Fabrication of ultra thin and aligned carbon nanofibres from electrospun polyacrylonitrile nanofibres

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Abstract. Ultra thin and aligned carbon nanofibres (CNFs) have been fabricated by heat treatment from aligned polyacrylonitrile (PAN) nanofibre precursors prepared by electrospinning. The alignment of the precursor nanofibres was achieved by using a modified electrospinning set up developed recently, where a tip collector was used to collect and align the nanofibres. The average diameter of the aligned CNFs is about 80 nm. The stabilization and carbonization behaviour were studied mainly based on the randomly oriented PAN nanofibres. The effects of stabilization and carbonization temperatures, temperature-increasing rates, and with and without substrates on the morphology and structure of the CNFs were investigated. Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, transmission electron microscopy and Raman spectroscopy were used to characterize the structure of the CNFs and thermogravimetric/differential temperature analysis was used to evaluate the thermal behaviour of PAN nanofibres.

Keywords. Nanofibres; carbon; nanotechnology; oxidation; aligned.

1. Introduction

Carbon is a material of great importance in industrial application owing to its diversity in structure and property. Among various carbon nanostructures, carbon nanofibres (CNFs) have recently attracted researchers from diverse areas due to their wide application potential, such as candidate materials for hydrogen storage (Zhu *et al* 2003), electronic components (Cui *et al* 2004), catalysts and catalytic supports (Endo *et al* 2004), bio-analytical tools (Yokoyama *et al* 2005), functional composites (Hammel *et al* 2004), field emission devices (Li *et al* 2005), and substitutes for carbon nanotubes (CNTs) (Singh *et al* 2002). It is known that the fibre mechanical properties improve substantially with a decrease in the fibre diameter. For example, the tensile strength of the CNF webs increased by two times when the average diameter decreased from 800 to 300 nm (Kim *et al* 2007). Although the fibres prepared by traditional spinning methods are generally 5–500 µm in diameter (Yang *et al* 2003), a novel fibre production technique known as electrospinning offers the possibility of preparing ultra-thin fibres below 1 µm readily (Reneker and Chun 1996; Reneker *et al* 2000; Deitzel *et al* 2001; Huang *et al* 2003).

In recent years, electrospinning has received great interest due to its simplicity and versatility for fabricating ultrathin and continuous nanofibres. In electrospinning a polymer solution or melt is kept in a reservoir with a capillary for fluid spinning and high voltage is applied between the fluid and ground collector. Under the action of applied electrical field the charged drop of the polymer solution at the tip of the capillary becomes conical, termed as Taylor cone (Reneker *et al* 2000). At a critical field when the electrostatic force overcomes the surface tension force holding the droplet, a charged solution jet is ejected from the Taylor cone. The charged jet then undergoes a complex process of whipping, stretching, and solidification as moving towards the grounded collector, which results in the formation of solid fibres as small as tens of nanometers in diameter. By using appropriate organic electrospun fibres as precursors, various inorganic nanofibres such as CNFs can be prepared by subsequent calcinations. However, reports on the preparation of CNFs from the electrospun precursor fibres are lacking. The diameters of CNFs so far prepared are generally several micrometers to more than 100 nm (Chun *et al* 1999; Kim and Yang 2003; Li *et al* 2003; Yang *et al* 2003; Kim 2004; Kim *et al* 2004a, 2007; Chung *et al* 2005; Rutledge *et al* 2006; Sutasinpromprae *et al* 2006). In addition, although the aligned CNFs were prepared by rotating the collector (Kim *et al* 2004b; Rutledge *et al*

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2006) and double-electrode collector (Li *et al* 2003), it is necessary to develop simple and new technique for producing the aligned CNFs on large scale at low cost.

In this paper, the aligned CNFs with the average diameter of 80 nm were fabricated from the electrospun polyacrylonitrile (PAN) nanofibres by stabilization and carbonization. The alignment of the precursor polymer nanofibres was achieved by using a newly developed technique. This study helps to reveal the stabilization and carbonization behaviour of the CNFs and provides a simple and effective method for preparing ultra-thin aligned CNFs.

2. Experimental

PAN (Aldrich, $M_w = 86200$) and *N,N*-dimethylformamide (DMF) solution was prepared in the range from 9–12.5% (w/v) by magnetic stirring for about 12 h.

The aligned precursor nanofibres were electrospun from PAN solution by using a newly developed electrospinning set up (Rafique *et al* 2007). Figure 1 shows a schematic of the modified electrospinning set up.

