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

Xuezhu Xu^a, Jian Zhou^b, Long Jiang^{a,*}, Gilles Lubineau^{b,*}, Scott A. Payne^c,
David Gutschmidt^a

^a Department of Mechanical Engineering, North Dakota State University, Fargo, ND 58108, United States

^b King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia

^c Microscopy Core Facility, North Dakota State University, Fargo, ND 58108, United States

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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.

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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 elec-

trospun 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

* Corresponding authors: Fax: +1 701 231 8913 (L. Jiang).

E-mail addresses: long.jiang@ndsu.edu (L. Jiang), gilles.lubineau@kaust.edu.sa (G. Lubineau).

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carbon materials have been discussed. Increased surface area, electrical conductivity and electrochemical performance of the materials have been achieved.

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, thioli lignin and lignin-sulfonate 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, $\geq 99.8\%$), iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98\%$) 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. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 ($\varnothing$ 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 subsequently grown on the obtained CFs in the same furnace through chemical vapor deposition (CVD). During the pyrolysis furnace temperature was raised from 21 to 550 °C at 10 °C/min and maintained at 550 °C for 2 h under a hydrogen/argon (500:1 ml/min) gas flow. The temperature was then increased to 1000 °C at 10 °C/min and maintained for 1 h under 500 ml/min argon flow to achieve complete carbonization. To grow CNTs on the obtained CFs, the temperature was decreased to either 750 or 850 °C and the gas was changed to an acetylene/argon mixture (100:300 ml/min). The CVD process lasted for 20 min.

2.3. Nanostructure characterization

Structures of the CFs were studied using a FEI Quanta 3D FEG scanning electron microscope (SEM) operating at 10 kV. The precursor fibers were sputter-coated with gold using an Emitech K575× sputter coater before imaging and the CFs were imaged directly. Energy-dispersive X-ray spectroscopy (EDS) was performed using an EDAX EDS detector operating at 20 kV. Data were analyzed using Genesis Spectrum software (Version 6.39, EDAX Inc.). For transmission electron microscope (TEM) imaging, fiber samples were first embedded in epoxy (Epon-Araldite-DDSA with DMP-30 accelerator) and then cut into 50–70 nm thick slices using a RMC MT XL ultramicrotome (Boeckeler Instruments, Tucson AZ). The imaging was performed using a JEOL JEM-2100 LaB₆ TEM operating at 200 kV. Electron energy loss (EELS) data were acquired using a Gatan ENFINA 1000 EELS spectrometer equipped on the TEM. Zero and core loss EELS data were collected using a 1 mm entrance aperture and a dispersion of 0.3 eV/channel. Background and plural scattering was removed from each spectrum using Digital Micrograph software (Gatan, Inc., version 1.84.832).

2.4. Other characterizations

Thermal properties of the precursor fibers and the CFs were studied using differential scanning calorimetry (DSC, NETZSCH 204F1 Phoenix) and thermogravimetric analysis (TGA, NETZSCH 209F1 Iris). In DSC, samples were scanned from 25 to 350 °C at a rate of 10 °C/min under continuous nitrogen flow. In TGA, samples were heated from 30 to 950 °C at 20 °C/min under nitrogen flow. Wide angle X-ray diffraction

(WAXD) tests were performed from 10° to 50° (2 θ) at 0.1°/min using a Bruker D8 advance powder X-ray diffractometer operating at 20 kV and 5 mA. Raman spectra of the carbon fibers were obtained and analyzed using a LabRam Aramis Raman spectroscopy system (HORIBA Jobin Yvon) equipped with a 473 nm Cobolt laser source and LabSpec software (Version 5.78.24). Wettability of the precursor fiber mats and the CF mats was evaluated by measuring the contact angle of distilled water. A FTA1000B drop shape analyzer from First Ten Angstroms was used and the contact angle was analyzed using its FTA32 Video software. The surface area of the CFs was measured based on Brunauer–Emmett–Teller (BET) method using an Accelerated Surface Area and Porosimetry (ASAP) 2420 system from Micromeritics Instrument Corporation. The samples were dried at 100 °C for 2 h to eliminate adsorbed water before the measurements. Data were analyzed using ASAP 2420 V2.03 software.

