Quantitative appraisal of the interfacial anchoring state of polyaromatic hydrocarbons during the formation of C/C composites

Cheng-Te Lin [a], Min-Chiao Tsai [a], Chi-Young Lee [a,b], Hsin-Tien Chiu [c], Tsung-Shune Chin [d,*]

[a] Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan
[b] Center of Nanotechnology, Materials Science, and Microsystems, National Tsing Hua University, Hsinchu 30013, Taiwan
[c] Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan
[d] Department of Materials Science and Engineering, Feng-Chia University, Taichung 40724, Taiwan

ARTICLE INFO

ABSTRACT

The preferred anchoring state for polycyclic aromatic hydrocarbons (PAHs) pyrolyzed onto carbon substrates has been studied by semi-quantitative methods, examining their interfacial lattice arrangements. The samples were prepared by decomposing petroleum pitch inside carbon nanotubes resulting in a variety of crystallinities forming one-dimensional C/C composites. Studies indicate that the preferred anchoring state of PAH molecules depends on the nature of the substrate. Accordingly the PAHs in mesophase pitch should exhibit a face-on orientation on the carbonaceous substrates, including a graphite sheet, glassy carbon, and pyrolytic carbon. However, it showed that the anchoring state (face-on or edge-on) of PAH units can be altered even on carbonaceous substrates. The results demonstrated that in C/C composites the anchoring state is predominantly determined by the relative degree of crystallinity of the pitch/carbon substrate, and can be semi-quantitatively estimated using the I_D/I_G ratio from Raman spectra. Face-on anchoring is preferred when the I_D/I_G ratio of substrate is smaller (higher crystallinity) than that of the pyrolyzed precursor, whereas edge-on anchoring is favored when it is larger. Such an estimation method is useful in tailoring microstructures in the fabrication of C/C composites using PAH precursors.

1. Introduction

The investigation of the surface anchoring effect at the boundaries between polycyclic aromatic hydrocarbon (PAH) molecules/substrates attracts academic interest. There are two categories of surface anchoring states, edge-on and face-on, expounded by Hurt et al. [1–3]. The preference of the anchoring state is dependent on the competition between intermolecular forces *within* PAH molecules and *between* PAH units/substrate. Usually the sample is prepared by spreading and pyrolyzing the PAH precursor on the substrate for observation under a polarized optical microscope. However, the conventional method cannot provide direct evidence of the anchoring state in the vicinity of the boundary between PAHs/matrices. This is because the ordered anchoring region is sometimes on the scale of sub-micrometers and therefore beyond the optical resolution limit [2]. Another effective way to obtain information of interfacial anchoring states is

to examine the arrangement of graphene layers within the sample using high-resolution transition electron microscopy (TEM). Since the penetration depth of electron beams at 200 kV is only tens of nanometers, the sample prepared for optical microscope analysis is not appropriate for TEM observation.

Recently, the template synthesis method using nanoporous anodic alumina (AAO) has been extensively applied to produce various one-dimensional carbon nanomaterials, like nanofibers [4–6] or nanotubes [7–9]. The microstructure of such nano-sized materials can be easily studied under TEM. In addition, it is known that the alignment of PAHs, which is affected by interaction with the surface of the substrate (the surface anchoring effect), can be extended into the sample body in the range of sub-micrometers [1,6]. Although the anchored molecules are restricted to the superficial region of a bulk material, the arrangement of the PAH molecules can dominate the entire microstructure as the dimension of the products approaches nanoscale. Therefore, such one-dimensional carbon nanomaterials are ideal intermediates to study the interfacial microstructure because of the pronounced anchoring behavior.

Present-day studies imply that the anchoring states of mesophase pitches depend on the type of substrate [1–3,10]. Edge-on anchoring is found on most substrates, whereas face-on anchoring is only observed on carbon, mica, polyimide, and silver. These reports also indicate that PAH molecules always exhibit a face-on orientation on a graphite-based surface and carbonaceous substrates, such as glassy carbon, carbon fibers, and pyrolytic carbon. The results inspired our interest in investigating whether PAHs can exhibit alternative anchoring states on a certain substrate and, if so, what interfacial anchoring patterns will be shown.