This set up consists of a syringe with needle, a collector, and a support plate. Different from the conventional electrospinning set up, the grounded collector electrode here is a metal wire of only 2 mm in diameter, fixed in a hole centred at an electrode holder such as a wooden board. Because of the small size of the grounded electrode this collector has been termed 'tip collector'. In this set up, the opening of the hypodermic needle was towards the collector, as shown in figure 1. Positive terminal of the power supply was dipped into the solution and the counter electrode was placed in the electrode holder during this work. In response to the applied electrospinning voltage, the droplet formed at the needle tip was deformed into the conical shape called 'Taylor cone' and a further increase in the applied voltage ejected a jet from the apex of the Taylor cone which travelled towards the counter electrode. As the electrospun fibre travelled towards the

counter electrode, due to higher consumption of solution than the supply at the needle tip, the fibre jet broke and a single fibre was produced in this way. Just after the rear end of a single fibre left the needle tip a new solution drop started to accumulate at the tip again and the next single fibre formed by a similar process. In this way the fibres are produced one by one. At the moment, the front end of the fibre reached the collector and it adhered to the collector surface and was fixed. Subsequently, the rear part of the fibre fell towards the support plate and lied on its surface. During the above processes, the whipping spiral relaxed gradually due to the repelling force between the adjacent circular segments of the charged fibres and a straight nanofibre was finally obtained spanning the gap between the collector and the support plate. Once a single fibre was formed as described above, the next fibre was repelled by the formerly deposited fibre when it approached the collector and landed towards the support plate, as a result of which the next fibre arranged itself in parallel to the former one. The detailed results on the set up and production mechanism of the aligned nanofibres have been published elsewhere (Rafique *et al* 2007).

Conversion of the PAN nanofibres into the CNFs was accomplished in two steps, viz. stabilization and carbonization. Stabilization was carried out in the temperature range from 200–350°C at different heating rates from 0.5–5°C/min in air for 1 h. Carbonization was carried out in the temperature range from 750–1100°C at different heating rates from 0.5–5°C/min under nitrogen for 1 h. The PAN nanofibres were also electrospun and subsequently carbonized on quartz substrate in order to observe the effects of applying tensile stress during stabilization and carbonization.

3. Characterization

In order to determine the stabilization temperature of the electrospun PAN nanofibres thermogravimetric/differential temperature analysis (TG/DTA, WCT-2C) was performed at a heating rate of 5°C/min in air. Fourier transform infrared spectroscopy (FTIR, NICOLET-380) was used to characterize the chemical bonding of the as spun and heat treated nanofibres. The morphology of the fibres was characterized by scanning electron microscope (SEM, Hitachi S-4700). All the nanofibre samples were gold coated for 90 s before SEM measurements. Raman spectroscopy (RM-1000 Micro Raman Spectrometer) and X-ray diffraction (XRD, XD-2) were used to characterize the structure of the CNFs. High-resolution transmission electron microscopy (HRTEM, JEOL-2010F) was used to investigate the crystallinity of the CNFs.

4. Results and discussion

Initially, randomly distributed PAN nanofibrous mats were prepared by using the conventional electrospinning

Figure 1. Schematic of modified electrospinning set up for the production of aligned polymer nanofibres.

system, where the plate collector was placed vertically below the syringe needle. Figure 2 shows typical SEM image of random nanofibre mat and the diameter of the nanofibres range from 180–220 nm. The fibres are straight and average diameter is about 200 nm. In our study it was found that diameters of the electrospun nanofibres depend to a great extent on the concentration of the solution, needle diameter and the electric field strength. Higher solution concentrations result in thicker fibres and lower concentration produces thinner fibres. Bigger diameter needle supplies more solution to the tip as compared to smaller diameter needle and hence the result in thicker fibres. Generally, the fibre diameter decreases with increasing electric field strength. By choosing the solution concentration of 10% (w/v) and electric field strength of 2kV/cm the diameter of the PAN nanofibres was controlled around 200 nm as shown in figure 2.

Conversion of polymer nanofibres into CNFs was performed through stabilization and carbonization. To determine the stabilization temperature, TG/DTA was performed in air from room temperature to 600°C and is shown in figure 3(a). The sharp exothermic peak at about 290°C indicates the cyclization of the nitrile group in PAN and corresponds to the oxidative stabilization process. The weight loss around 280–290°C is due to the evaporation of volatiles and then from 300–600°C due to combustion.

Figure 3(b) shows FTIR spectra of the nanofibres thermally cured at 200, 350 and 750°C in comparison with that of as spun polymer nanofibres. The FTIR spectrum of the sample treated at 200°C showed a notable reduction in peak intensities at 1452, 1733, 2241, and 2920 cm^{-1} indicating abrogation of aliphatic C–H bands (1452, 2920 cm^{-1}), C=O bond for methyl acrylate (1733 cm^{-1}) and saturated nitriles at 2241 cm^{-1} in com-

parison to the as spun polymer nanofibres. FTIR spectrum of the sample thermally cured at 350°C showed some features related to the structural changes. The band at 804 cm^{-1} is probably due to C=C=H bonding and that at 1590 cm^{-1} band is due to C=N, C=C, N=H mixed bonds. Another band at 1370 cm^{-1} might be due to the nascent amorphous structure (inception of D-peak). Based on the above investigations, 300°C was chosen as the stabilization temperature for the preparation of CNFs in this study.