3. Results and discussion

3.1. Morphology of carbon fibers

Sample codes and descriptions for all the tested fibers are given in Table 1. Fig. 1 shows the morphologies of the precursor fibers and CFs. All the CFs underwent the same pyrolysis but different CVD processes. Two CVD temperatures (750 and 850 °C) were chosen and the purpose was to show the effect of temperature on the growth of CNTs. As shown in Fig. 1A, the LP fibers exhibit a uniform diameter of approximate 1100 nm, which is relatively large compared to lignin/PAN [53] or pure PAN [54] based carbon fibers prepared by other researchers. The large fiber diameter is ascribed to high polymer concentration (15%) and large needle gauge (17) used in this study. After the CVD process, LP850 maintains structural perfection of LP with a reduced average diameter (~615 nm) as shown in Fig. 1B and Table 2. TEM imaging of the cross-section of a LP850 fiber reveals that the fiber consists of regions with different levels of carbon layer ordering. The region defined between the two lines in Fig. 1C shows primitive long-range order with a d_{002} of 0.439 ± 0.049 nm. The graphene layers are not strictly parallel to each other with apparent bends and branches, suggesting their turbostratic nature. The inset in the bottom left corner of Fig. 1C shows a region with even less long-range order. A complete amorphous carbon region is located in the top left corner of the picture.

Fe nanoparticles are able to catalyze the growth of CNTs at 750 °C. As shown in Fig. 1D, “bud”-like CNTs with an average diameter of 243 ± 62 nm grow on the surfaces of the Fe-LP750

Table 1 – Sample codes and descriptions.

LP	Electrospun lignin/PAN composite fibers
Fe-LP	Electrospun Fe(NO ₃) ₃ ·9H ₂ O-doped lignin/PAN composite fibers
Pd-LP	Electrospun PdCl ₂ -doped lignin/PAN composite fibers
LP850	Carbonized LP fibers (pyrolysis at 1000 °C followed by CVD at 850 °C)
Fe-LP750	Carbonized Fe-LP fibers (pyrolysis at 1000 °C followed by CVD at 750 °C)
Fe-LP850	Carbonized Fe-LP fibers (pyrolysis at 1000 °C followed by CVD at 850 °C)
Pd-LP750	Carbonized Pd-LP fibers (pyrolysis at 1000 °C followed by CVD at 750 °C)
Pd-LP850	Carbonized Pd-LP fibers (pyrolysis at 1000 °C followed by CVD at 850 °C)

Fig. 1 – (A) SEM image of LP; SEM (B) and TEM (C) images of LP850; SEM images of Fe-LP750 (D) and Fe-LP850 (E); (F) TEM image of the cross-section of Fe-LP850; SEM images of Pd-LP750 (G) and Pd-LP850 (H); (I) TEM image of Pd-LP850. The insets are locally magnified images. (A color version of this figure can be viewed online.)

Table 2 – Diameters and lengths of the precursor fibers, CFs and grown CNTs.

Sample	Precursor fiber or CF diameter (nm)	CNT diameter (nm)	CNT length (nm)
LP	1100 ± 340	–	–
Fe-LP	1002 ± 141	–	–
Pd-LP	1190 ± 223	–	–
Fe-LP750	981 ± 309	243 ± 62	–
Pd-LP750	989 ± 203	223 ± 42	13,916 ± 2533
LP850	615 ± 133	–	–
Fe-LP850	942 ± 195	–	–
Pd-LP850	909 ± 293	164 ± 54	13,933 ± 4568