In this study, a variety of tubular carbon substrates were prepared and investigated for their preferred orientations of the graphene layers at the interface of pitch/carbon composites. The anchoring states of carbonized pitch in C/C composites were identified by high-resolution TEM and quantitatively characterized by Raman spectroscopy for their crystallinity.

2. Experimental

Thin carbon layers (5–50 nm) with different degrees of crystallinity were coated on a channel surface of AAO (Whatman Ltd.) becoming a carbonaceous substrate. Because each chemical vapor deposition (CVD) process has its own limitations, several kinds of depositions, such as acetylene decomposition (Samples B and D) [11,12], ethanol pyrolysis (Sample C) [13,14], and Wurtz-type reaction (Sample E) [15–17] were employed to coat the AAO channels. The details of preparation can be found in Supporting Information. The adopted PAH precursor is isotropic petroleum pitch (A-240, Ashland Inc.), which is composed of hetero-PAH molecules. The precursor was spread on top of the templates with or without carbon coating for pyrolyzing the PAHs inside the channels during subsequent thermal treatment. In a tube furnace the temperature was held at 300 °C for half an hour under flowing Ar to soften the precursor, and then gradually raised to 700 °C for 2 h for the pyrolysis. The oxide template was removed by

immersing in hydrofluoric acid. For the study of interfacial microstructure, all the products were annealed at 2500 °C to enhance their lattice orientation. The samples were characterized by high-resolution TEM (HRTEM, JEOL JEM-2010) and Micro-Raman scattering measurements (CHROMEX 501is: 488 nm).

3. Results and discussion

The petroleum pitch carbonized at 700 °C in the bare channels of AAO template without carbon coating (Sample A) was first examined. After leaching off the template, the product was found to be composed of uniform nanofilaments, as shown in Fig. 1a. Their diameter and length were evaluated to be 300 ± 50 nm and 60 μm, respectively, which accurately correspond to the channel size of the template. This implies that during the softening process, the channels of the template were fully impregnated with liquid-phase pitch, in which the alignment of PAH molecules is strongly influenced by the oxide inner surface of the channels. In the lattice image (Fig. 1b) it can be seen that the orientation of graphene layers is normal or oblique to the longitudinal axis of the nanofilaments. This suggests that the interaction between PAHs and alumina would result in an edge-on anchoring state. The result is in agreement with that of previous observations [5,18,19].

Carbon substrates made by coating carbon on AAO channels with different methods (Samples B–E) were obtained after the removal of template. Their appearance in scanning electron micrographs (SEM) is similar to that in Fig. 1a. However, in TEM (see Fig. S2) these substrates exhibit a tubular structure, and their hollow cores will be used in pitch-filling to form C/C composites with a core–shell structure. The diffraction spots in Fig. S2a can be assigned to the (0 0 2) lattice plane of graphite. It indicates that after graphitization the carbon substrate of Sample B comprises of graphite basal planes, whereas other samples show nanocrystalline carbon. In order to determine their interfacial anchoring state, the lattice images at the boundary of C/C composites (Samples B–E) were observed by high-resolution TEM. These core–shell materials were also treated at >2500 °C to develop crystallinity, thus enhancing the contrast of the lattice framework. Such a high-temperature treatment does not change the graphene orientation of the sample post-carbonization [2,20].

