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Development and Structural Integration of Electrospun Carbon Nanofibers with Multi-layer Graphene Patches

Ali A.B^{1,2,3}, Dreyer B^{1,2,3}, Aprojanz J^{4,5}, Tegenkamp C^{2,4,5}, Renz F^{1,2} and Sindelar R^{2,3}

¹Institut für Anorganische Chemie, Leibniz Universität Hannover, Callinstr. 7, 30167 Hannover, Germany.

²Hannover School for Nanotechnology, Laboratorium für Nano und Quantenengineering (LNQE), Leibniz Universität Hannover, Schneiderberg 39, 30167 Hannover, Germany.

³University of Applied Sciences and Arts, Faculty II, Hochschule Hannover, Ricklinger Stadtweg 120, 30459 Hannover, Germany.

⁴Institut für Festkörperphysik, Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover, Germany.

⁵Institut für Physik, Technische Universität Chemnitz, Reichenhainer Str. 70, 09107 Chemnitz, Germany. *Correspondence:

Annas Bin Ali, Hannover School for Nanotechnology, Laboratorium für Nano und Quantenengineering (LNQE), Leibniz Universität Hannover, Schneiderberg 39, 30167 Hannover, Germany, E-mail: annas.bin.ali@acd.uni-hannover.de.

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ABSTRACT

Among the carbon based nanostructured materials, Carbon Nanofibers (CNF) have got unique prominence since past decade due to excellent mechanical and electrical properties combined by their cheap and easy fabrication process. CNF with graphene layered structure were developed by electrospinning of PAN (Polyacrylonitrile) and subsequent post treatments under specialized conditions. The assembly of graphene layers in the form of patches on the CNF surface was examined by Raman spectroscopy and TEM. Structural changes of CNF under different temperatures from 800°C - 1500°C in reducing atmosphere have been investigated. Crystallite size, ID/IG, and FWHM for D and G characteristic bands were evaluated via Raman peak fitting and X-ray diffraction spectroscopy. Results have shown that CNF carbonized at 1500°C with prior external straining (creep stress) applied during the oxidative stabilization process showed emergence of a symmetrical sharp 2D peak in Raman spectrum with I2D/IG ratio of nearly multi-layer graphene. High temperature heat treatment along with creep stress during the stabilization process results in transforming more of the amorphous carbon into the ordered graphitic domains, leading to assembly of graphene layers on carbon nanofiber surface.

Keywords

Carbon nanofibers, Carbonization, Electrospinning, Graphene layers.

Introduction

Carbon nanofibers (CNFs) are among the prominent class of carbon based nanomaterials (CNTs, carbon nano-walls and graphene), that have been widely explored for different applications ranging from industrial scale mechanical setups to nano-electronic systems [1]. The uniqueness of its wide usage is based on high surface area, superior mechanical and electronic properties, light weight and easy fabrication as compared to its peers [2,3]. Traditional carbon fibers (CF) have diameter around 7 μ m and it has been concluded that for such carbon fibers, the graphitic content starts reducing at radial distance of 20 % from surface to core [4]. Carbon nanofibers (CNFs) with typical diameters less than 500 nm do not show this large structural inhomogeneity, due to the fact that their diameter is smaller than the typical skin of traditional CF with less defects [4]. The nano-scale structure with high surface to volume ratio, makes them among the most researched material for lithium ion battery, fuel cells and sensor related electronic applications [5].

Polyacrylonitrile (PAN) is the most used precursor to achieve CNFs, among pitch and rayon due to its high carbon yield and

stable structure [6]. CNFs with typical diameter less 1 µm are developed by electrospinning technique. In a typical process, solution to be electrospun is loaded in a syringe with metallic needle and pumped continuously. Droplet formed at the tip of needle is attracted by Coulombs force from the collector due to application of high voltage. Fibers are formed when electric field exceeds the surface tension of solution to be spun and the Taylor cone formation takes place, which results in whipping movement of fiber jets towards the collector. The typical electrospinning conditions (applied voltage, collector to needle distance, flow rate) determine the size of nanofibers ranging from 50 nm to few microns. Electrospun fibers are then subjected to oxidative stabilization and high temperature carbonization to obtain carbon nanofibers. In general, electrospinning is an efficient facile way to create nanofibers, however it has been reported that due to residual solvent induced chain relaxation in as spun nanofibers, there exists a lower degree of chain alignment [7,8]. The mechanical properties of such electrospun carbon nanofibers are lower due to low molecular orientation and chain alignment along fiber axis. Fibers are drawn as part of post spinning process to induce chain alignment during stabilization process to start the chemical cyclization process leading to oriented graphitic domains in carbonization process [8,9].

