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Lignin-based carbon fibers: Carbon nanotube decoration and superior thermal stability

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ABSTRACT

Lignin-based carbon fibers (CFs) decorated with carbon nanotubes (CNTs) were synthesized and their structure, thermal stability and wettability were systematically studied. The carbon fiber precursors were produced by electrospinning lignin/polyacrylonitrile solutions. CFs were obtained by pyrolyzing the precursors and CNTs were subsequently grown on the CFs to eventually achieve a CF–CNT hybrid structure. The processes of pyrolysis and CNT growth were conducted in a tube furnace using different conditions and the properties of the resultant products were studied and compared. The CF–CNT hybrid structure produced at 850 °C using a palladium catalyst showed the highest thermal stability, i.e., 98.3% residual weight at 950 °C. A mechanism for such superior thermal stability was postulated based on the results from X-ray diffraction, Raman spectroscopy, scanning and transmission electron microscopy, and electron energy loss spectroscopy analyses. The dense CNT decoration was found to increase the hydrophobicity of the CFs.

1. Introduction

Carbon materials, in their various forms such as nanotubes, fibers (diameter ranging from nanometers to micrometers), graphene, aerogels and activated carbons, feature high strength and modulus [1–3], good flexibility [4], low density [5], high surface area and excellent electrical conductivity [6–8]. They have been used for applications in energy storage, catalysis, adsorption, filtration, chemical sensing and fire-resistant materials [9–12]. Among these carbon materials, carbon fibers (CFs) produced via thermal treatments of electrospun polymeric precursors have attracted intensive research attention [13–15]. Polymeric precursors including poly(ethylene terephthalate) (PET) [12], polyacrylonitrile (PAN) [16] and poly(vinyl alcohol) (PVA) [17] have been electrospun into nanofibers and subsequently converted into CFs with high carbon yield and excellent mechanical properties. Moreover, functionalization of the obtained CFs by growing carbon nanotubes (CNTs) on their surfaces has also been attempted by several research groups using the chemical vapor deposition (CVD) method [15,18–20]. CNT growth mechanism and the composition and nanostructures of the hybrid carbon materials have been discussed. Increased surface area, electrical conductivity and electrochemical performance of the materials have been achieved.

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It is worth noting that CNT decoration (growth) is more widely used on micron-sized commercial CFs. When used in polymer composites, these CNT-decorated CFs increase interfacial shear strength, interfacial load transfer, flexural strength and fracture toughness of the composites due to the increased surface area and improved wettability of the decorated CFs and strengthened mechanical interlocking between the CFs and the matrix [21–25]. However, growth of CNTs on CFs often causes decreases in CF tensile strength and modulus because of the structural and chemical damages to the CFs during the high-temperature catalytic growth process of CNTs [22,24,25]. The damages have been attributed to the reactions between the carbon and the catalyst particles and local CF oxidation and gasification [22], and more recently to mechanochemical changes in the CF microstructures (i.e., loss of highly oriented surface graphite of the fibers) when heated above a critical temperature [23]. Two recent studies have shown that it is possible to maintain and even increase the strength/modulus of the CFs by applying tension on the fibers during CNT growth and lowering the CVD temperature [23], or via a method to repair CF surface damages, increase carbon crystal size and cross-link the neighboring crystals [26].