Fig. 2a (Sample B) shows that the arrangement of carbonized PAH units on the right side prefer to align parallel to the basal planes of the substrate on the left side, representing a face-on anchoring behavior. A similar result is seen with the pyrolysis of naphthalene polymer into multi-walled carbon nanotubes [21]. The lattice images become slightly clearer after thermal treatment, and the alignment tendency does not change (see Fig. 2b). As liquid-phase pitch carbonized in the channel coated with nanocrystalline carbon layer, the C/C interface becomes ambiguous and difficult to distinguish, as shown in Fig. S3a and c. After high-temperature treatment, the lattice alignment of PAH units in both Samples C and D can be discriminated as having a face-on anchoring preference (see Fig. S3b and d), in agreement with previous observations as well [1,2].
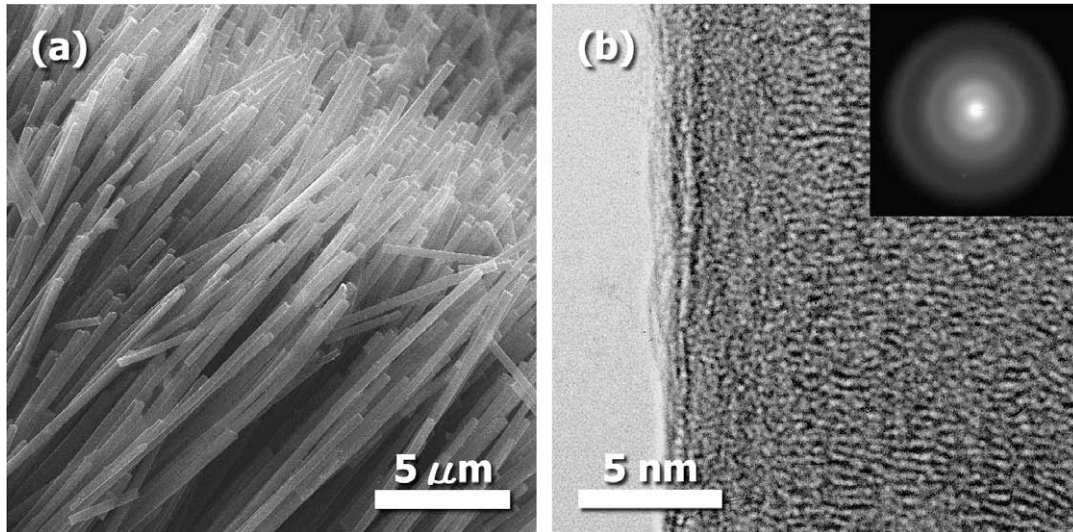
Fig. 1 – (a) SEM and (b) high-resolution TEM images of carbon nanofilaments (Sample A) produced by carbonizing the pitch in the channels of nanoporous AAO. The lattice image exhibits an edge-on anchoring state.
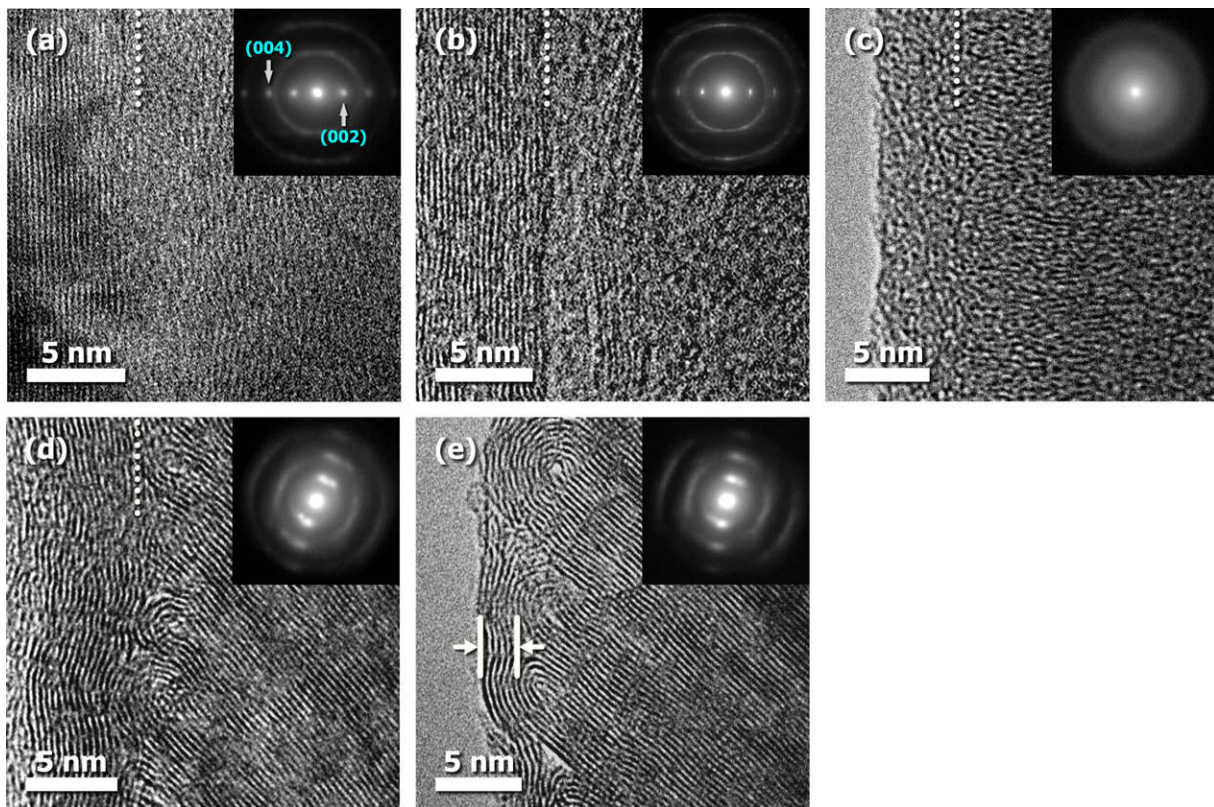

