remove the analyzer point spread function what resulted in improved resolution of the spectra for peak deconvolution [30].

Fourier-transform infrared (FTIR) analyses of MWCNTs, MWCNT(KMnO4)s and MWCNT(HNO3)s were performed on FTIR spectrometer Nicolet 6700. Transmission accessory was used for MWCNTs, MWCNT(KMnO4) and MWCNT(HNO3) samples in powder form prepared by potassium bromide.

MWCNT/EOC composites were prepared by ultrasonication of dispersions of MWCNTs in EOC/toluene (5% solution of EOC in toluene). The chosen filler concentration in the composites was 30 wt% what is well above the percolation threshold. The sonication process was carried out using thermostatic ultrasonic bath (Bandelin electronic DT 103H) for 3 h at a temperature of 80 °C. Then the dispersion was poured into acetone which is not solvent of EOC but mixes with toluene and forms a precipitate. Finally, the composite sheets were prepared by compression molding at 100 °C.

The electrical conductivity of MWCNT stripes (length 20 mm, width 15 mm, thickness ca 0.3 mm) cut out from the prepared MWCNT network structures of disc shape was measured along the stripe length by the two-point technique using multimeter Sefram 7338.

The thermoelectric power of a material is a measure of the magnitude of an induced voltage in response to a temperature difference across that material, as induced by the thermoelectric effect. The thermoelectric power measurement was carried out for all the samples using a set-up illustrated in Fig. 1. A circular composite sample (diameter 20 mm, thickness 2 mm) was placed between two copper electrodes. The ends of each Cu electrode were immersed in a thermostatic silicone oil baths set to different temperature. The temperature at the copper/composite interfaces was measured by a digital thermometer. The arising thermoelectric current was measured with a Multiplex datalogger 34980A.

Similar technique as in the case of electrical conductivity