has been observed when the temperature exceeds an optimal value [56–57]. This trend is attributed to two competing factors affecting CNT growth: the rate at which carbon is incorporated into the growing CNTs versus the rate at which metal nanoparticles become inactive [55]. The catalytic metal particles are deactivated after the formation of graphitic carbon overcoating on their surfaces. The softening of the particles at high temperatures may allow easy particle encapsulation by the overcoating and therefore cause the cessation of CNT growth [56,57]. In this study, the zero length of CNTs on the Fe-LP850 fibers is possibly caused by rapid encapsulation of the metal particles even before CNT growth. The highly ordered graphitic overcoating ($d_{002}=0.340 \pm 0.026$ nm) around the Fe particles can be clearly seen in Figs. 1F and 5B. This d_{002} agrees well with the standard spacing of the graphene layers in MWNTs [58].

Pd nanoparticles were found to have different catalytic effects on the growth of CNTs. Fig. 1G shows dense “hair”-like CNTs with an average diameter of 223 ± 32 nm grown on the

Pd-LP750 fibers, whereas Fig. 1H shows smaller CNTs (164 ± 54 nm) on the Pd-LP850 fibers. The decrease in the CNT diameter is possibly caused by the temperature-dependent energies associated with CNT growth. [59] Fig. 1I at higher magnification clearly shows the distribution of Pd particles in the CFs and in the grown CNTs. Some particles in the CFs agglomerate whereas the particles in the CNTs are elongated by the growing nanotubes [60,61]. The graphitic layers of one CNT are distinct in the inset.

3.2. Thermal properties of precursor fibers

Thermal properties of the LP, Fe-LP and Pd-LP fibers were studied using DSC and TGA. Pure lignin and PAN in their powder forms were also tested under the same condition for comparison. All the materials were vacuum dried before the tests. In Fig. 2A, the pure lignin shows an intensive endothermic peak centered at ~ 110 °C due to the removal of bonded water and a series of low-temperature radical coupling reactions [62]. Major thermal decomposition of lignin starts at ~ 320 °C as indicated by the onset of an exothermic peak, during which cleavages of the α -ether linkages in lignin ether chains occur [63]. Pure PAN exhibits an exothermic peak at ~ 300 °C, suggesting the start of PAN degradation which involves cyclization of the adjacent nitrile groups [64]. The three precursor fibers in general show the thermal events of both pure PAN and pure lignin. The iron nitrate and palladium chloride salts added in the fibers do appear to have an impact on the events. For instance, PAN degradation temperature in the Fe-LP fiber

is increased by ~ 20 °C and the peak intensity of the Pd-LP fiber is substantially decreased, suggesting possible interactions between the salts and the polymers.

The TGA weight losses of the five samples during the carbonization process are shown in Fig. 2B and C and the results are summarized in Table 3. Pure PAN exhibits only one significant weight loss at ~ 318 °C, which corresponds to the degradation event determined by DSC at a similar temperature. On the other hand, pure lignin shows a more gradual multi-step weight loss due to its bound water and its complicated chemical structures and reactions [39]. The highest weight loss rate occurs at ~ 320 °C, which is attributed to the cleavages of the α -ether linkages as indicated by the DSC results. The LP fiber in general exhibit a weight loss curve in between those of pure PAN and pure lignin. The Fe-LP and Pd-LP fibers behave differently. The weight loss of Fe-LP is lower than those of the two pure materials below ~ 320 °C, whereas the weight loss of Pd-LP is higher (~ 320 – 560 °C) and lower (>620 °C) than those of the pure materials (Fig. 2B). The highest weight loss rate for Pd-LP occurs at 578 °C, 210 °C higher than that of pure PAN. These phenomena may be attributed to the same salt-polymer interactions that cause the differences in DSC results. The final carbon yields, i.e. the residual weights after one-hour isothermal degradation at 950 °C and cooling, are similar for all the samples (30–40%). These carbon yields are comparable to or even higher than the yields of pure lignin-based CFs reported earlier, especially considering that the one-hour isothermal process was not used in many of the earlier studies [65,47,66].