Fig. 2 – Interfacial lattice images of PAHs pyrolyzed on graphite (Sample B) and nanocrystalline carbon (Sample E) substrates: Sample B after (a) carbonization, and (b) graphitization; Sample E after (c) carbonization, and (d) (e) graphitization. A dot line indicates where the C/C boundary is.

An entirely different result was obtained when the PAHs were carbonized on a carbon substrate with very low crystallinity (Sample E). After carbonization, an ambiguous C/C boundary with different lattice orientations can be roughly observed, as shown in Fig. 2c. In lattice images of Fig. 2d and e, the inclined edge-on anchoring from graphitized Sample E is shown. The semi-circular loops on the edge of the pitch filler imply that the dangling sites, rather than basal planes of PAH units, are exposed at the C/C interface, confirming edge-on alignment. Such loops on the surface of graphene edge are usually found in graphitized carbon materials [5,20]. Two sets of (0 0 2) diffraction spots exhibited in the

inset of Fig. 2d also signifies that at the C/C boundary it is composed of two groups of graphene stackings. The significant influence of surface anchoring effect in nanoscale can be manifest in Fig. S4. Even though the thickness of carbon shell (substrate) is only ~2% of the diameter of the nanofilament (see Fig. 2e), the appearance of the C/C composite is still substantially altered as the anchoring state changes. In nanoconfined environments, the enlarged elastic strain can dominate the anchoring arrangement as well. Four possible face-on configurations considering surface anchoring strength and elastic strain were proposed by Jian et al. [21]. The graphitic microstructure of Sample E is disagreement with any proposed face-on configuration, indicating that two anchoring states can not be interchanged by internal elastic strain. In addition, edge-on state on disordered carbons might be affected by oxygen-containing functional groups on the surface of substrates. Although during thermal treatment most of adsorbed molecules should be expelled by reaction with carbons.

The degree of graphitization of all samples was determined by Raman scattering spectroscopy to systematically investigate the correlation between anchoring states and substrate crystallinity. Although the crystallinity of samples can be identified by the diffraction patterns of TEM as well, it is difficult to do quantitative comparison. Additionally, average grain size of samples can be estimated by peak width collected from X-ray diffractometer using Scherrer's equation. However, as the crystallinity of carbon samples is low, only tiny (0 0 2) peak can be found in the pattern and others are hidden in the background. Therefore, the I_D/I_G ratio estimated from Raman pattern is suitable to semi-quantitatively denote the degree of graphitization of samples in a low-crystalline state. In this study, I_D/I_G ratios of samples were calculated as the ratio of peak heights using Breit–Wigner–Fano (BWF) + Lorentzian fits for comparison with Ferrari's work [22]. The BWF function that has an asymmetric line shape, is given by:

$$I(\omega) = \frac{I_0[1 + \frac{2(\omega - \omega_0)}{Q\Gamma}]^2}{1 + [\frac{2(\omega - \omega_0)}{\Gamma}]^2} \tag{1}$$

where I_0 is the peak intensity, ω_0 is the peak position, Γ is the full width at half-maximum (FWHM), and Q is the skewness coefficient. The symmetrical Lorentzian shape is recovered in the limit as $Q^{-1} \to 0$ [22–24]. Such a curve-fitting method is expounded to be satisfactory for the case of nanocrystalline and amorphous carbons [25]. All the fitting results were summarized in Table 1, including the I_D/I_G ratios obtained using a Gaussian fitting routine [26,27]. The correlation of the I_D/I_G ratios between using two kinds of fitting procedures is shown in Fig. S5.

