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Multifunctional graphene nanoplatelets/cellulose nanocrystals composite paper

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ABSTRACT

We demonstrate a water-based method to fabricate strong, electrically and thermally conductive hybrid thin films (papers) made from the combination of graphene nanoplatelets (GnP) and cellulose nanocrystals (CNC). Unpressed and hot-pressed GnP papers containing CNC ranging from 0 wt% to 25 wt% were prepared. It is found that the GnP is well aligned within the hybrid paper, and a higher degree of alignment is induced by the hot-pressing process. The mechanical properties of the resulting papers increased with increasing content of CNC. The hot-pressed 25 wt% CNC hybrid paper showed the best mechanical properties among all the papers studied and improved the tensile strength by 33% and the modulus by 57% compared to neat GnP paper. Both the highest in-plane and though-plane thermal conductivity of 41 W/m K and 1.2 W/m K were measured respectively for the hot-pressed 15 wt% CNC hybrid paper. The electrical conductivity decreased continuously with increasing content of CNC but the thin film was still conductive at the highest CNC content in this study. The low-cost, environmental-friendly, thermally and electrically conductive flexible GnP/CNC hybrid papers have a set of properties making them suitable for many potential applications.

1. Introduction

Graphene has attracted world-wide attention due to its outstanding mechanical, thermal and electrical properties [1]. Some other novel carbon materials such as carbon nanotubes and helical carbon nanofibers/nanotubes also show good properties. However, their applications are limited by the high fabrication cost and low production rate [2–5]. In contrast, graphene nanoplatelets can be produced at a much lower price by a top-down approach [6,7]. Recent published research has shown that graphene-based materials are suitable to be used in a wide range of potential applications, such as lithium ion batteries [8], ultracapacitors [9], polymer composites [10,11], ultra-thin films [12,13], electronic circuits [14], and transparent and flexible electrodes for displays and solar cells [6,15].

Graphene can be prepared by employing both top-down (mechanical cleavage or liquid phase exfoliation) and bottom-up (such as chemical vapor deposition, arc-discharge, chemical conversion, unzipping carbon nanotubes, and epitaxial growth on SiC) approaches [16]. In general, the top-down process starting with natural graphite flakes, which is more suitable for large scale production, and offers significant economic advantages over the bottom-up methods [11,16]. Research in the Drzal's Group at Michigan State University successfully developed a process that can produce graphene nanoplatelets with thickness ranging from 1 nm to 10 nm and diameters from 300 to 50,000 nm [17,18]. Graphene nanoplatelets (GnP), which consists of a few layers of single layer graphene was produced by either thermal expansion of acid intercalated natural graphite or microwave radiation followed by pulverization using ball milling or ultrasonication [17]. The cost of GnP flakes produced by this method is estimated to be around $15/lb which makes it possible for the large-scale application in various fields [19].

Recently, a nanostructured graphene paper which is assembled by well-ordered graphene sheets has attracted increasing attention due to its wild potential application for solar cell, electronic and heat transfer devices [13]. Thin films (papers) of graphene oxide (GO) usually show excellent mechanical properties, however, the lack of electrical and thermal conductive limits their use [20].

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Although GO paper can be rendered conductive by thermal annealing, the structure and mechanical properties can be seriously deteriorated after thermal treatment. In addition, the cost of producing single layer graphene sheet is high which limits its applications. The early work in our group showed that papers made from commercially available GnP exhibited excellent in-plane thermal and electrical properties [21,22], while the GnP paper is not strong as compared with the graphene oxide or reduced graphene oxide paper. This study reports on the modification of GnP papers and the mechanical, thermal and electrical properties of the resulting materials.

Cellulose is the most abundant renewable organic material with annual production of over 7.5×10^{10} tons [23]. Recently, attention has been directed to nanosized cellulose (fibrils and whiskers) because of their exceptional high specific strength and modulus, low density, chemical versatility, renewable 'green' nature, and their relatively low cost [24–26]. Chun et al. [27] utilized cellulose powders as the starting material and fabricated cellulose nanofiber paper with a vacuum filtration method, the tensile modulus and strength of the prepared cellulose paper can be as high as 6.4 GPa and 55 MPa respectively. Sen et al. [28] fabricated 0.1–0.5 wt% graphene nanoplatelets–cellulose composite films by a solution casting method. The 0.25 wt% graphene nanoplatelets/cellulose composite film produced 0.8 GPa in tensile modulus and 22.6 MPa in strength, an increase of 45% and 31% respectively. The highest electrical conductivity of 5.1×10^{-3} S cm^{-1} was obtained at 0.50 wt % graphene loading. Si et al. [29] prepared graphene oxide-bacterial cellulose (GO/BC) nanocomposites with a GO content of 0.19, 0.29, and 0.48 wt%. The 0.48 wt% case showed the best mechanical properties with an increase of 38% in tensile strength and 120% in tensile modulus. A relatively low electrical conductivity of 1.24×10^{-9} S cm^{-1} was noted due to the partial reduction of GO to rGO during the sample preparation. Soheilmoghaddam and co-workers [30] successfully prepared green hybrid films through regenerating cellulose/exfoliated graphite nanosheets in ionic liquid. The tensile strength and Young's modulus of the prepared nanocomposites were increased by 97.5% and 172% respectively after the incorporation of 0.75 wt% and 1 wt% graphite nanoplatelets, and oxygen barrier properties and water absorption resistance were also improved as compared to the pure cellulose film.

