



Electrical and optical properties of reduced graphene oxide and multi-walled carbon nanotubes based nanocomposites: A comparative study



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ARTICLE INFO

Article history:

Received 17 April 2016

Received in revised form

19 June 2016

Accepted 9 July 2016

Keywords:

Graphene

Multi-wall carbon nanotubes

Poly (vinyl alcohol)

Conductivity

Seebeck coefficient

Optical properties

ABSTRACT

Graphene and multi-walled carbon nanotubes have attracted interest for a number of potential applications. One of the most actively pursued applications uses graphene and carbon nanotubes as a transparent conducting electrode in solar cells, displays or touch screens. In this work, in situ reduced graphene oxide/Poly (vinyl alcohol) and multi-walled carbon nanotubes/Sodium Dodecyl Sulfate/Poly (vinyl alcohol) composites were prepared by water dispersion and different reduction treatments. Comparative studies were conducted to explore the electrical and optical properties of nanocomposites based on graphene and multi-walled carbon nanotubes. A thermal reduction of graphene oxide was more effective, producing films with sheet resistances as low as 10^2 – 10^3 Ω /square with 80% transmittance for 550 nm light. The percolation threshold of the thermally reduced graphene oxide composites (0.35 vol%) was much lower than that of the chemically reduced graphene oxide composites (0.57 vol%), and than that of the carbon nanotubes composites (0.47 vol%). The Seebeck coefficient of graphene oxide films changes from about 40 μ V/K to -30 μ V/K after an annealing of three hours at 200 °C. The optical absorption of the nanocomposites showed a high absorbance in near UV regions and the photoluminescence enhancement was achieved at 1 wt% graphene loading, while the carbon nanotubes based composite presents a significant emission at 0.7 wt% followed with a photoluminescence quenching at higher fraction of the nanofillers 1.6 wt% TRGO and 1 wt% MWCNTs.

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1. Introduction

Since graphene and carbon nanotubes were discovered in 2004 and 1991 [1,2] respectively, researchers have envisioned them as important materials able to create a turning point in nanotechnology. Both graphene and carbon nanotubes have exceptional electric transport [1,3], optical [4,5], thermal [6,7] and mechanical [8,9] properties which make them excellent candidates as conducting fillers of composites. The morphology and orientation of nanofillers have a significant effect on the electrical properties of composites [10]. Graphene is known as more effective in conductivity enhancement than carbon nanotubes, and both fillers lead to much reduced percolation threshold and substantially higher conductivity in composites [11]. Graphene oxide (GO) is a water-soluble nanomaterial due to the presence of hydroxyl, epoxy, and

carboxyl groups on its surface [12]. These functional groups in GO impart the good dispersion with polymer, while carbon nanotubes are difficult to be uniformly dispersed in polymer matrix by simply mechanical mixing [13]. But in the case of GO, the charge conducting structure is destroyed due to the lattice defects caused by oxygenation, thus, the nanocomposites based on GO have much weaker electrical conductivity [14]. The oxidation-reduction process is an efficient and common method to improve the dispersibility of graphene sheets in many polymer matrices and to remove these polar groups in order to restore the electrical conductivity of reduced graphene oxide (RGO) sheets. However, the carbon nanotubes are generally randomly distributed in polymer matrix, and have no contribution to the formation of a conductive network. Besides, the ultrasonic treatment could assist the dispersion of fillers, but it would decrease the size of filler sheets and increase the structure defects of the sheets, these factors are disadvantageous to the improvement of the final electrical conductivity of filler sheets [15]. Our aim is to achieve the highest

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electrical conductive nanocomposites with large aspect ratio nanofillers while optimizing the dispersion.

The conductive fillers are distributed in the polymer matrix where their network formation probability increases and contact resistance decreases, so that the composite has a lower percolation threshold and a higher electrical conductivity. There are many experimental works studying the composite materials filled with multi-walled carbon nanotubes (MWCNT) and graphene. Tishkova [16] has found a percolation threshold in the electrical conductivity for a double wall carbon nanotubes (DWCNT)/Poly(ether-ether-ketone)(PEEK) composite at 0.2–0.3 wt%, and a maximum electrical conductivity of 3×10^{-2} S/cm. A composite based on PVA has been prepared from a solution with MWCNT, and displayed percolation thresholds of 0.4 vol% [17]. During the thermal reduction process, the large-area graphene oxide (LrGO) sheets improved the electrical conductivity and the percolation threshold of 0.189 wt% for LrGO/Poly (vinyl alcohol) (PVA) nanocomposites [15].

Graphene is a zero gap semiconductor due to its continuous sp^2 hybridized structure [18]. However, GO has a substantial band gap due to the presence of both sp^2 and sp^3 hybridized carbons [5,19] giving it a great potential in optoelectronic applications. Graphene has highly delocalized π -electrons similar to the case of carbon nanotubes [20]. The GO has a high optical absorption and a broadband fluorescence in the visible-near infrared (Vis-NIR) spectral regions between 600 and 1100 nm wavelengths [21]. The optical fundamental properties of carbon nanotubes have been investigated for quite a long time; they include their absorption and their photoluminescence (PL). For example, PL with different colors including green, yellow and red were observed [22].