In Raman spectra (Fig. 3a and b), the G-band (at 1550–1605 cm^{-1}) is attributed to the stretching-vibration mode of sp^2 sites, such as in aromatic compounds or olefins (C=C chains), whereas D-band (near 1350 cm^{-1}) is caused by the breathing mode of those sp^2 sites solely in aromatic rings. Ferrari et al. indicated that ranging from graphite (~100% sp^2 sites) to tetrahedral amorphous carbon (~100% sp^3 phase) visible Raman spectra can be elucidated using a three-stage model [22]. In our case while the G-band moves to the lower frequency, the I_D/I_G ratio decreases, and the FWHM of peak decreases as well. Therefore it can be concluded that all studied samples are composed of from micro- to nanocrystalline graphite without sp^3 hybridization. The average I_D/I_G ratios of Sample A after pyrolysis (at 300 °C) and carbonization (at 700 °C) evaluated from Fig. 3a are 0.74 and 0.75, respectively. At the pitch/AAO interface the dispersive interaction between pitch/oxide is much weaker than the internal π–π bonding within PAH units, resulting in strong edge-on anchoring (see Fig. 1b). Typical Raman spectra of as-prepared carbon substrates before pitch-filling are shown in Fig. 3b. The average I_D/I_G ratio of Sample B is 0.15, indicating a well-developed graphite structure. The ratios of other samples with lower crystallinity were estimated to be in the range 0.60–1.09. Sample E has the highest I_D/I_G ratio, representing a very low-crystalline phase.

It was noted from the average I_D/I_G ratios, that if the crystallinity of carbon substrate (I_D/I_G ratio: 1.09, Sample E) is inferior to that of pyrolyzed pitch (I_D/I_G ratio: 0.74), the edge-on anchoring state is created. On the contrary, when the crystallinity of substrate is close to or better than that of pyrolyzed pitch, a face-on anchoring arrangement will be formed. Fig. 3c interprets that the interfacial microstructure is related to the I_D/I_G ratios (degrees of graphitization) of filler/substrate. This suggests that as the liquid-phase pitch pyrolyzes inside the carbon-coated channels, a competition in degree of order between self-assembling PAH molecules and the interfacial bonding with substrate will determine its ultimate anchoring state. Edge-on anchoring occurs on nanocrystalline carbon substrates because the PAH molecules assemble with themselves having higher surface energy than align along the substrate surface. As the degree of graphitization of substrate increases, the intermolecular attraction between pitch/substrate is enhanced, resulting in face-on anchoring to reach a lower energy conformation. An illustration of the two anchoring states at the boundary of pitch/carbon substrate is shown in Fig. 4. Such a semi-quantitative estimation method using

Table 1 – Fitting parameters using BWF + Lorentzian and double-Gaussian fits for all samples.						
	Sample A (300 °C)	Sample A (700 °C)	Sample B	Sample C	Sample D	Sample E
G-band position[a] (cm^{-1})	1598.5	1594.8	1587.0	1589.5	1602.2	1581.3
FWHM[a] (cm^{-1})	75.1	72.1	119.9	76.0	53.1	20.0
Peak ratio[a] (I_D/I_G)	0.74	0.75	1.09	0.69	0.60	0.15
Peak ratio[b] (I_D/I_G)	2.60	2.73	4.11	2.63	2.45	0.42