Figure 4 shows SEM images of the CNFs prepared at different conditions. The heating rates are 1°C/min for all the three samples. Figure 4(a) shows SEM image of the CNF mat carbonized at 750°C for 1 h. Before carbonization the nanofibres were stabilized for 1 h at 300°C with a heating rate of 1°C/min. The average diameter of the nanofibres was found to be around 100 nm.

Figure 4(b) shows SEM images of the CNF mat carbonized at 1100°C. The average diameter of the nanofibres at this temperature was about 80 nm. The decrease in diameter for the CNFs carbonized at 1100°C compared

Figure 2. A typical SEM image of the random PAN nanofibres.

Figure 3. (a) DTG/TGA traces of PAN nanofibres in air and (b) FTIR spectra of different samples: (I) PAN nanofibres; (II) PAN nanofibres stabilized at 200°C; (III) PAN nanofibres stabilized at 350°C; and (IV) CNFs.

with that at 750°C may be caused by higher density changes at higher temperature. This reduction in diameter from polymer nanofibres to the CNFs is in agreement with the previous reports (Zussman *et al* 2005). Figure 4(c) shows the SEM image of the CNFs that were electrospun directly on the quartz substrate. It is indicated

Figure 4. SEM images of the CNFs prepared at different conditions: (a) carbonized at 750°C, (b) carbonized at 1100°C, (c) carbonized at 1100°C for the sample deposited on the substrate.

that the nanofibres carbonized on substrates are much straighter and thinner than that of the free mats. The fibres will inevitably be densified and shrink during stabilization and carbonization. The nanofibres were fixed on the substrate from many points and these remained fixed during stabilization and carbonization process, so during stabilization and carbonization the fixation of the nanofibres has an effect similar to that of applied stretching on the nanofibres. In this case the densification due to the loss of non-carbon species was mainly accommodated by the shrinkage along the radial direction during heat treatment. Consequently, due to the fixation of the nanofibres onto the substrate from many points the CNFs on the substrates (these nanofibres cannot move) are straighter due to applied stretch and thinner than that of the free samples due to higher densification along the radial direction. As shown in figures 4(b) and (c), the diameter of CNFs decreased to 60 nm for the sample on the substrate from 80 nm for the free sample.

Figure 5. SEM images of the CNFs prepared at different conditions. (a) Stabilized at 300°C with a heating rate of 1°C/min and carbonization at 1100°C with a heating rate of 5°C/min and (b) stabilized at 200°C with a heating rate of 1°C/min and carbonization at 1100°C with a heating rate of 5°C/min.

The processes of stabilization and carbonization were further investigated by varying the stabilization and carbonization conditions. Figure 5(a) shows the SEM image of the CNFs stabilized at 300°C and carbonized at 1100°C with a heating rate of 5°C/min. It is clearly observed that the nanofibres tend to break during carbonization at higher heating rate. The production rate of the volatile by-products increases with increasing temperature-increasing rate during carbonization.

The nanofibres may be damaged or broken by the rapid swelling of the volatile by-products if their production rate is too high at high heating rate. Meanwhile, the rapid release of the by-products also generates stress inside the fibres that causes the fibres to break sometimes. Figure 5(b) shows SEM image of the nanofibres stabilized at 200°C and carbonized at 1100°C at a heating rate of 5°C/min. It is evidently observed that the nanofibres lost their integrity and merged together. This is because the nanofibres were not properly stabilized at 200°C and melt during heating for carbonization, and thus result in the emergence of the nanofibres. XRD was utilized to verify the carbonization of the nanofibres. Figure 6 shows XRD pattern of the CNFs carbonized at 1100°C and the PAN nanofibres. A broad XRD peak at about $2\theta = 17^\circ$ for PAN nanofibres indicates low crystallinity, suggesting that PAN molecules in the fibres did not have enough time to crystallize before solidification during electro-spinning.

Two distinct XRD peaks at about 25° and 44° for the CNFs carbonized at 1100°C indicates (002) and (10) layers of graphite structure (Babu and Seehra 1996). It is attested that the PAN nanofibres were well carbonized and graphitized.

Figure 7 shows the Raman spectra of PAN-based CNFs derived at different temperatures. Two peaks around 1360

and 1580 cm^{-1} were clearly observed for all the samples carbonized at temperatures from 750–1100°C, which are typical characteristics of the graphitic carbon. The peak around 1580 cm^{-1} can be identified as the G peak of crystalline graphite arising from zone-centre E_{2g} mode, and the peak around 1360 cm^{-1} as the D peak assigned to an A_{1g} zone-edge phonon induced by the disorder associated with finite crystalline size.