Recent studies by our group have demonstrated highly anisotropic carbon nanofibers achieved during the mentioned spinning and post spinning fabrication process. The prepared carbon nanofibers showed high electrical conductivity along the fiber axis [10]. The current work is based on investigation of structure and morphology of these carbon nanofibers as well as the effect of different carbonization temperatures on the crystal structure and defects of CNFs. Moreover, effect of creep stress (hot drawing) during the stabilization process on the crystal structure after carbonization has been studied and compared. Scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR) and transmission electron microscopy (TEM) measurements were done for examining the morphology of carbonized nanofibers. X-ray diffraction (XRD) as well as Raman spectroscopy has been employed to study the effect of different annealing temperatures and time on the crystal growth and defects of graphitic domains.

Materials and Methods

Preparation of carbon nanofibers

The carbon nanofibers (CNFs) were fabricated by a three stage process. Firstly, the electrospinning was done using Polyacrylonitrile (PAN) as precursor material. 16wt% of PAN (150,000 Mw, Sigma-Aldrich) was dissolved in dimethylformamide (DMF, Carl Roth). Fibers were spun at 16 kV voltage, 0.85 ml/h flow rate, 10 m/s collector speed and 16 cm needle to collector distance for 7 hrs. In the second stage, the fiber mat was taken off from rotating collector and exposed to stabilization in air. Stabilization process was carried out in two different ways. One set of electrospun fibers were stabilized assisted with permanent loading (strain) during this stage, i-e creep stress. Second set of electrospun fibers were only clamped (no strain) with the fixtures during the stabilization step without creep stress applied, so the only stress is mechanical stress

due to retardation. For the third case, no external stress applied nor the fiber mat was clamped.

In the third and final stage of fabrication process, samples were subjected to high temperature carbonization process. The strained samples were heat treated at different temperatures (800°C, 1000°C, 1200°C, 1500°C) for 1 hr under reduced atmosphere (2% H_2 in Ar) with 5°C/min ramp rate, and with one set of fibers for 10 hrs at 1500°C, table 1(a). The unstrained fibers were heated to 1500°C for 10 hrs under the same reducing atmosphere to observe the difference of application of creep stress, table 1(b). For the unstrained unclamped samples, complete loss of product resulted during high temperature carbonization stage, table 1(c). The detailed experimental matrix with sample designation is shown in table 1.

STEP 1: Electrospinning	STEP 2: Stabilization (conditions)	STEP 3: Carbonization (conditions)	
PAN precursor	With strain (Load) - Creep 230°C, at 10 hrs, Air No strain (Fixation only) retardation stress	800°C, 1000°C, 1200°C, 1500°C - 1 hr, Ar /H ₂ 1500°C - 10 hrs, Ar /H ₂ Denoted by: (1500°C - 10 hrs - strain)	
	230°C, at 10 hrs, Air	- no strain)	
	No Fixation Free retardation without stress	No samples lasts during high temperature carbonization	

 Table 1: Detailed experimental and sample matrix.

Characterization and Analysis

Morphology of as spun, stabilized and carbonized fibers was analyzed using scanning electron microscope SEM (Zeiss LEO 1455VP, Germany). The as spun and cyclized fibers were sputter coated with gold prior to imaging. Structural changes in PAN were observed using FTIR (Perkin Spectrum Two, UK) with in wavenumber of 400-4000 cm⁻¹. Carbonization study was done by employing X-ray diffraction (Bruker D2 Phaser, Germany). Samples were scanned from 10°-70° using CuKa with step size of 0.03°. The interlayer spacing for primary diffraction peak (002) was estimated using Bragg diffraction law using Scherrer formula (crystallite size (Lc) = $K\lambda/B\cos\theta$, where K = 0.91) [11,12]. Raman spectroscopic analysis (Thermo Fisher Scientific DXR2, US) was done with a laser excitation wavelength of 532 nm with incident power of 1 mW. Origin-Pro peak Gaussian fitting analysis was applied to D, G and 2D peaks obtained in the Raman spectrum for ID/IG and I2D/IG calculations. Later, TEM (FEI Tecnai G2 F20, US) was also done for the 1500°C - 10 hrs - strain sample to complement the findings for Raman analysis.