[a] The parameters were obtained using BWF + Lorentzian fits; the I_D/I_G ratio was evaluated from the ratio of peak heights.
[b] The I_D/I_G ratio was evaluated from the ratio of integrated peak areas using two Gaussians.
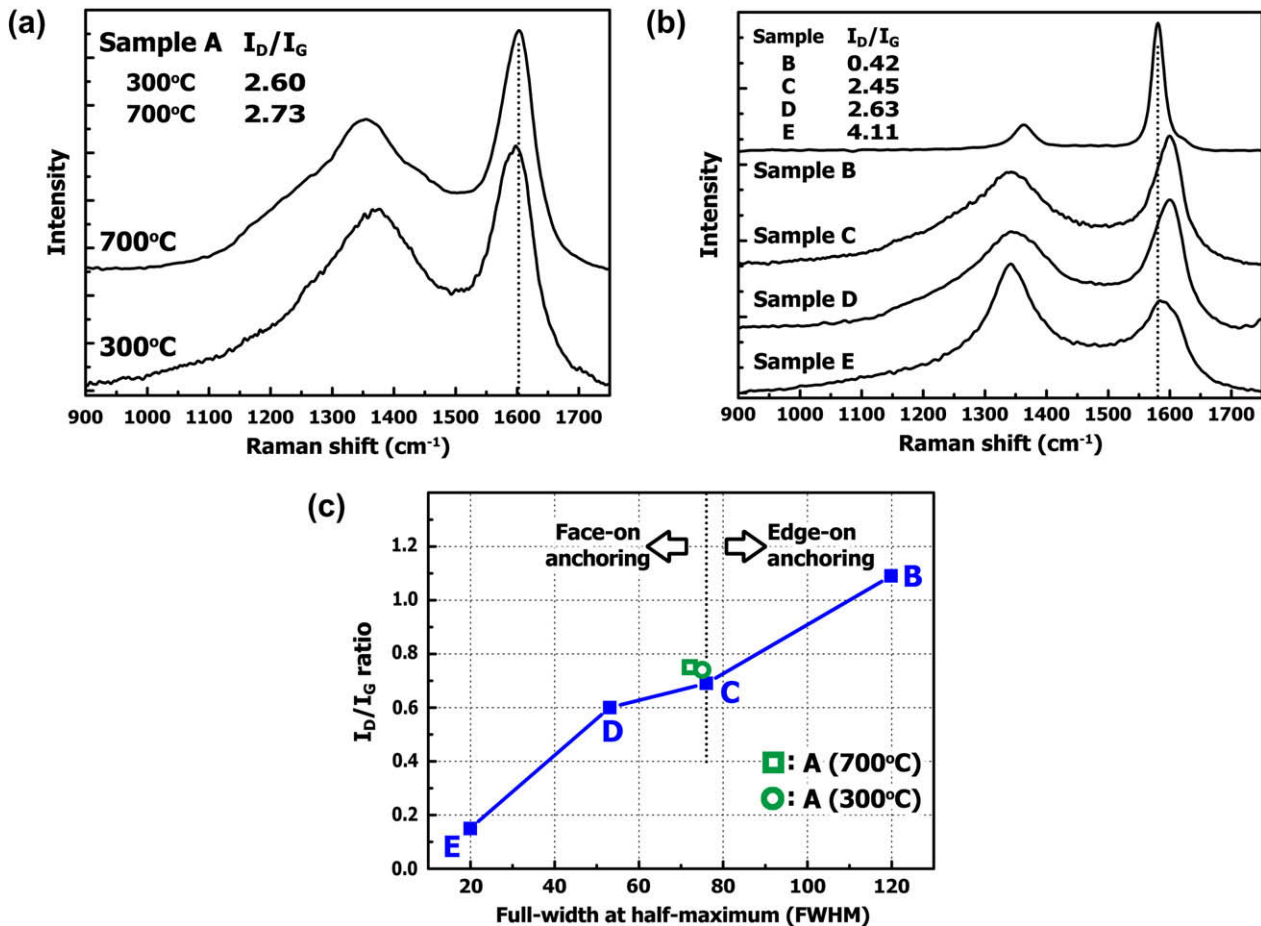
Fig. 3 – Raman spectra measured from (a) pitch carbonized inside the channels of AAO, and (b) various carbon substrates before pitch-filling, (c) the I_D/I_G ratios of samples versus their FWHM showing a linear relationship.
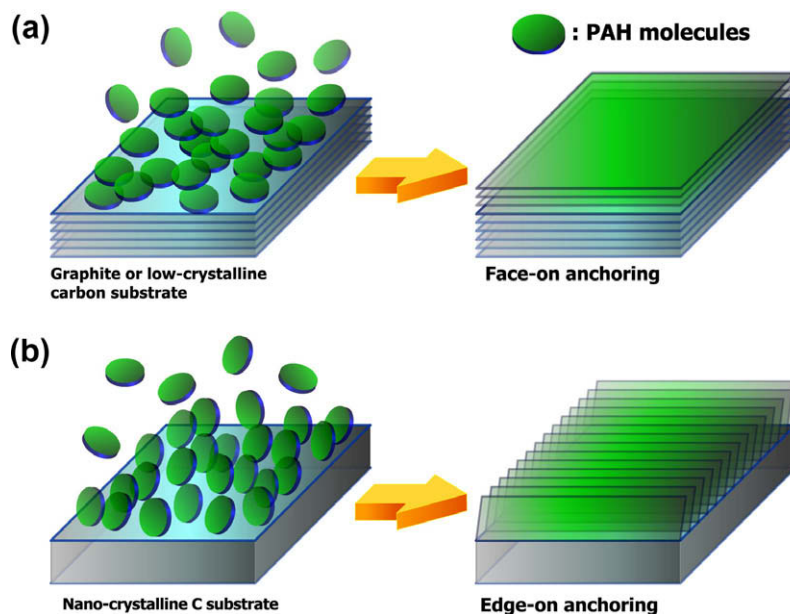

