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Gamma radiation induced distribution of gold nanoparticles into carbon nanotube-polyaniline composite

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Abstract

Composites of single-wall nanotubes, polyaniline and gold nanoparticles were prepared by a one pot synthesis using γ-radiation as source for initiation of polymerization and generation of Au nanoparticles. The nanocomposites were characterized for the structure, morphology and electronic properties through X-ray diffraction analysis (XRD), Fourier transform infra red spectroscopy (FT-IR), field emission transmission microscopy (FETEM) and UV–visible spectroscopy.

Keywords: Nanocomposites; D. Transmission electron microscopy (TEM); D. X-ray diffraction (XRD); D. Infrared (IR) spectroscopy; D. Optical microscopy

1. Introduction

Carbon nanotubes (CNTs) are being the focus of current research due to their special mechanical and electronic properties [1,2]. Electrically conducting polymers, the "fourth generation polymeric materials", are receiving importance in modern technology as they find applications in optical, microelectronic devices, sensors, catalysts, drug delivery, energy storage systems, electrochromic display devices, light emitting devices, etc. [3–6]. Recent research interest has been focused on the preparation of nanomaterials/nanocomposites involving the combination of carbon nanotubes (CNTs), conducting polymers and metal nanoparticles by employing various methodologies such as sol-gel process, self-assembly, electrochemical and chemical methods [7–11].

Polyaniline (PANI) one of the most important conducting polymer has been extensively studied primarily owing to its high electrical conductivity upon doping combined with its environmental stability [12], unique dopability [13], electrochromism [14], variable electrical conductivity, ease of preparation, etc. Preparation of PANI-CNT composite with enhanced electronic properties has been reported [15,16].

Recently, attaching metal nanoparticles on the surfaces of nanotubes or to sidewalls to obtain hybrid nanocomposite is gaining interest. Such nanocomposites find applications in devices such as catalysts for fuel cells [17], transistors [18], logic gates [19] and sensors [20]. A search for the method to prepare CNT/nanoparticle composites has now been an important goal for many researchers [21–23]. Various approaches for the preparation of CNT/nanoparticle composite were reported, such as, physical evaporation, chemical reaction with functionalized CNTs and electroless deposition methods [23–26].

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Wet chemical treatment methods were used to activate the surface of CNTs for linking metal nanoparticles to them. Jiang et al. [27] attached gold nanoparticles to nitrogen-doped multi-wall carbon nanotubes. Au nanoclusters were attached to single wall nanotubes (SWNT) via thioamide interaction at carboxyl group-modified SWNT surfaces. Apart from this method, other methods were also tried [28,29]. Functionalized Au nanoparticles were attached on non-covalently functionalized CNTs [30]. Polymer coated CNTs were prepared using template synthesis [31]. However, all these methods that have been used for the synthesis of nanocomposites consisted of two steps; covalent or non-covalent functionalization of CNTs and the reduction of metal ions to result nanocomposites [32].

As an initiation route, radiolysis provides several advantages over conventional chemical methods. The main advantage stems from the absence of using an additional agent (like oxidizing agent) in the polymerization medium. γ-Radiation has been applied extensively in initiating polymerization reactions, grafting polymer chains onto polymeric backbones, modifying polymer blends, and in preparing interpenetrating polymer networks.

Nanocomposites of Pt–Ru nanoparticles and electronically conducting polymers were effective for anode catalysts in direct methanol fuel cell (DMFC) applications [33]. Pt nanoparticles of the order of 2–2.5 nm were loaded onto CNTs using the sulfonic acid functionalization of CNTs [34]. PANI/Au nanoparticles composite were synthesized and used as glucose sensor [35]. A non-volatile plastic digital memory device was fabricated based on nanofibers of PANI decorated with Au nanoparticles [36]. The reports reveal that the composites consisting of CNT, PANI and Au nanoparticles can find applications as sensor or electrocatalyst.

To the best of our knowledge, a single step or one pot synthesis of preparation of nanocomposite, comprising of CNT, conducting polymer and Au nanoparticles has not been reported so far. The method received important as it reduces the number of steps including complex sequence of processes for making the nanocomposites. Also, the nanocomposites will be free from impurities from each step.

In the present work, we have established a one pot synthesis of SWNT-PANI-Au nanocomposites using γ-radiation as source for initiation of polymerization and generation of Au nanoparticles in the medium consisting of SWNTs. The nanocomposites prepared were characterized for morphology and electronic properties.

2. Experimental

2.1. Materials

Aniline (Aldrich) was distilled and used. Single-wall carbon nanotubes (SWNTs) obtained from CNT Co., Ltd. Incheon, Korea were rinsed with double-distilled water and dried. Cetyltrimethyl ammonium bromide, auric acid, hydrochloric acid of analytical grade from Aldrich were used as received.

2.2. Preparation of PANI–SWNT–Au nanoparticles composite

In a typical synthesis of the nanocomposite, a solution of aniline in 1 M HCl (10 mM), 0.005 g SWNT in 0.5 M CTAB was added and sonicated for 1 h. To this, 0.04 mM $HAuCl_4$ in 1 M HCl was added. Nitrogen gas was bubbled through the above solution (30 min) to remove oxygen and then the solution was irradiated by γ-ray (Co-60 source) to a total dose of 3 kGy under atmospheric pressure and room temperature. After γ-irradiation, precipitation occurred. The precipitate (SWNT–PANI–Au nanocomposites) was filtered and washed with 1 M HCl until the filtrate became colorless. The composite was then dried under dynamic vacuum at room temperature.

2.3. Characterization

Fourier transform infrared (FT-IR) spectrum of the composite was recorded using a Bruker IFS 66v FTIR spectrophotometer in the region 400–4000 cm^{-1} using KBr pellets. The morphology of the composite was examined by field emission transmission microscope (FETEM) – JOEL JEM-2000EX with a field emission gun operated at 200 kV. UV–visible spectrum was recorded using Shimadzu UV–visible spectrophotometer. A Ds-Advanced Burker AXS Diffractometer was employed using a Cu·Kα source to obtain XRD spectrum of the composite. The spectrum was scanned from $2\theta = 0°$ to $80°$. The amount of gold nanoparticles in the composite was determined though inductively coupled plasma-mass spectrometry (ICP-MS VG Elemental-Plasma Quad 3).

3. Results and discussion

We have successfully prepared nanocomposites comprising of single wall carbon nanotube-polyaniline-Au (SWNT–PANI–Au–NC) by a one pot synthesis. SWNT–PANI–Au–NC was prepared by irradiating γ-ray to a solution consisting of SWNT, aniline and $HAuCl_4$ in 0.5 M CTAB and 1 M HCl. Interestingly, we have neither used a conventional oxidizing agent like ammonium persulphate for polymerization of aniline nor used a reducing agent for generating Au nanoparticles from $HAuCl_4$. Polymerization of aniline and formation of Au nanoparticles were simultaneously achieved in the presence of γ-irradiation. It is to be noted that after the γ-irradiation of the solution consisting of $HAuCl_4$, SWNT and aniline, green colored precipitate was formed. At the first instance, it was felt that the green precipitate might be polyaniline (PANI) in its emaraldine salt form [37]. Field emission transmission micrograph (FETEM) analysis of the precipitate (details are provided later) indicated the presence of Au nanoparticles along with PANI and SWNT. Hence, we confirmed that