Fig. 2 – (A) DSC thermograms of pure lignin, pure PAN, LP, Fe-LP and Pd-LP; (B) TGA and (C) DTGA curves of the five samples. (A color version of this figure can be viewed online.)

Table 3 – Fractional residual weights of the pure polymers and precursor fibers in TGA measurements (26–950 °C).

Material	Residue weight (wt.%)					
	150 °C	300 °C	450 °C	600 °C	950 °C	950 °C (after 1 h)
Lignin	94.1 ± 8.1	85.7 ± 8.4	65.3 ± 7.8	60.1 ± 6.2	41.4 ± 4.2	33.2 ± 3.7
PAN	99.6 ± 11.5	98.9 ± 9.5	51.2 ± 6.6	45.0 ± 5.1	37.7 ± 3.6	32.3 ± 3.4
LP	98.9 ± 10.6	90.7 ± 8.5	61.7 ± 7.7	51.2 ± 6.7	39.8 ± 4.2	36.1 ± 4.5
Fe-LP	96.0 ± 8.7	82.3 ± 8.3	56.9 ± 5.4	49.9 ± 4.8	36.3 ± 2.3	31.4 ± 2.1
Pd-LP	98.6 ± 9.3	91.2 ± 10.1	76.4 ± 8.2	51.6 ± 6.4	34.4 ± 4.1	31.1 ± 4.2

Fig. 3 – TGA curves of various carbon fibers. (A color version of this figure can be viewed online.) **Fig. 4 – Residue weight at ca. 900 °C of various carbon materials as reported in literature; the inset image presents Pd-LP850 carbon sponge on an alcohol flame. (A color version of this figure can be viewed online.)**

3.3. Thermal properties of carbon fibers

TGA was also used to assess the thermal stabilities of the obtained CFs. Fig. 3 compares the TGA curves of various CFs up to 950 °C and the residual weights (W_t) at 200, 400, 800 and 950 °C are summarized in Table 4. All tested CFs demonstrated good thermal stability up to 400 °C. W_t of the LP850 precipitates starting from 450 °C (T_{onset}) and levels off at 76.1% at 700 °C. In contrast, W_t s for the Fe-LP750, Fe-LP850, Pd-LP750 and Pd-LP850 fibers are much more stable and they only slightly decrease to 95.1%, 94.1%, 95.5% and 98.3% at 950 °C, respectively. The residual weights remain up to 90% for Pd-LP750 and Pd-LP850 CFs even after one hour isothermal heating at 950 °C (Table 4). These high residue weights show high thermal stability of the obtained CFs. The superior thermal stability is also demonstrated in the inset of Fig. 4, where a Pd-LP850 carbon sponge is burned on an alcohol flame and its structure remains intact after repeated burning [9].

A great number of studies have been conducted on the synthesis of various carbon materials such as C₆₀ [67], carbon black [68], single walled carbon nanotubes (SWNTs) [69–72],

double walled carbon nanotubes (DWNTs) [73], multi-walled carbon nanotubes (MWNTs) [74–76], graphite [67,71], graphene paper/sheets [77,78], carbon nanofibers (CNFs) [79–83], vapor grown carbon nanofibers (VGCF) [70,84], electrospun PAN-based carbon fibers [83], cellulose-based carbon fibers [85], and lignin-based carbon fibers [86]. Many of these carbon materials have shown relatively low thermal stability. For instance, T_{onset} s of many of the studied materials fall well below 900 °C and the residual weights of these materials at 900 °C are much lower compared to the CFs tested in this study (Fig. 4). Especially, the W_t s at 950 °C for the carbon fibers having biological origins (e.g., lignin-based and cellulose-based CNFs) have been reported to be ~40% [86] and 50% [85], respectively. The fact that the melting temperature of pure graphite approaches 3726.8 °C (4000 K) [87,88] implies that there is large room for the improvement in the thermal stability of carbon materials. Carbon materials with high thermal stability, including highly crystalline graphene paper [77], MWNTs [76], and highly purified VGCF [84], have been reported recently. High temperature synthesis

Table 4 – Residue weights for the CFs at different temperatures determined by TGA.

