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In situ build coaxial bilayer shell with decreasing conductivity from the surface of carbon nanotubes

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ABSTRACT

To control the dielectric loss of polymer/carbon nanotube (CNT) composites, we developed coaxial double-layer coated CNTs to form a diminishing conductive gradient from the CNT center to its outside through a dual-functional polyaniline (PANI) interlayer. The conductive multiwalled CNTs were covered with a semiconductive PANI first shell through in situ redox polymerization with ferric chloride as the oxidizing agent; moreover, this agent is the precursor of the second iron hydroxide shell. The inorganic outer layer of iron hydroxides was directly coated on the PANI interlayer surface through in situ deposition method to obtain an insulating property. Depending on the conductivity that decreases from the inside to the outside of the core-shell structured CNT hybrids, the epoxy resin-based composites showed gradually reduced dielectric losses because the double-coating layers hindered the reunion and connection of conductive CNTs.

1. Introduction

Carbon nanotubes (CNTs) are widely used in electrochemistry, mechanics, optics, catalysis, and absorbing stealth fields [1]. Moreover, CNT-related composites exhibit excellent application value in the dielectric field [2–6]. Chen et al. used CNTs as conductive fillers to compound with poly(vinylidene fluoride) to prepare dielectric composites; moreover, they discovered that the dielectric constant reaches 200 at 1 kHz with controlled dielectric loss [7]. However, the mechanism to decrease the dielectric loss is a challenge when using such conductive filler-polymer composites. Reports on surface-modified CNTs have been published in the last decade regarding obtaining high dielectric constant and low dielectric loss [8]; in these studies, covering metals, inorganic materials, and polymers on CNT surface to form a core-shell structure are the main and efficient methods [9,10]. Wang et al. utilized polyaniline (PANI) as a capping layer to modify CNT and assembled it with graphene oxide to form a sandwich hybrid. The dielectric constant of PANI@CNT-rGO/epoxy composite reached 210 with low dielectric loss at 100 Hz [11]. Li et al. discovered various iron oxides, including Fe_3O_4 or Fe_2O_3 particles, adhering on the walls of CNTs, and the hybrid effectively improved the dispersion of CNTs and reduced dielectric loss [12].

To control the conductivity of CNTs and obtain low dielectric loss, we devised a double-cladded coaxial structure to cover the CNT surface. The first CNT layer was PANI and the second cladding layer was iron hydroxide. Ferric chloride was selected as the oxidizing agent of aniline polymerization and the metal precursor of iron hydroxide. The external inorganic layer provided an insulating shell that prevented the contact between the conductive particles and hindered the migration of electrons between the CNTs. The intermediate layer of PANI provided the bonding between iron hydroxide and the conductive core of CNTs, which exhibited lower conductivity than CNTs. Moreover, epoxy resin-based composites were prepared using the homemade filler, which gradually reduced dielectric loss and guaranteed a high dielectric constant.

2. Experimental

The multiwalled CNTs (MWCNTs) with length: 10–20 μm and outer diameter: 30–50 nm (purity: >95%, Chengdu Organic Chemicals Co., Ltd.) were dispersed in mixed solution (H_2O and ethanol, Beijing Chemical Works) with HCl. The aniline (J&K Company) was added under the protection of argon. The mixture was continually ultrasonically dispersed for 2 h. Ferric chloride (Alfa Aesar (China) Chemicals Co., Ltd.) solute was dropwise added to the solution and constantly stirred for 16 h in an ice bath. The PANI-coated

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MWCNTs (PANI@CNTs) were obtained after direct washing, filtration, and drying. The PANI- and iron hydroxide-coated MWCNTs ($Fe(OH)_3$/PANI@CNTs) were obtained when the lye (KOH, Beijing Chemical Works) was continually added into the above solution and stirred for 24 h; afterward, the mixture was washed, filtrated, and dried. The preparation diagram of the hybrids is shown in Fig. 1. The hybrid structure was characterized by transmission electron microscopy (TEM, Tecnai $G^2$20) and X-ray photoelectron spectroscopy (XPS, ESCALAB250). Epoxy matrix composites were prepared using a mature process: certain amounts of fillers (pure MWCNTs, PANI@CNTs, and $Fe(OH)_3$/PANI@CNTs) were mixed with epoxy resin (E51). The polyether ammonia hardener (D230) was added to the above mixture (E51:D230 = 3:1), and the uniform prepolymer was rapidly transferred to the mold after degassing in a

