



One-step hybridization of graphene nanoribbons with carbon nanotubes and its strong-yet-ductile thermoplastic polyurethane composites

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ABSTRACT

A hybrid of reduced graphene nanoribbon (GNR)–carbon nanotube (CNT) (i.e. R-GNR/CNT hybrid) with unique three-dimensional (3D) nanostructures has been prepared via a facile unzipping and reducing method. Interlocked structures are formed within the nanohybrids where one-dimensional (1D) CNTs act as bridges connecting individual two-dimensional (2D) GNRs, which not only prevent the aggregation of GNRs but also promote the formation of 3D hybrid with cross-linked nanostructure. Thermoplastic polyurethane (TPU) composites with different R-GNR/CNT hybrid loadings have been fabricated via solution casting. With the addition of small amount of R-GNR/CNT hybrids, apart from the largely improved tensile strength and Young's modulus, the toughness of the TPU composites is surprisingly enhanced. Here, the toughening mechanisms are also discussed. Furthermore, the electrical conductivities of the TPU composites are also significantly enhanced in the presence of this 3D R-GNR/CNT nanohybrid due to the formation of conductive pathways within the matrix.

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1. Introduction

Graphene nanoribbon (GNR), a single atomic layer of sp^2 carbon atoms with straight edges, could be prepared by chemical vapor deposition (CVD) method [1], spirally or longitudinally unzipping the multi-walled carbon nanotube (MWCNT) [2,3] with unique characteristics including high aspect ratio, low-defect, as well as controllable morphology, which makes it a promising candidate for use in electronic devices, such as field effect transistors [4], and dye-sensitized solar cells [5]. Compared to the commonly used graphene oxide produced by Hummers' method, the length-to-width ratio and dimension of this GNR produced by splitting carbon nanotube (CNT) can be exactly predetermined by the length and diameter of the initial CNT [6,7]. Although GNR with narrower width less than 10 nm behaves as semiconductor independent of its edge pattern, the wider GNRs exhibit high electrical conductance characteristic of large graphene flakes and could be further used for bulk applications, such as flexible transparent electrodes [7]. Furthermore, the high aspect ratio of wide GNRs makes them particularly attractive of carbon fiber spinning and fabrication of conductive polymer composites [8].

Recently, although hybrid materials of CNTs and graphene (or graphene oxide) have been successfully prepared by solution mixing [9–13] or CVD method [14,15], except for the sophisticated preparation process, the obtained hybrids could hardly ensure a close interaction between CNTs and graphene sheets [16], which seriously limits the further application of the prepared hybrid materials. So, developing a convenient and efficient method for preparing hybrid material of CNTs and graphene (or graphene derivatives, such as GNR) with strong interfacial interaction between these two kinds of carbon materials and realizing their synergistic effect is urgent and of great importance.

In this work, we have facily prepared a hybrid of oxidized graphene nanoribbon–carbon nanotube (i.e. O-GNR/CNT) by one-step unzipping the MWCNTs. After the pristine MWCNTs have been partially unzipped, unique three-dimensional (3D) cross-linked nanostructures are formed where residual CNTs act as “bridges” connecting the unzipped nanoribbon sheets. Reduced graphene nanoribbon–carbon nanotube (R-GNR/CNT) hybrid is obtained after the O-GNR/CNT hybrid was treated with hydrazine hydrate. With the presence of residual CNTs, not only the aggregation of GNR is prevented, but also the electron transfer efficiency of the hybrid is greatly improved, resulting in an electrical conductivity as high as 120 S cm^{-1} compared with the 65 S cm^{-1} of the pristine CNTs. Using this 3D R-GNR/CNT hybrid as nanofillers, a series of thermoplastic polyurethane (TPU) composites were

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fabricated by solution casting method. To our interesting, with the addition of merely 1.0 wt% R-GNR/CNT hybrid, not only the Young's modulus and ultimate tensile strength of the composite are significantly enhanced, but also the toughness of the composites is greatly improved. Furthermore, due to the excellent dispersion of this 3D R-GNR/CNT hybrid in the TPU matrix, the electrical conductivity of the composites has been enhanced by 9 orders of magnitude with the incorporation of 1.0 wt% R-GNR/CNT hybrid compared with neat TPU matrix.

2. Experimental

2.1. Materials

The pristine CNTs used in this work are MWCNTs, which is produced by chemical vapor deposition method with diameter of 20–30 nm and length larger than 20 μm and purchased from Chengdu Organic Chemicals Co. Ltd. Thermoplastic polyurethane (TPU, Product No. 58277, with a M_w of 100,000 and hard segment content of 44.7%) used throughout the experiments was supplied by Noveon Inc., USA. Chemical reagents were obtained from Sino-pharm Chemical Reagent. Milli-Q ultraclean water was used throughout the experiments. All the materials were directly used in the experiments without further purification.