Carbon Fibers	Residue weight (wt.%)				
	200 °C	400 °C	800 °C	950 °C	950 °C after 1 h
LP850	99.0 ± 7.2	98.3 ± 7.4	87.1 ± 5.8	76.0 ± 7.1	68.7 ± 8.0
Fe-LP750	97.5 ± 6.2	97.0 ± 5.3	96.2 ± 6.6	95.1 ± 8.3	82.8 ± 7.5
Fe-LP850	99.9 ± 8.4	99.7 ± 6.8	97.0 ± 6.4	94.1 ± 5.2	80.7 ± 6.1
Pd-LP750	98.5 ± 10.1	97.8 ± 7.5	96.0 ± 8.3	95.5 ± 7.3	90.6 ± 7.2
Pd-LP850	99.7 ± 6.5	99.4 ± 6.9	98.5 ± 5.8	98.3 ± 7.4	89.4 ± 5.2

Fig. 5 – (A–C) TEM of the cross-section of the Fe-LP850 fiber; EDS mapping for Fe-LP850 (D) and Pd-LP850 (E) showing 3 wt.% Fe and 7 wt.% Pd particles within the carbon fibers; (F) schematic structure of the carbon fiber containing catalytic nanoparticles. (A color version of this figure can be viewed online.)

(1500–2600 °C), high structural perfection and repeated purification are the similarities between the three studies and are believed to contribute to the fibers' high thermal stabilities [89].

3.4. Mechanism of high thermal stability

The nanostructures of the carbon fibers and their carbon forms were studied using TEM, XRD, Raman spectroscopy and EELS to determine the mechanism behind their high thermal stability. TEM micrographs in Fig. 5A–C show that the Fe nanoparticles embedded in the carbon fibers are coated with graphitic carbon layers measuring ~20 nm in thickness. The

non-graphite carbon in contact with the particles was converted into lower energy graphitic carbon during the CVD process [90,91]. The distribution of the Fe and Pd nanoparticles is fairly homogenous as shown by the EDS mapping graphs in Fig. 5D and E. A schematic model for a typical carbon fiber is shown in Fig. 5F.

XRD patterns of the LP850, Fe-LP850 and Pd-LP850 fibers are shown in Fig. 6A. The LP850 exhibits a major peak at ~24°, which is attributed to the (002) plane of graphitic carbon [82]. The same peak also occurs on Fe-LP850 and Pd-LP850, suggesting the presence of graphitic carbon in all the three fibers, in accordance to the results from TEM imaging. The other peaks on Fe-LP850 are attributed to the diffractions

Fig. 6 – XRD patterns (A) and Raman spectra (B) of carbon fibers. (A color version of this figure can be viewed online.)

from the (111), (200) and (220) planes of Fe [92,93], whereas on Pd-LP850 the peaks are attributed to the (111), (200), (220), (311) and (222) planes of Pd [94,95]. It also appears that all the three CFs show a weak peak at $\sim 44^\circ$, which can be associated with the diffraction of the (111) plane of diamond [96,97].

Peak width, peak intensity and intensity ratio of the so-called D and G bands in Raman spectra are often used to indicate the level of structural order of carbon materials. G band occurs due to in-plane stretching motion of all sp^2 bonded carbon atoms. D band only occurs in the presence of defects in the sixfold rings and its intensity is related to the number of the defects. As shown in Fig. 6B, the intensities of D and G peaks remain relatively constant for all the fibers and their I_D/I_G ratios are all close to 0.85, indicating similar structural perfection of graphitic carbons [98]. Peak shifts on both D and G peaks can be observed for the fibers containing Fe or Pd nanoparticles, which is presumably caused by electron doping or mechanical strain effects of the nanoparticles [99]. The increase in the fraction of sp^3 carbon can also shift the G peak to a lower wavenumber [96,100]. From this prospective, the downshift of the G peak for the Fe or Pd doped carbon fibers may indicate their higher fraction of diamond-like sp^3 carbon compared to the neat LP850 fiber, as discussed below.