Cellulose nanocrystals (CNC) are fibrillar in nature and have a diameter of around 5 nm and their length can vary depending on their source and method of preparation [31]. In this work, we first formed GnP dominated-CNC (wood pulp) composite papers, and investigated the morphology, mechanical, electrical and thermal properties of the unpressed and hot-pressed papers.

2. Experimental

2.1. Exfoliated graphene nanoplatelets (GnP)

Graphene nanoplatelets (GnP) was produced by thermal expansion of acid intercalated graphite compounds (Asbury Mills, NJ), followed by pulverization in isopropanol using ball milling and ultrasonication to produce the desired aspect ratios. GnP was heat treated in a furnace at 400 °C for 2 h before use to remove any impurities remaining after the particle fabrication procedure. GnP-5 refers to the graphene nanoplatelets with an average diameter of around 5 μm and a thickness less than 10 nm. Only GnP-5 flakes were used in all the experiments of this paper and GnP mentioned throughout the paper means GnP with an average diameter of 5 μm.

2.2. Cellulose nanocrystals (CNC)

Aqueous cellulose nanocrystals in the never-dried state were obtained in a slurry with a cellulose content of 6.2 wt% produced from wood pulp by the University of Maine (Orono, Me). The as received cellulose nanocrystals are rod-like particles with dimensions of approximately 5 nm in diameter and 150–200 nm long (http://umaine.edu/pdc/cellulose-nano-crystals/).

2.3. Exfoliated graphene nanoplatelet paper and GnP/CNC hybrid paper preparation

The suspension of CNC was diluted in water to approximately 1 mg/ml and dispersed using shear mixing (Ultra Turrax T25 basic, IKA Werke GmbH & Co. KG, Germany) for 5 min at 13,500 rpm. Polyethyleneimine (PEI) which works well for dispersing GnP was purchased from Aldrich (branched, Mw = 25,000) and used as received.

GnP powders were dispersed in water at a concentration of ~1 mg/ml with the aid of PEI (GnP:PEI:Water = 2:1:2000, by weight) by high energy ultrasonication for 3 min at a true power output of 120 W. The solution was then stirred overnight to ensure sufficient interactions between GnP flakes and PEI. A variety of cellulose nanocrystals (1 mg/ml) were slowly added to 50 ml of the above mentioned solution with continual stirring to produce mixtures with CNC content ranging from 5 wt% to 25 wt%. The mixed solution was vigorously stirred for 24 h, and GnP/CNC hybrid papers were prepared by filtration of the obtained solution through a 0.22 μm pore size PVDF membrane (Millipore). The films were not rinsed to avoid affecting the GnP alignments of the resulting papers. After filtration, the GnP/CNC paper on the membrane was dried at room temperature for 24 h then carefully peeled off. This paper was identified as 'as-made' in later discussions. The as-made papers were then further vacuum dried at 70 °C for 24 h. The GnP paper without any CNC was also prepared by the same method. These papers are identified as 'unpressed'. The as-made papers that were compressed in a dual platen press under 65 MPa at 125 °C for 30 min were identified as 'hot-pressed'.

2.4. Characterization

An environmental scanning electron microscopy (ESEM, Philips Electroscan 2020) with energy dispersive spectrometer (EDS) equipment at accelerating voltage of 20 kV was used to image the fracture of the cross section of both the unpressed and hot-pressed papers. The distribution of GnP/CNC in solution was examined using an Olympus optical microscope (BX-51M). Transmission electron microscope (TEM) analyses were conducted on a JEM 2100F STEM/EDS electron microscope at 200 kV, and the samples were prepared by drop casting on carbon-coated cooper grids followed by solvent evaporation in air at room temperature.

Raman spectroscopy was carried out using a Micro Raman spectrometer (Renishaw, system 100, UK) in the range of 500–3500 cm^{-1}. The excitation wavelength was 785 nm from He–Ne laser with a laser power of 28.2 mW at the sample surface. Results are the average of at five Raman measurements per group.

Mechanical properties of the papers were measured under controlled air conditions of 23 °C and 50% relative humidity by a Dynamic Mechanical Analyzer (DMA, Q800, TA instruments). GnP based papers with different thickness were cut with a razor blade into rectangular strips of 30 mm in length and 6.6 mm in width for measurements. The dimensions were measured by calipers, and the thickness of each type of paper was measured with a digital micrometer. The samples were gripped using a film tension clamp with a clamp compliance of about 0.25 μm N^{-1}. After the specimens