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Fabrication of robust and highly thermally conductive nanofibrillated cellulose/graphite nanoplatelets composite papers

Genghui Li, Xiaojuan Tian, Xiuwen Xu, Chen Zhou, Jiaye Wu, Qi Li, Liqiang Zhang, Fan Yang, Yongfeng Li*

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, Changping, 102249, PR China

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ABSTRACT

In this work, a lightweight and flexible composite paper has been successfully fabricated by incorporating nanofibrillated cellulose (NFC) with graphite nanoplatelets (GNPs). The NFC, with a high tensile strength but a low thermal conductivity, forms interconnected networks existing in the interspace of GNPs, which can significantly improve the tensile strength of the as fabricated composite paper. Interestingly, with the presence of NFC, graphite nanoplatelets are well aligned within the composite, thus forming effective thermal transport paths along the in-plane direction. Benefiting from the reinforcement and guiding effect derived from the incorporation of NFC, the composite paper exhibits considerably enhanced tensile strength while maintaining its high thermal conductivity. Specifically, the hybrid film with 75 wt % GNPs shows an in-plane and through-plane thermal conductivity of 59.46 W m^{-1} K^{-1} and 0.64 W m^{-1} K^{-1}, respectively, with a satisfactory tensile strength of 46.39 MPa, thereby exhibiting great potential as an appropriate choice for lateral heat dissipation applications. Our findings provide a promising candidate, manufactured by a facile and low-cost process at industrial scale, for lateral heat dissipation applications.

1. Introduction

With rapid development of high power density electronics industry, highly thermally conductive paper designed for thermal dissipation are nowadays in great demand, which has already captured massive research attentions worldwide [1–7]. With the high thermal conductivity up to 1750 W m^{-1} K^{-1}, graphite films, produced by carbonizing and graphitizing polymers such as polyimide, have got access to the market [8]. However, the extremely high temperature (2800 °C) used during the graphitization process leads to huge energy consumption and inevitably causes damage and shrinkage within the graphite films, which enormously raise their price concomitantly with unsatisfactory flexibility. It is widely accepted that being used as the supreme lateral heat spreader, an ideal thermally conductive paper should not only possess excellent thermal conductivity, but also have the features of flexibility, light weight and low cost [9,10]. Graphene, with a stunning thermal conductivity of 5000 W m^{-1} K^{-1} at room temperature [11], brings hope to the exploration of more advanced thermally conductive paper. Considering that the mature and industrial production of graphene can merely be achieved via a reduced graphene oxide method to date [12], graphene oxide (GO) has thus gained extensive attention and been widely employed to fabricate thermally conductive paper [9,10,13,14]. Unfortunately, the paper consisting of GO usually exhibits a very low thermal conductivity due to the defects caused by functional groups [15]. Hence, heat treatment is usually introduced at this stage to remove the functional groups [9,10,13], which does enhance its thermal conductivity but sacrificing its mechanical properties due to the weakened interaction of graphene sheets. Moreover, although the reduction temperature (700–900 °C) is significantly reduced compared to that during graphite paper production, it still causes unacceptable energy consumption. It is therefore of great significance to explore the low-cost preparation protocols that can endow conductive paper with high thermal conductivity and excellent mechanical strength using graphene or their analogue.

Graphite nanoplatelets, as one of typical graphene analogues that can be industrially produced at low cost, share a lot in common with graphene, thereby being proposed as a promising substitution of graphene in conductive paper fabrication [16–18]. Xiang et al.

* Corresponding author.
E-mail address: yfli@cup.edu.cn (Y. Li).

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used polyethyleneimine as the stabilizer to disperse the nanoplatelets and prepared GNPs papers through a standard filtration process, followed by a combination of thermal-annealing and hot-press treatments. The obtained conductive paper achieved an in-plane thermal conductivity of 313 W m^{-1} K^{-1} [18]. However, composed of all the stiff nanoplatelets, the papers appeared to be brittle when it comes to some practical applications. To enhance the mechanical property of the conductive paper, most research attention has been paid to introduce various polymers as standing framework within the conductive composites [19–24]. For instance, Shahil et al. employed graphene as fillers associated with epoxy as framework to fabricate thermally conductive composite [21]. It was found that the obtained composite at 10 vol % loading showed good mechanical properties with a thermal conductivity of 5.1 W m^{-1} K^{-1}. Evidently, with the addition of polymers, the thermal performance of the composites is rather disappointing compared to that of carbon based conductive papers. It is necessary to note that the strikingly decreased thermal conductivity is due to the random distribution of the fillers and the high thermal interface resistance between the filler and matrix [2,25]. In this context, strategies that can significantly improve the mechanical properties of the composite paper without sacrificing its thermal conductivity are urgently needed.