In the present study, to ensure a lower electrical percolation threshold, we used Poly (Vinyl alcohol) (PVA) as a polymer matrix and the in-situ thermal reduction at 200 °C enabled to prepare thermally reduced graphene oxide (TRGO)/PVA composites. A comparative study on the electrical and optical properties of chemically reduced graphene oxide (CRGO)/PVA, TRGO/PVA and MWCNT/PVA composites was carried out. The photoluminescence (PL) measurements on these nanocomposites were achieved at 320 nm to find the origin of their emissions. We also compare the efficiency of chemical and thermal reduction methods and report that a high temperature treatment is more effective in deoxygenating the films and restoring conductivity with a blue fluorescence.

2. Experimental

2.1. Materials

Graphene oxide (GO) nanofillers with a bulk density of 1.8 g/cm^3 , with a layer number between 15 and 20 and with an oxidation level of 4–10% were purchased from Sigma-Aldrich. Multi-walled nanotubes produced by catalytic chemical vapor deposition (CCVD) were purchased from Nanocyl S.A. Belgium. The average diameter and length are respectively 9.5 nm and $1.5 \mu\text{m}$ with a density of 2.1 g/cm^3 and the purity is greater than 95%. Poly (vinyl alcohol) matrix with a molecular weight of 47,000 g/mol, a density of 1.3 g/cm^3 and a degree of hydrolysis of 98% was supplied by Sigma Aldrich. The reduction of GO was performed by a chemical method using hydrazine hydrate (N_2H_4) as reducing agent. The surfactant for the dispersion of the MWCNTs was Sodium Dodecyl Sulfate (SDS; 99%) provided by Sigma-Aldrich. All dispersion experiments were carried out with distilled water.

2.2. Sample preparation

2.2.1. Preparation of GO/PVA, CRGO/PVA and TRGO/PVA nanocomposites

Amounts of graphite oxide powder of 5, 7, 10 and 16 mg were dispersed in 10 ml distilled water. Moreover, we used ultrasonication method for 30 min at a room temperature to obtain GO nanosheets.

GO/PVA nanocomposites containing different amounts of the filler were prepared as follows: PVA (4 g) was dissolved in 80 ml of deionized water using a magnetic stirrer for 5 h at 80 °C. Then, 20 ml of the PVA solution was added into solutions of GO and reacted for 48 h at room temperature under uniform stirring.

To prepare CRGO/PVA nanocomposites, hydrazine hydrate was added into the GO/PVA blend, stirred for 3 h at 95 °C. The mass ratio of hydrazine hydrate:GO was 1:10.

Four series of nanocomposite films were prepared separately with GO contents of 0.5, 0.7, 1 and 1.6 wt% with respect to the PVA content. The homogeneous solutions obtained were slowly dropped onto glass substrate, and dried at 60 °C for 24 h. A pure PVA film was also prepared in the same conditions and used as a reference. The thicknesses of the obtained films were between 15 and 30 μm . The TRGO/PVA nanocomposite films were reduced through in-situ thermal reduction and placed in a vacuum oven at 200 °C for 30 min.

Dry GO films were placed in a quartz tube with one closed end. The tube was introduced into a tubular furnace (Adamel Lhomargy) and the open end was fitted to a turbo-pump vacuum line (Adixen Drytel). The temperature was maintained constant at 200 °C for 30 min, 1 h, 2 h and 3 h. At room temperature, ambient air was admitted to the tube and the films were recovered.

2.2.2. Preparation of MWCNTs/PVA nanocomposites

In a typical dispersion procedure, two steps were realized in order to obtain better dispersion for preparing the suspensions of MWCNTs. The Sodium Dodecyl Sulfate (SDS) was used for the exfoliation of the nanotubes with the ratio 1:5 of MWCNTs:SDS. All solutions were ultrasonicated for 60 min in distilled water. The MWCNTs/SDS suspension was added to an aqueous solution of PVA. Four series of nanocomposite films were prepared with MWCNT contents of 0.5, 1, 2 and 3 wt%. The solution was briefly sonicated and stirred for 48 h at room temperature. The homogeneous solutions obtained were slowly dropped onto a glass substrate, and dried at 60 °C for 24 h.

2.3. Characterization

The thermogravimetric analysis (TGA) of dry GO powder was performed using Setaram TG-ATG 92 from 20 to 600 °C and under purified nitrogen gas flow with a 6 °C/min heating rate. Microscopic morphology observations were conducted on a JEOL 7400F FEG scanning electron microscopy (SEM) under an acceleration voltage of 5 kV. The conductivity of the thin films was measured by the four point method. Optical absorption measurements were recorded using a 200 Double Energy System UV-visible-near-infrared spectrophotometer working in absorption and transmission mode in the wavelength range varying from 1000 nm (0.31 eV) to 200 nm (6.2 eV). Photoluminescence measurements (PL) were performed using a fluorometer FL980, at room temperature, excitation wavelength of 325 nm using a xenon lamp. The film thicknesses were measured using a mechanical profilometer DEKTAK XT.

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