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Structural, optical, and electrical properties of multi-walled carbon nanotubes/polyaniline/Fe_3O_4 ternary nanocomposites thin film

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ABSTRACT

Multi-walled carbon nanotubes/polyaniline/magnetite (MWCNTs/PANI/Fe_3O_4) ternary nanocomposites were synthesized. The ternary nanocomposites were synthesized through two main steps, namely; (i) polymerization of aniline in the presence of a carboxyl functionalized multi-walled carbon nanotubes to form binary MWCNTs/PANI. (ii) Co-precipitation of magnetite on the surface of MWCNTs/PANI binary composites to prepare MWCNTs/PANI/ Fe_3O_4 ternary composites. MWCNTs/PANI/ Fe_3O_4 ternary composite thin films were also fabricated via thermal evaporation technique in a vacuum at 1×10^{-4} Pa. The characterization of the prepared ternary nanocomposites either powder or thin films were described by numerous techniques including FT-IR, TGA, TEM, XRD. The magnetic properties were investigated by the vibrating sample magnetometer (VSM). XRD showed the polycrystalline nature of a monoclinic crystal system with space group $P2_1/c$ of ternary nanocomposites powder and showed nanostructure of thin films as well. Optical properties (transmittance and reflectance) of the thin films with 300 nm thickness in the wavelength range of 300–850 nm were studied. The optical complex dielectric constant, optical conductivity, and optical energy band gaps $E_g$were calculated. The optical absorption data indicated that MWCNTs/PANI/Fe_3O_4 thin films have mainly both indirect and direct energy band gaps allowed transitions in the energy range of 2.90–3.41 EV. The dark current-voltage characteristics of the MWCNTs/PANI/ Fe_3O_4 thin films were non-linear and showed rectification behavior. The Rectification ratio (RR) of the forward and reverse currents at the same voltages (V = $\pm$ 3 V) was found to be 5 at room temperature.

1. Introduction

Composites of carbon nanotubes (MWCNTs) and polyaniline (PANI) represent a new class of carbon-based functional composites which display enhanced several properties, such as mechanical and electronic aspects due to the existence of MWCNTs. MWCNTs and PANI have similar solubility [1–5]. PANI exhibits semiconductor performance with a relatively high conductivity because of extended π-conjugation along the polymeric backbones. Different types of carbon nanotubes, for instance, single-walled nanotubes (SWNTs), double-walled nanotubes (DWNTs), and multi-walled nanotubes (MWNTs) have potential applications in the manufacture of novel classes of multifunctional composites due to their exceptional thermal strength, mechanical and electrical properties [6,7]. When MWCNTs are presented inside the polymer matrix, it improves the mechanical and electrical properties of the polymer. In addition, the formation of MWCNTs-polymer networks leads to innovative composites for use in numerous applications such as electromagnetic shielding, storage devices and electrostatic dissipation. Aniline monomer has been polymerized in the presence of the MWCNTs, which are stabilized by strong π-π interactions between MWCNTs and polyaniline chains. Several investigations of MWCNTs/conducting polymer composites have been reported [8–16]. On the other hand, metal oxides (MOs) such as TiO_2, MnO_2, Magnetite, NiO and RuO_2 have been incorporated onto MWCNTs/PANI composites as a thin layer on MWCNTs or nanoflakes [17,21]. These ternary composites have shown attractive applications in several fields, specifically, magnetite is of great importance for its good magnetic properties. MOs were deposited onto MWCNTs before, instantaneously or after PANI

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Table 1
Typically, composition of MWCNTs/PANI/ Fe_3O_4 ternary nanocomposites.

Code	% MWCNTs	Amount of MWCNTs g		Volume of iron salt (ml) (0.1 M)	
				Fe(II)	Fe(III)
TC1	0.62	0.057	Aniline Monomer	1.56	3.12
TC2	1.25	0.115	7.52 (g)	3.12	6.25
TC3	2.50	0.225		6.25	12.5
TC4	5.00	0.450		12.5	25.0
TC5	10.0	0.900		25.0	50.0