2.2. Preparation of O-GNR/CNT and R-GNR/CNT hybrids

The O-GNR/CNT hybrid was prepared by the method of unzipping the MWCNTs [17]. The fabrication process can be described as follow: firstly, 100 mg of pristine carbon nanotubes were suspended in 25 mL of concentrated H_2SO_4 and stirred for 1 h. H_3PO_4 (85 wt%, 3 mL) was then added and the mixture was allowed to stir for another 20 min at room temperature until the reaction temperature increased to 70 °C. After that, 200 mg of KMnO_4 was gradually added into the mixture in 2 h. The reaction was stirred for another 2 h at 70 °C. After being cooled to room temperature naturally, the mixture was poured into 100 mL of ice-water containing 4 mL H_2O_2 (30 wt%). The mixture was allowed to coagulate for 24 h and the obtained precipitates were dialyzed against ultraclean water for 1 week to remove the residual reagents. After that, a homogeneous dispersion of O-GNR/CNT hybrid was prepared. After being reduced with hydrazine hydrate at 98 °C with stirring for 5 h, a stable dispersion of R-GNR/CNT hybrid in *N,N*-dimethyl formamide (DMF) was achieved by ultrasonication with sonication power of 250 W for 20 min at room temperature.

2.3. Fabrication of neat TPU, TPU/(R-GNR/CNT) composite films

The TPU/(R-GNR/CNT) composite films were prepared using a typical solution casting method. Typically, 500 mg of TPU pellets were dissolved in 15 mL of DMF at 90 °C. Then, a desired amount of DMF dispersion of R-GNR/CNT hybrid was gradually added into the TPU solution. After being carefully stirred for 30 min followed by sonication for another 30 min, the mixture was subsequently poured into a culture dish. The solvent was slowly evaporated at 70 °C for 24 h to get the TPU/(R-GNR/CNT) composite film with 1.0 wt% nanofiller loading. Similarly, TPU/(R-GNR/CNT) composite films with different hybrid loadings of 0, 0.2, 0.5, 1.5, and 2.0 wt%, respectively, were also prepared.

2.4. Characterization and instruments

X-ray diffraction (XRD) measurements were carried out using a PANalytical X'Pert PRO XRD with Cu $K\alpha$ radiation ($\lambda = 0.1548$ nm; operating energy, 40 keV; cathode current, 40 mA; scan rate,

2° min^{-1}). Fourier transform infrared (FTIR) analysis was performed on a Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS detector by signal-averaging 64 scans at a resolution of 4 cm^{-1} . Raman spectra were collected using an Avalon Instruments Raman Station using a 632.8 nm He–Ne laser. Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2100 TEM instrument with an accelerating voltage of 200 kV. The TPU/(R-GNR/CNT) composites for TEM observations were microtomed under cryogenic conditions to obtain ultrathin sections using a Leica ultramicrotome with a diamond knife. Thermogravimetric analysis (TGA) was performed by using a Perkin Elmer Pyris-1 TGA under nitrogen atmosphere. The tensile tests of the TPU and its composite films were carried out using an Instron universal material testing system at 25 °C with a crosshead speed of 5 mm min^{-1} . Mechanical property values reported here present an average of the results for tests run on at least five specimens. The conductivities of the pristine CNTs and the obtained R-GNR/CNT hybrid were measured using a 4-point probe method (RTS-8) by coating the samples on the glass slides. The electrical conductivities of the TPU composites were measured by a two-probe method using a picoammeter (ZC-36, Shanghai Precision & Scientific Instrument Co., Ltd, China), and at least five data points were measured for each sample.

3. Results and discussion

3.1. Characterization and micrographs of pristine CNTs, O-GNR/CNT and R-GNR/CNT

Fig. 1 schematically illustrates the unzipping procedure and the formation process of the unique 3D “ribbon-to-bridge-to-ribbon” nanostructure, where CNTs act as “bridge” connecting different GNR sheets. The pristine CNTs were partially unzipped under treatment of mixed acid and KMnO_4 , thus forming the O-GNR/CNT hybrid. Under ultrasonication and reduction, the hybridization of the GNR and residual CNTs occurred, resulting in the formation of R-GNR/CNT hybrid with a 3D electrically conductive structure. It is noted that, compared with the amount of KMnO_4 used in Ref. [17], here less KMnO_4 (2 wt% equal of pristine CNTs) was used in order to

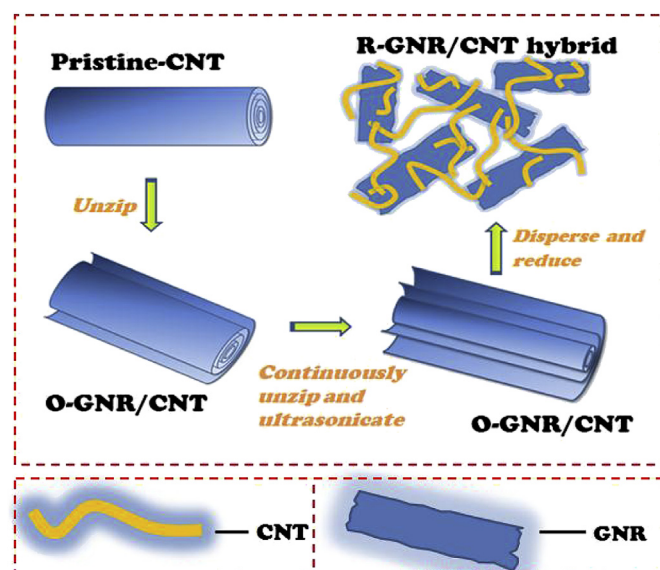


Fig. 1. Schematic illustration showing the preparation steps of O-GNR/CNT and R-GNR/CNT hybrid.

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