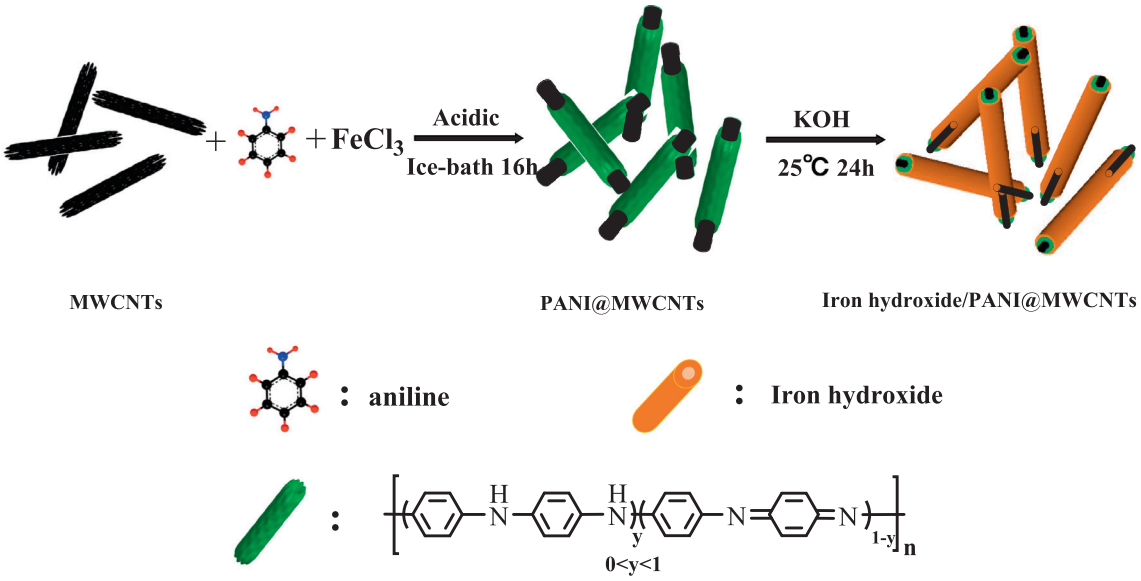

Fig. 1. Mechanism of coating of MWCNTs.

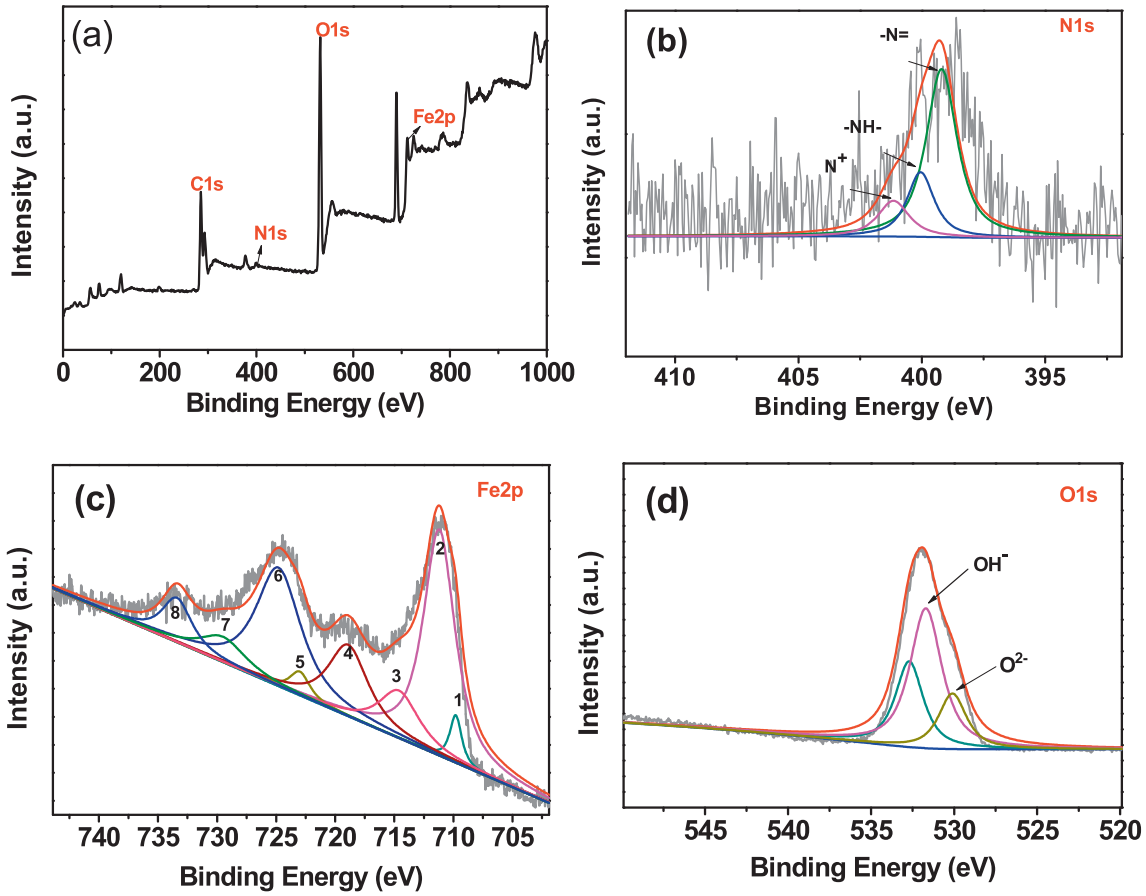

Fig. 2. XPS curves of (a) $Fe(OH)_3$/polyaniline (PANI)@carbon nanotubes (CNTs), (b) N1s peak-fit processing (c), Fe2p peak-fit processing, and (d) O1s peak-fit processing.