Energy and environmental concerns have initiated and energized the research on the development of CFs from renewable resources, much like the research histories of many recent “green” chemical products, such as paints, resins, and detergents. Cellulose is regarded as the most abundant natural polymer on the planet and it has been attempted as the precursor for CFs. Nano-CFs have been developed from the cellulose nanofibrils that are isolated from plant cell walls [27–30]. The cellulose nanofibrils exuded by bacteria has also been converted into nano-CFs [9]. On the other hand, lignin, the second most abundant natural polymer and the most commonly occurring aromatic natural polymer in the world, has also been used as a natural feedstock for CF production. Lignin mainly consists of phenylpropane units connected through various ether-type and condensed-type linkages. It contains high content of carbon (30% of non-fossil organic carbons on the Earth) [31] and its phenolic rings facilitate the formation of carbon rings during the carbonization process [32]. Research on lignin-based CFs can be traced back to the patents issued in the 1960s and 1970s. Otani et al. describe methods to make carbon fibers from alkali lignin, thiolignin and ligninsulfonate using melt, wet and dry spinning processes [33]. Mansmann et al. mix a series of carbon sources including lignin with spinnable polymer solutions to produce CF precursor fibers and eventually CFs [34]. Producing lignin-based CFs via melt spinning has been the main research direction in the last two decades because of its obvious economic advantages compared with other methods. Pure lignin from different sources is melt-spun and carbonized under different conditions and the properties of the obtained CFs are tested [35–39]. Thermoplastic polymers including poly(ethylene oxide) (PEO) [36], PET [40] and polypropylene [41,42] are blended with lignin to increase its spinning performance. The melt-spinning performance has also been improved through using chemically modified lignin [43–45]. Electrospinning has become an important tool in the pursuit of submicron level CFs because of its ease of use and low cost [46,47]. Ethanol and dimethylformamide (DMF) are the most commonly used solvents. PEO, PVA and PAN are added to lignin solutions to increase their spinning performance [48–52]. Fiber spinning and carbonization conditions and CF morphology, mechanical properties and electrochemical performance have been determined through these studies.

Although the research on lignin-based CFs started fifty years ago, most of the studies, especially those using the melt-spinning method, focus on the processing techniques, structural investigations and mechanical properties of the obtained CFs. The first study on lignin-based submicron CFs via electrospinning did not appear until 2007; only twenty journal papers in this field can be found using Web of Science database to date. No study on CNT decoration on the electrospun lignin-based CFs has been reported. The processing, nanostructures and thermal properties of such hybrid carbon fibers are of importance to their potential applications, but yet to be explored.

In this study alkali lignin was used as the main raw material to prepare CF–CNT hybrid fibers via electrospinning followed by carbonization and CNT growth. Fe and Pd nanoparticles were used to catalyze CNT growth and their effects on the nanostructure, carbon crystallization, thermal properties and carbon yield of the CFs were systematically compared. The obtained hybrid CFs exhibited superb thermal stability that surpassed most of the reported carbon materials. CNT “hairs” grown on the carbon fiber surface led to a hierarchical nano-micro surface structure that imparted super-hydrophobicity to the fibers. To the best of our knowledge, this is the first work that compares the effects of Fe and Pd on the growth of CNTs on the lignin-based CFs. The obtained hybrid fibers also exhibit the highest thermal stability reported so far.

2. Experimental

2.1. Electrospinning of CF precursors

Alkali kraft lignin (M_w = 10,000), polyacrylonitrile (PAN, M_w = 150,000), N,N-dimethylformamide (DMF, ⩾99.8%), iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, ⩾98%) and anhydrous palladium(II) chloride ($PdCl_2$) were purchased from Sigma–Aldrich. Lignin and PAN (1:1 wt.:wt.) were dissolved in DMF to produce a 15 wt.% homogeneous solution. A catalyst precursor, i.e. $Fe(NO_3)_3 \cdot 9H_2O$ or $PdCl_2$, was added into the solution (2 wt.% with respect to the total mass of the lignin and PAN) and the mixture was stirred at 60 °C for 24 h. The final solution was loaded into a 12-ml syringe equipped with a 17-gauge needle. Electrospinning of Lignin-PAN precursors was performed using an EC-DIG (IME Technologies) electrospinning system under ambient conditions (temperature 23 °C, relative humidity 50%). The applied voltage was 17 kV and the flow rate was 0.1 ml/h. The fibers were collected on a rotating aluminum disc (Ø 30 cm) that was placed 25 cm from the needle.

2.2. Synthesis of CFs

The synthesis was performed on the electrospun CF precursors by pyrolysis using a tubular quartz furnace. CNTs were