Results and Discussion

SEM and FTIR: as Spun, Stabilized and Carbonized nanofibers Figure 1 (a-c) shows SEM micrographs for PAN based nanofibers at each of the three stage processes. The diameter for as spun fibers was 330 ± 22 nm, with stabilized fibers around 314 ± 40

nm. Decrease in diameter was observed for carbonized fibers $(1500^{\circ}\text{C} - 10\text{hrs})$ with 188 ± 39 nm. The decrease in diameter can be attributed to weight loss accompanied by densification of CNF at elevated temperatures during stabilization and carbonization stages. The fibers observed are uniform and continuous with no apparent porosity. FTIR results, figure 1(c), for as spun fibers indicated sharp peaks at 2940 cm-1, 2240 cm-1, 1452 cm-1 which is attributed to C-H stretching, -C≡N stretching and CH2 bending [13,14]. As the fibers went through stabilization process the evolution of -C=N peak was observed at 1600 cm-1 and the peak for -C≡N disappeared, figure (f). Transformation of -C≡N to -C=N- in the PAN backbone is most crucial step for stabilization process that is indicative for ladder structure formation. Also the peak for -C-H at 2940 cm-1 disappears after the stabilization process. The processes reported to take place during the oxidative stabilization process are dehydrogenation (to eliminate hydrogen and form -C=C- in PAN back bone) and cyclization. Cyclization is the most important reaction in stabilization process, resulting in formation of ladder structure that is vital for fibers to last during high temperature carbonization process [15]. The process is an exothermic process with evolution of gaseous products and aids in holding the molecule together and make the structure stiffer [13,16]. IR results after high temperature carbonization process, figure (i), show absence of all above indicated peaks corresponding to -C=N and C-H, pointing out that carbonization has taken place. The schematic, figure 1 (b,e,h), shows randomly oriented PAN chains from the sample for as spun process, partial alignment of PAN fibers after hot drawing (creep assisted stabilization process) and formation of graphitic domains after carbonization process.



Figure 1: SEM, FTIR and graphical abstract for structure of as spun, stabilized and carbonized nanofibers.

Crystallography and structural analysis of carbonized nanofibers

The effect of heat treatment on the crystallite size of stabilized PAN fibers at different temperatures is shown in figure 2(a). It can be seen that as the carbonization temperature increases from 800° C to 1500° C, an increase in crystallite size is observed in the range of 10.71 Å to 13.20 Å. The highest increase is observed for fibers carbonized at 1500° C for 10 hours. Along with an increase in crystallite size, a decrease in the FWHM is observed for the (002) signature peak for graphite. Inset in figure 2(a) shows the XRD pattern for fibers carbonized at 1500° C - 10 hrs. The (002) and (100) peaks at 25.4° and 43.8° are typical for diffraction from

graphitic carbon. A sharp (002) peak is typical of ordered graphite. FWHM decreases with increase in heat treatment temperature indicating that more of the amorphous carbon is turning into ordered graphite and the degree of crystallinity has increased. A decrease in the interlayer spacing (Table 2) from 3.61 Å to 3.49 Å is observed, with a value reaching close to typical graphite (3.36 Å) [17]. CNF were also carbonized at 1500 °C for 10 h without creep stress during stabilization stage figure 2(b). It is evident from the graph that a greater increase in crystallite size is observed for fibers which are stabilized with creep stress. Moreover, FWHM for the (002) peak is also increased (5.27 Å) for 1500°C - 10 hrs - no strain samples as compared to the 1500°C - 10 hrs - strain samples (6.29 Å).



Figure 2: (a) Crystallite size and FWHM (002) as function of heat treatment temperature for carbon nanofibers (b) Crystallite size and FWHM (002) for 1500° C - 10 h - strain and 1500° C - 10 h - no strain samples.

Structural characterization was further explored using Raman spectroscopic analysis. Typical Raman spectra for carbon materials show D and G bands from 1332 cm-1 to 1360 cm-1 and 1500 to 1630 cm-1 approximately, ascribed to defects in the graphitic structure and ordered graphitic structure. The R ratio is measure of defects in graphite/graphene systems, defined as integral intensity ratio of D to G band (R=ID/IG) [18]. Figure 3(a) shows a decrease in R ratio as the carbonization temperature is increased. R decreases from 3.72 to 1.46 as temperature is increased from 800°C to 1500°C, which is attributed to more of the amorphous

carbon transforming into ordered graphite structure. Increased annealing temperature for CNFs leads to ordering of graphene domains and effectively helps to reduce the amount of graphitic defects, also reported in other studies [19-21]. The 1500°C - 10 hrs - strain sample showed the least value for ID/IG and FWHM for the G peak. Decrease in FWHM for G peak shows that sp2 content is increased and more graphitic ordering takes place for samples with dwell time of 10 hrs, however for the 1500°C - 10 hrs - no strain samples, the value of disorder and FWHM increases as compared to 1500°C - 10 hrs - strain samples.