deposition to give MWCNTs/MO/PANI or PANI deposited onto MWCNTs followed by deposition of MO to give MWCNTs/PANI/MO ternary nanocomposites. MWCNTs/PANI containing magnetite NPs were made in two main steps; the first step is the deposition of magnetite nanoparticles (NPs) on the MWCNTs' sidewalls by in situ co-precipitation of Fe^{2+} and Fe^{3+} ions [23] or in situ thermal decomposition process [19]. The second step is the deposition of the PANI layer by the in situ polymerization of aniline monomer using $FeCl_3$ salt [18] or APS [19,20] as different oxidant to give MWCNTs/Magnetite/PANI composite. To avoid destruction of the nanostructure of MWCNTs/ Fe_3O_4 NP, no types of acids were used and $FeCl_3$ (rather than APS) was used as an oxidant in the second step [18]. MWCNTs were functionalized with negative carboxylic groups to have affinity with positive ferrous and ferric ions through the in situ co-precipitation of magnetite nanoparticles. Wang et al. [22] used these ternary composites to immobilize trypsin. Conducting polymers suffer from cracks or breaking during cycling due to volumetric alterations during the doping/dedoping process. MWCNTs suffer from low specific capacitance (5–200 F g^{-1}) [24]. On the other hand, the transition metal oxides suffer from poor intrinsic electrical conductivity. The combination of MWCNTs, PANI and metal oxide in composite electrodes decrease the previous drawbacks essential to the individual components [25]. In this paper, an attempt to decrease particle agglomeration, increase dispersion and homogeneity in resulting ternary composites through a synthesis process in two main steps, namely; (i) Binary MWCNTs/PANI nanocomposite is prepared by oxidative in situ polymerization of aniline in the existence of MWCNTs. (ii) Ternary nanocomposites of MWCNTs/PANI/Fe_3O_4 were prepared by co-precipitation of magnetite nanoparticles on the surface of resulting MWCNTs/PANI binary composites in the mother liquid from the previous. MWCNTs/PANI/Fe_3O_4 thin films were fabricated by thermal evaporation technique. The electrical properties of the ternary nanocomposite thin films were studied.

2. Experimental

2.1. Raw materials

All reagents and solvents were used as received without extra treatment except aniline (Aldrich) (Double distillations of aniline were carried out before the polymerization process), ammonium persulphate (APS) LOBAL Chemie, ethanol and polyethylene glycol (PEG4000) purchased from Fisher Scientific UK limited, $FeCl_3.6H_2O$, $FeSO_4.4H_2O$ (AppliChem Panreac), ammonia solution (Scharlau), KNT-ICH_{24}, -COOH functionalized industrial, Grade: Multi-walled carbon nanotube, Diameter: 20–40 nm, Length: 10–20 μm, Carbon purity ˜90%, Specific surface area: 110 m^2/g, and -COOH content 1.4% wt. was used.

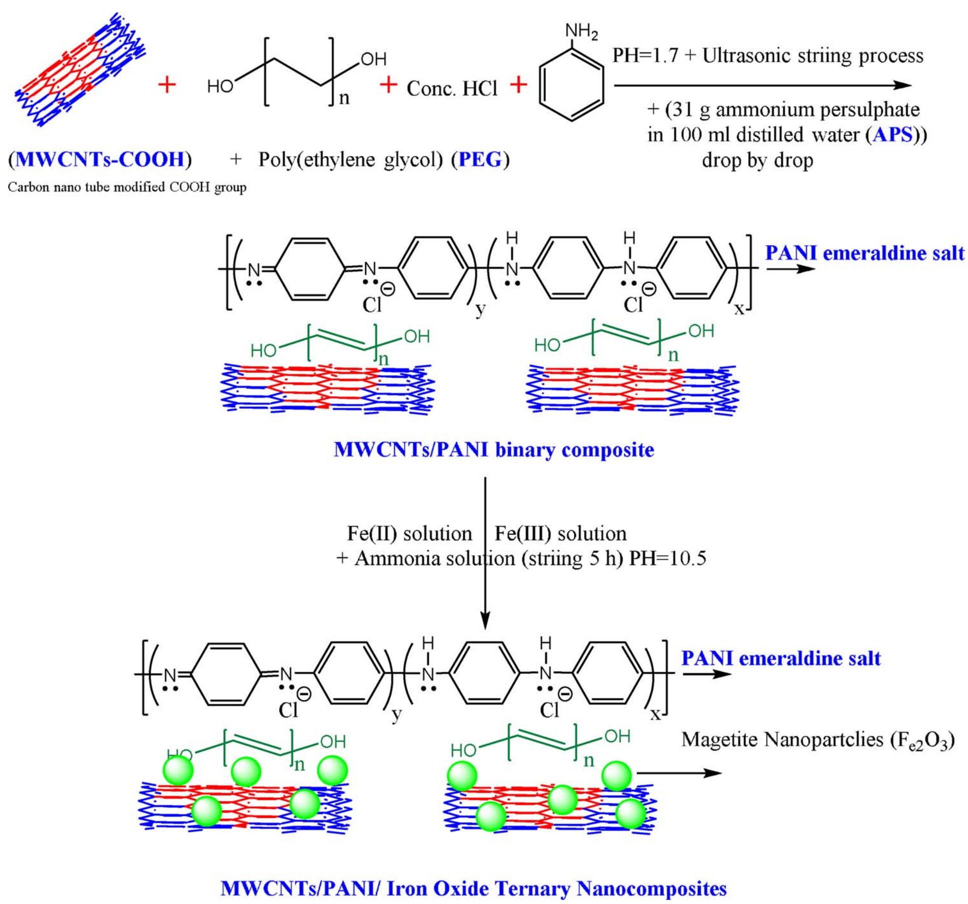

Fig. 1. Synthesis sequence of MWCNTs/PANI/ Fe_3O_4 ternary nanocomposites.