Recently, nanofibrillated cellulose (NFC) has emerged as an alternative for conventionally used polymers in the fabrication of thermally conductive papers [14,26,27]. The elastic modulus of individual cellulose microfibril in the axial direction is reported to be as high as 145 GPa [28], which makes the NFC appropriate matrix for fabricating composites with favorable mechanical property. Unlike conventional polymers, the NFC would not wrap the fillers completely, thus providing a large contact area of the thermally conductive fillers, which significantly minimized the interfacial thermal contact resistance. Moreover, the introduction of the NFC has also been proved to be effective to improve the alignment of the fillers, leading to a highly ordered hierarchical structure [26]. Owing to the excellent mechanical property and unique one-dimensional structure, the introduction of NFC is anticipated to simultaneously obtain the conductive composite with outstanding mechanical property and high thermal conductivity by minimizing interfacial thermal resistance and forming well-aligned structure.

In this work, the highly thermally conductive paper has been fabricated by incorporating NFC with graphite nanoplatelets. Notably, the graphite nanoplatelets can be industrially produced via massive exfoliation of expanded graphite using supercritical carbon dioxide, which has been proved to be a facile, green and cost-effective process [29]. The thermally conductive paper is prepared from a standard filtration of homogenously dispersed solution of GNPs and NFC, and no thermal treatment is involved. It is found that due to the reinforcement and guiding effect derived from the incorporation of NFC, the composite paper shows a robust structure where GNPs are orderly aligned along in-plane direction and the voids between nanosheets are completely filled by the microfibrils. With this hierarchical structure, the composite paper inherits the fascinating mechanical properties of the NFC, and remains to be highly thermally conductive.

2. Experimental section

2.1. Materials

Expanded graphite was purchased from commercial products (99.5%, Qingdao Jinrilai Graphite Co. Ltd., China), with the lateral size of 10–30 μm and the thickness of 10–50 nm. Carbon dioxide (99.5%) was obtained from Beijing AP BAIF Gases Industry Co. Ltd. China. Sodium bromide, 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO), sodium hypochlorite solution, sulfuric acid, nitric acid and other chemicals were of laboratory grade and used without further purification.

2.2. Fabrication of NFC/GNP paper

The NFC was prepared from recycled sulfite paper using the modified method reported by Satio et al. [30]. Briefly, 2 g paper was homogenized with a blender, and then the as obtained slurries were mixed with TEMPO (0.025 g) and sodium bromide (0.25 g). TEMPO-mediated oxidation was initiated by adding 10 ml 13% NaClO solution at room temperature with gentle agitation. During the oxidation process, the pH was maintained at 10.5 by adding 0.5 M NaOH. When no more decrease in pH was observed, the reaction was finished. Subsequently, the product was centrifuged at 4000 r/min for several times until the PH turned to 7. The obtained pulp was then homogenized with a shear mixer for 30 min. The suspension was then centrifuged at 5000 r/min for 30 min to separate large particles from the microfibrils. The collected supernate was diluted and stored at 4 °C.

The GNPs were prepared from expanded graphite according to the method proposed in our previous work [29]. The detailed experimental conditions were as follows: temperature of 55 °C, pressure of 12 MPa, graphite powder mass of 1 g, rotating speed of 2000 rpm and reaction time of 1 h. The resultant nanoplatelets (250 mg) were then treated by a precooled (less than 30 °C) nitric acid–sulfuric acid mixture [1:3 (v/v), 80 ml] under ultrasonication for 24 h. Then, the mixture was transferred into water (1 L), followed by stirring at room temperature for 1 h to obtain aqueous dispersed GNPs.

The GNPs solution was dropped into a NFC solution during stirring, and the mixture was kept stirring for 30 min and then sonicated for 5 min to form a uniform dispersion. The prepared dispersion was vacuum-filtered on a PVDF membrane (47 mm in diameter, 0.45 mm in pore size). The obtained wet film was then placed in a vacuum oven at about 50 °C for 12 h and then pressed under 10 MPa for 1 min.

2.3. Characterization

Thermogravimetric analysis (TGA) was conducted using a T.A. Instruments Q500 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) images were acquired with a Hitachi-SU8010 emission scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2 F20 transmission electron microscope. Raman spectra were measured on a Renishaw inVia confocal Raman microscope system using green (532 nm) laser excitation. The four-probe resistivity tester (KDY-1-type, Guangzhou Kunde Technology Co. Ltd.) was used to investigate the electrical conductivity of the composite paper. The thermal conductivity of the films was studied using the “laser flash” technique (LFT) with a Netzsch LFA 447 Nanoflash at 25 °C. The LFT transient method directly measured the thermal diffusivity, α, of the material. The thermal conductivity is then determined from the equation $K = \rho\alpha C_p$, where ρ is the mass density and C_p is the specific heat of the sample. Tensile strength of the composite paper was measured by an instron (INSTRON 5865), and the test is performed under the condition of the testing speed of 0.5 mm/min.

3. Results and discussion

Fig. 1(a) presents the typical TEM image of the graphitic layer structure of the GNPs. It is observed that the platelet is composed of