SAMPLE	2 theta (002)	d-spacing (002)(Å)	Crystallite size (Å)	FWHM (002) (°)
800°C - 1 hr	24.61°	3.615	10.71	7.93
1000°C - 1hr	24.52°	3.628	11.68	7.27
1200°C - 1hr	24.734°	3.598	12.5	6.8
1500°C - 1hr	24.856°	3.579	13.2	6.44
1500°C - 10 hrs	25.433°	3.499	16.15	5.27

Table 2: Interlayer spacing, FWHM (002) and crystallite size for different carbon nanofibers after carbonization.



Figure 3: (a) 'R' ratio (ID/IG) and FWHM (G peak) as function of carbonization temperatures, (b) Typical Raman spectrums for CNFs carbonized at different temperatures.

Figure 3(b) shows typical Raman spectra for differently treated samples. From the outset, D and G peaks can be seen along with the hump at ~ 2600 cm-1 to 2900 cm-1 Raman shift. It is quite clear that for samples carbonized at 1500°C for 10 hrs, there is an evolution of peak at Raman shift of 2675 cm-1, namely 2D peak. The 2D peak is second order of D band, and is referred as

Nano Tech Appl, 2018

quantitative indicator for the number of graphene layers, ranging from single to few layers of graphene [22,23]. Figure 4(a) shows the 2D/G and FHMW for 1500°C - 10 hrs - strain and 1500°C - 10 hrs - no strain samples. FWHM (2D peak) is around 95 cm-1 for strained samples whereas the unstrained sample show higher FWHM of approximately 130 cm⁻¹. Also, from the integral intensity ratios (I2D/IG), 1500°C - 10 hrs - strain sample shows a value of 0.78 while for 1500°C - 10 hrs - no strain sample value of 0.45 is observed. The typical FWHM (2D peak) for few layer graphene is around 66-75 cm⁻¹ with the 2D/G ratio of 0.8 (22-24). Hence, 1500°C - 10 hrs - strain sample, figure 4(b), shows a Raman spectrum similar to structures with few to higher numbers of graphene layers unlike the traditional graphite structure. To confirm further the presence of multilayer graphene (MLG) structure, TEM imaging was done and the results are shown in figure 5.



Volume 1 | Issue 1 | 4 of 5

Figure 4: 2D/G ratio and FWHM (2D peak) for 1500° C - 10 hrs - stain and 1500° C - 10 hrs - no strain samples, (b,c) Typical Raman spectrum for 1500° C - 10 hrs - stain and 1500° C - 10 hrs - no strain.





The TEM image shows the presence of graphene patched layers along the surface of 1500° C - 10 hrs - strain samples. Multilayer graphene patches are evident, however along with that, amorphous carbon and typical graphite in the core structure. Figure 4(a) also shows formation of loops and stacking of cup shaped loops, these loops formation reduces the number of free edges between adjacent graphene layers, also leading to a decreased value of 'R = ID/IG', as observed from Raman spectroscopy results. Similar findings have been reported elsewhere [25].

Conclusion

CNFs were developed by electro spinning process and were subjected to stabilization using two different approaches, namely applying strain and no strain. Subsequently, these fibers were carbonized under reducing environment. Strained samples during stabilization process were carbonized at different temperatures ranging from 800°C to 1500°C. To observe the impact of creep stress, the unstrained samples were also carbonized at 1500°C for 10 hrs and were compared with strained samples carbonized at 1500°C. To summarize the findings, Increase of carbonization temperature results in ordering of graphitic crystals and defect density decreases as observed from XRD and Raman analysis. The presence of multilayer graphene patches along the carbon nanofibers surface is assumed to be the reason for high electron conductivity as measured in previous studies [10]. Raman 2D peak (Gaussian fitted curve) analysis and its FWHM for 1500°C - 10 hrs - strain sample shows that the structure is more like a few to multilayer graphene rather than typical graphite structure. The application of creep stress during oxidative stabilization stage results in orientation of PAN chains such that, it leads to the formation for highly ordered graphitic domains during the high temperature carbonization stage and is instrumental in assembling of multilayer graphene patches on the surface of carbon nanofiber.

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