From Raman spectra it is observed that R -value, the intensity ratio of the D and G peaks, decreases with increasing carbonization temperature, indicating that the degree of graphitization increases correspondingly. Knight and White (1989) developed an empirical formula for the relationship between R and the crystallite domain size L_a of graphite as $L_a = 4.4/R$ nm. Using this equation, L_a was estimated to be in the range from 4.17–4.62 nm with increasing carbonization temperature from 750–1100°C as shown in figure 7(b).

Finally, the aligned PAN nanofibres were prepared by using the set up shown in figure 1. Figure 8(a) shows the

Figure 6. XRD patterns of (a) electrospun PAN nanofibres and (b) CNFs carbonized at 1100°C.

Figure 7. (a) Raman spectra of the CNFs carbonized at different temperatures: (I) 1100°C; (II) 1000°C; (III) 800°C; (IV) 750°C and (b) crystal size and fibre diameter vs carbonization temperature.

SEM image of aligned PAN nanofibres electrospun from a concentration of 11% (w/v) with diameter in the range from 120–170 nm and the average diameter is about 140 nm. Such a thin diameter of PAN nanofibres was achieved by using new electrospinning set up and adjusting the electrospinning parameters properly. Here the advantage of this set up lies in that the nanofibres were further thinned during suspension across the gap between tip collector and support plate (figure 1). These aligned

PAN nanofibres were stabilized at 300°C at a heating rate of 1°C/min and then carbonized at 750°C with a heating rate of 1°C/min.

Figures 8(b) and (c) are the SEM images at different magnifications of the aligned CNFs after carbonization. Majority of the fibres after carbonization were in the diameter range from 60–90 nm and average diameter was about 80 nm. The production of so thin carbon nanofibres with alignment on large scale was not reported so far apart from the present results.

Figure 9 shows TEM images of the CNFs, where figure 9(c) is the HRTEM image measured at the edge area of the CNF shown in figures 9(a) and (b). It is clearly observed that the structure of the surface layer is different from that of the inner part of the CNF. The inner part is composed of the ordered domains of graphitic layers and the amorphous area. The size of the ordered domain is from several layers to 4–3 nm, which is in agreement with the calculated results from the Raman peaks shown in figure 7(b). However, the surface layer is much better graphitized and preferential orientation of the graphitic layers along the fibre axis is clearly observed in the

Figure 8. (a) Aligned PAN nanofibres; (b) and (c) SEM images of the CNFs prepared at 750°C at a heating rate of 1°C/min.

Figure 9. TEM (a), (b) and HRTEM (c) images of the CNFs.

surface layer. Formation of the oriented atomic layers in the surface part is likely to originate from the preferential orientation of the molecular chains in the precursor PAN fibres. The molecular chains in the surface layer are easier to be aligned during elongation of the electrospinning than those in the inner part. So the surface layer shows much better crystallinity and orientation of the atomic layers than that in the inner part. The thickness of the surface layer is 15–25 nm. In addition, more or less orientation along the fibre axis was also observed for the graphitic layers in the inner part of the CNF, which also resulted from the alignment of the molecular chains in the PAN fibres caused by the large elongating strain during electrospinning. The orientation of the atomic layers along the fibre axis is helpful for improving the mechanical properties of CNFs.

5. Conclusions

In conclusion, this paper presents the fabrication route of the ultra thin and aligned CNFs from electrospun PAN nanofibres using a modified electrospinning set up followed by heat treatment. This modified electrospinning set up can readily produce ultra thin precursor nanofibres, which is a prerequisite for obtaining the ultra thin CNFs. The ultra thin and aligned CNFs with an average diameter of about 80 nm were prepared successfully by this modified set up. DTA/TG analysis and FTIR spectra revealed the chemical reaction occurring during stabilization and carbonization. The stabilization temperature of 300°C was determined, whereas lower stabilization temperature of 200°C caused the nanofibres to merge together during carbonization. Higher temperature increase up to 5°C/min caused the CNFs to break during carbonization, which can be avoided by decreasing the temperature rate to 1°C/min. The CNFs carbonized on substrates are straighter and thinner than that of the free samples, which is because the nanofibres cannot shrink freely on the substrates. Raman spectra and XRD pattern confirmed the carbonization of the PAN nanofibres and it was found that with increasing carbonization temperature the degree of graphitization increases. The crystallite size calculated from the Raman peaks is in the range of 4.17–4.62 nm depending on the carbonization temperature, in agreement with the observation results by HRTEM. The outer part of the CNFs shows much better crystallinity than that in the inner part. The preferential orientation of the atomic layers along the fibre axis was clearly observed for the outer part, which is because the molecular chains in the outer part have higher mobility, and thus aligned much better during elongation process of electrospinning.

The ultra thin and aligned CNFs are especially useful for composite materials.

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