The fractions of the graphitic and diamond carbons in the fibers were further studied using TEM-EELS. Fig. 7A compares the low loss region EELS spectra of LP850, Fe-LP850 and Pd-LP850. LP850 exhibits a plasmon energy of 23 eV, which is typical of amorphous carbon [101]. Fe-LP850 shows a higher plasmon energy at 26 eV while Pd-LP850 features a broad peak with multiple smaller peaks ranging from 27 to 32 eV, which are the energy for graphite and diamond-like carbon, respectively. The different carbon forms in the three fibers are explained as below. Since LP850 contains no metallic catalyst, growth of graphitic CNTs and the catalyzed graphite conversion in the fiber did not occur during the CVD process. Instead, amorphous carbon was deposited on the fiber surface due to acetylene thermal decomposition. Therefore, the EELS spectrum of LP850 shows predominantly the peak of

amorphous carbon. The intensive peaks between 27 and 32 eV for Pd-LP850 suggest the coexistence of graphitic and diamond-like carbon in the fiber [79–81]. The graphitic carbon exists in CNTs and the overcoating of Pd nanoparticles whereas the diamond-like carbon is located in the carbon fiber matrix. For Fe-LP850, it contains graphitic overcoating on Fe nanoparticles, but no CNTs due to catalyst deactivation. In the later stage of its CVD process, amorphous carbon could be deposited on its surface after the Fe nanoparticles were deactivated. The addition of amorphous carbon could cause the downshift of the plasmon energy of Fe-LP850 from 27 eV (for graphitic carbon) to 26 eV.

The $sp^2:sp^3$ ratios for the three carbon fibers can also be assessed by comparing their C 1s (K-edge) EELS spectra (Fig. 7B). Each spectrum in the figure features two peaks: one at ~ 284 eV due to excitation from 1s level to unoccupied π^* of sp^2 and the other one at ~ 292 eV due to excitation to σ^* of sp^2 and sp^3 sites [102]. The peak intensity ratio of $\pi^*:\sigma^*$ is routinely used to indicate the fraction of sp^3 bonds – lower ratio suggesting higher sp^3 fraction. The $\pi^*:\sigma^*$ ratios for LP850, Fe-LP850 and Pd-LP850 are 0.71 ± 0.04 , 0.65 ± 0.03 and 0.56 ± 0.04 , respectively, indicating an increasing fraction of sp^3 diamond-like carbon. Based on the results from TEM, XRD, Raman and EELS, it is concluded that all the carbon fibers (with or without metallic nanoparticles) contain at least graphitic (sp^2) and diamond-like (sp^3) carbons, which are the material bases for the high thermal stability of the carbon fibers. The substantially lower thermal stability of LP850 is due to its lack of the catalytic nanoparticles, which leads to the deposition of amorphous carbon on the CF surfaces instead of CNT growth and graphite conversion during the CVD process. The rapid decrease in W_t for LP850 between 450 and 700 °C is attributed to thermal decomposition of the amorphous carbon. W_t remains constant after all the decomposition is completed (Fig. 4A).

Although the mechanical properties of the CFs are not tested in this study, it is reasonable to assume that the high-temperature mechanical properties of the fibers are also improved because of the increased thermal stability. CFs tend

Fig. 7 – EELS spectra in the carbon low loss (A) and K-edge (B) regions for the LP850, Fe-LP850 and Pd-LP850 fibers. (A color version of this figure can be viewed online.)

