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Sono-assisted preparation of bio-nanocomposite for removal of Pb^{2+} ions: Study of morphology, thermal and wettability properties

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ABSTRACT

Multi-walled carbon nanotubes (MWCNT) loaded poly(ethylene terephthalate) (PET) composites, with different CNT contents, were fabricated through an ultrasound assisted method as a fast and green way. Then, the obtained composites were fully characterized via FT-IR, UV–Vis, XRD, TGA, FE-SEM and TEM, etc. For this purpose, PET bottle was recycled and applied as matrix of nanocomposites (NC)s. Then, we dispersed the covalent functionalization of MWCNTs with a protein dispersant and obtained a powder of protein-functionalized CNTs. Bio-functionalized MWCNTs showed higher Pb^{2+} removal efficiency compared to MWCNT-COOH as ascertained via batch equilibrium adsorption experiments. Also, the results indicated the novel NCs presents a high affinity for Pb^{2+} heavy metal owing to the presence of several good sites. The contact angle results indicated that the addition of MWCNT-BSA increased significantly the contact angle compared to the pure PET. It was concluded that inflame retarding feature of NC was higher than pure polymer.

1. Introduction

Poly(ethylene terephthalate) (PET) is attaining popularity as one of the most versatile engineering polymers due to its excellent mechanical and chemical properties. This material is fully recycled and change to new products such as cosmetics, carpets, packaging for detergents, car parts or back into PET bottles as well as polymer nanocomposites (NC)s [1–3].

Carbon nanotubes (CNT)s as the most popular nanomaterials after C_{60}, show remarkable properties including electrical conductivity, high mechanical strength and thermal conductivity [4,5]. They have great potential for technological and scientific applications particularly for use as composite fillers in polymers [6]. However, the CNTs have high aspect ratio and strong van der Waals forces, so they easily attract each other which cause poor compatibility with polymers and lack of solubility. The most effective approach to resolve this problem is surface functionalization of CNTs that could be categorized to covalent and non-covalent functionalization [7–10].

The conjugating CNTs with DNA, proteins, or carbohydrates is general bio-functionalization method which makes them possible to create a new class of bioactive CNTs. Proteins and polypeptides as a type of important biomaterials, are often used to functionalize CNTs [4].

Bovine Serum Albumin (BSA), one of the most widely studied proteins that is present in the body fluids of vertebrates [10]. Huang et al. covalently attached BSA to CNTs and showed the majority of the nanotube-bound BSA proteins remain bioactive [11]. Weng et al. reported that the single walled CNT-BSA conjugates have ideal enantioselectivity, stability and biocompatibility in separation of tryptophan enantiomers [12]. Research reports on the toxicity of CNTs revealed that the bindings of blood proteins on the CNT surface result in much reduced cytotoxicity for these protein-coated CNTs. A protein-modified nanotube was found to be nontoxic or less toxic than the pristine CNTs [13].

Pb^{2+} as a toxic and more hazardous heavy metals cannot be destroyed naturally, therefore its removal from wastewater is so important. The threshold limit of the Pb^{2+} ions for assessing quality of drinking water was reported by Iranian National Standards Organization (INSO) which was 0.05 mg L^{-1}. Owing to cost-effectiveness, easy handling and speediness green nature of adsorption method, it is extremely suggested for the remediation of water pollutants such as Pb^{2+} [14–18].

In this in mind, to decrease the pollution, we functionalized multi-walled CNTs (MWCNT)s covalently with BSA proteins to obtain MWCNT-BSA hybrids. Then, the obtained filler with a small quantity was incorporated into the recycled PET (rec-PET) matrix by sonication