Fig. 8 – (A) Measurements of contact angles for the glass substrate and three fiber mats; (B) areal fraction of wetted surface as a function of θ^* ; (C) adsorption isotherms for different carbon fibers. (A color version of this figure can be viewed online.)

to lose their strength and modulus under high temperatures because of the mechanochemical changes in their microstructures [22,23]. The dominant graphitic and diamond-like carbons in the CFs containing Pd and Fe catalysts are thermally stable and mechanically strong, thus imparting high mechanical properties to the CFs under high temperatures.

3.5. Surface area and wettability

Surface areas of the Fe-LP750, Fe-LP850, Pd-LP750 and Pd-LP850 fibers were measured using the BET method. Fig. 8C shows the adsorption isotherms of the four fibers. Based on the curves the surface areas of the four fibers were calculated to be 14.84, 5.74, 19.73 and 31.45 m²/g, respectively. Fe-LP850 exhibits the smallest surface area because no CNTs grow on its surface. Fe-LP750 has the second smallest surface area because of the presence of the “bud” like CNTs on its surface. Pd-LP750 and Pd-LP850 show increasingly larger surface areas due to their longer and thinner “hair”-like CNTs.

The nano-micro hierarchical surface structure of the carbon fibers can impart super-hydrophobicity to the fibers. Three representative fiber mats, i.e. LP (precursor fibers), Fe-LP850 (CFs without CNTs) and Pd-LP850 (CFs with the longest CNTs), were measured for their apparent contact angles (θ^*) as shown in Fig. 8A. The clean glass substrate underneath the fiber mats was also tested for comparison. θ^* s were found to be $78 \pm 5^\circ$, $104 \pm 6^\circ$, $130 \pm 7^\circ$ and $143 \pm 5^\circ$ for glass, LP, Fe-LP850 and Pd-LP850, respectively. The angles show that the glass surface is intrinsically hydrophilic and the addition of a LP fiber layer transforms the surface from being hydrophilic to hydrophobic. Since the LP fiber contains 50 wt.% highly hydrophilic lignin, the increase in hydrophobicity should be mainly attributed to the porous surface of the fiber mat, which effectively reduces the contact area between the liquid and the surface. The increase in θ^* for Fe-LP850 over LP can be

explained by the former's almost pure carbon composition, which is intrinsically more hydrophobic than lignin and PAN. The further increase in θ^* for Pd-LP850 is due to the “hair”-like CNTs on its surface, which further reduce the contact area between the liquid and the fiber mat as calculated below.

For non-ideal rough solid surface, the apparent contact angle is given by the Cassie–Baxter model [103]:

$$\cos \theta^* = -1 + \Phi_s(\cos \theta_E + 1)$$

Where Φ_s is the areal fraction of the surface wetted by the liquid and θ_E is the ideal Young's contact angle between the surface and the liquid. From the equation, Φ_s can be calculated by $(\cos \theta^* + 1)/(\cos \theta_E + 1)$. θ_E for Fe-LP850 and Pd-LP850 is taken to be 90° because of their pure carbon surfaces [104]. θ_E for LP is assumed to be the average θ_E value (86.8°) of PAN (100.8° [105]) and lignin (72.8° [106]). The glass surface is assumed to be a smooth ideal surface. Based on these values, the relationship between Φ_s and θ^* is given in Fig. 8B, which clearly shows that the fraction of the surface area wetted by water decreases for the four samples.

4. Conclusions

In summary, we have synthesized lignin-based, nano-micro hybrid CFs with high thermal stability and super-hydrophobicity. The high thermal stability was due to the high contents of graphitic and diamond-like carbons in the fibers containing Fe or Pd nanoparticles, which converted amorphous carbon into graphitic carbon and enabled the growth of CNTs. The carbon fiber without the metallic nanoparticles showed lower thermal stability because of the amorphous carbon deposited on its surface. The high thermal stability suggests high mechanical properties of the CFs under high temperatures. The super-hydrophobicity occurred on the fiber with long

548 CNTs, which created a nano-micro hierarchical surface struc-
549 ture that effectively reduced the surface area wetted by water.

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