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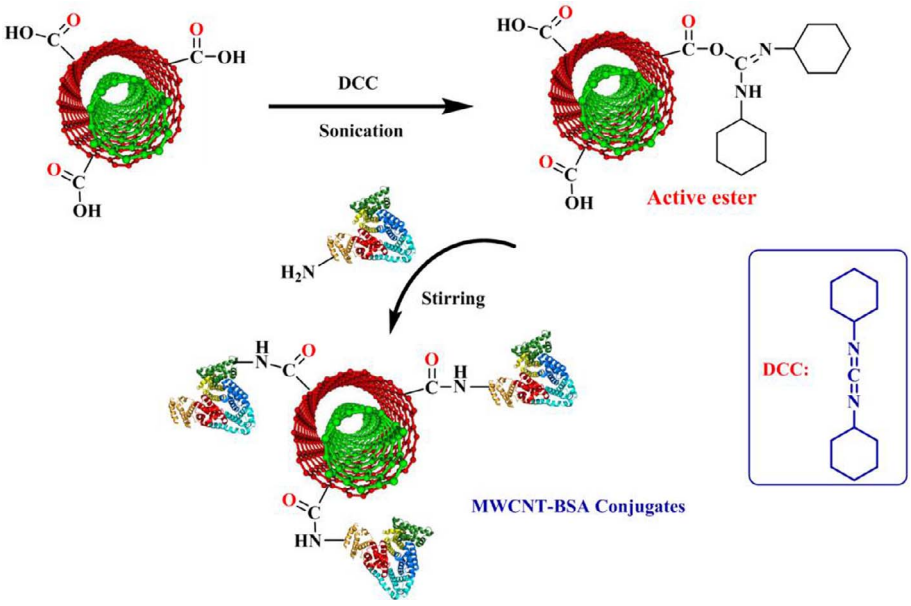
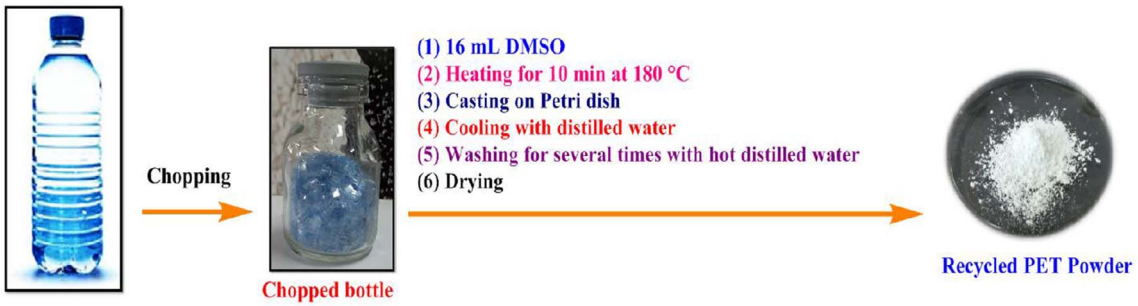


Scheme 1. Preparation scheme of the MWCNT-BSA conjugates via diimide-activated amidation process.



Scheme 2. Recycling of PET.

method. Sonochemical technology has attracted growing attention in the combination of organic and inorganic materials because it can provide a clean media and fine dispersion of fillers in a short time. To the best of our knowledge, there have been no reports on rec-PET/MWCNT-BSA NCs and their properties. Spectroscopic and morphological characteristics of MWCNT-BSA and rec-PET/MWCNT-BSA NCs were investigated using Fourier transform infrared spectrometer (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), respectively. The effect of MWCNT-BSA on the Pb^{2+} adsorption, morphology, wettability and thermal stability of rec-PET/MWCNT-BSA NCs was studied.

2. Materials and methods

2.1. Materials

PET was obtained from waste soft drink Poroshat bottle (1500 mL). The obtained MWCNT-COOH from Neutrino Co. (Tehran, Iran) had the following specifications: outer-diameter of 8–15 nm, length of 30 μm, carboxyl content 2.00 wt% and purity of > 95 wt%. Sigma Aldrich (USA) provided BSA or Fraction V (Mw: 66,463 Da). N,N'-Dicyclohexylcarbodiimide (DCC) was obtained from ACROS (USA). N,N-Dimethylacetamide (DMAc) as solvent was provided by Merck Chemical Co. (Darmstadt, Germany). Dimethylsulfoxide (DMSO) was obtained from DAEJUNG (Korea). $Pb(NO_3)_2$ was purchased from Cica-Reagent (Tokyo, Japan). Potassium dihydrogen phosphate (KH_2PO_4) was obtained from Merck Chemical Co. (Darmstadt, Germany).

2.2. Instruments and apparatus

The crystal structures of samples were identified using a powder XRD on a Philips X'Pert MPD X-ray diffractometer (Eindhoven, Netherlands) with Cu Kα radiation of λ = 0.154 nm. FT-IR spectra were recorded on a Jasco-680 instrument (Tokyo, Japan) after 22 scans within 4000–400 cm^{-1}. The FE-SEM images were recorded by a HITACHI S-4160 instrument (Tokyo, Japan) at 20 and 30 kV. TEM micrographs were obtained using a Philips CM 120 microscope (Netherlands) with an accelerating voltage of 150 kV. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer system (STA 6000) (Waltham, USA) over the range of 25 to 800 °C at a heating rate of 20 °C·min^{-1} under argon atmosphere (20 mL·min^{-1}). UV–Vis spectra were measured using a UV–Vis double beam PC scanning spectrophotometer (UVD-29550) equipped with a 10-mm quartz cell. A Perkin-Elmer 2380-Waltham flame atomic absorption spectrophotometer (FAAS) equipped with single element hollow cathode lamps, and air-acetylene was used for Pb^{2+} measurements. Static contact angle measurements were done by the sessile drop method with optical contact measuring apparatus. Data was taken using a U-VISION MV500 digital camera microscope (China). It was used to measure the contact angles created by the water droplets on the surface of specimen. Experiments were performed by means of probe sonicator (100 W, 20 kHz) using Topsonics homogenizer ultrasonic liquid