Fig. 4 – Comparative schemes: (a) face-on anchoring is preferred as the crystallinity of carbon substrate is better than that of pyrolyzed PAHs. (b) On the contrary edge-on anchoring will be created.

average I_D/I_G ratios provides a simple and useful way to pre-program the microstructure of pitch/carbon composites. The interfacial texture in C/C composites deeply influences their physical and mechanical behavior [28,29].

4.   Conclusions

The preferred anchoring state at C/C boundary in composites has been studied by directly observing their lattice orientation in high-resolution TEM. After examining the results of carbonized pitch on various carbon substrates, it has been demonstrated that the anchoring state is not only dominated by the nature of the substrates, but also the relative degree of crystallinity of pitch/carbon substrate. In addition, the resultant anchoring state can be determined by comparing the average I_D/I_G ratio of pyrolyzed filler with that of carbon substrates from Raman spectra. When the carbon substrate has higher crystallinity than that of pyrolyzed pitch, the interfacial graphene orientation shows face-on anchoring, otherwise edge-on anchoring is preferred. This is helpful in understanding the microstructural patterns in C/C composites using PAHs as precursor.

Acknowledgements

Appendix A.   Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.11.024.

R E F E R E N C E S

[1] Hurt R, Krammer G, Crawford G, Jian KQ, Rulison C. Polyaromatic assembly mechanisms and structure selection in carbon materials. Chem Mater 2002;14(11):4558–65.

[2] Jian KQ, Shim HS, Tuhus-Dubrow D, Bernstein S, Woodward C, Pfeffer M, et al. Liquid crystal surface anchoring of mesophase pitch. Carbon 2003;41(11):2073–83.

[3] Han KQ, Xianyu HQ, Eakin J, Gao YM, Crawford GP, Hurt RH. Orientationally ordered and patterned discotic films and carbon films from liquid crystal precursors. Carbon 2005;43(2):407–15.

[4] Jian KQ, Shim HS, Schwartzman A, Crawford GP, Hurt RH. Orthogonal carbon nanofibers by template-mediated assembly of discotic mesophase pitch. Adv Mater 2003;15(2):164–7.

[5] Lin CT, Chen WC, Yen MY, Wang LS, Lee CY, Chin TS, et al. Cone-stacked carbon nanofibers with cone angle increasing along the longitudinal axis. Carbon 2007;45(2):411–5.

[6] Chan C, Crawford G, Gao YM, Hurt R, Jian KQ, Li H, et al. Liquid crystal engineering of carbon nanofibers and nanotubes. Carbon 2005;43(12):2431–40.

[7] Bae EJ, Choi WB, Jeong KS, Chu JU, Park GS, Song S, et al. Selective growth of carbon nanotubes on pre-patterned porous anodic aluminum oxide. Adv Mater 2002;14(4):277–9.

[8] Zhi LJ, Gorelik T, Wu JS, Kolb U, Müllen K. Nanotubes fabricated from Ni-naphthalocyanine by a template method. J Am Chem Soc 2005;127(37):12792–3.

[9] Liu QY, Li Y, Liu HG, Chen YL, Wang XY, Zhang YX, et al. Nanotubes fabricated from sandwich-type mixed (porphryinato)(phthalocyaninato)europium complex by template technique. J Phys Chem C 2007;111(20):7298–301.

[10] Brooks JD, Taylor GH. Formation of graphitizing carbons from the liquid phase. Nature 1965;206:697–9.

[11] Sui YC, Acosta DR, Gonzalez-Leon JA, Bermudez A, Feuchtwanger J, Cui BZ, et al. Structure, thermal stability, and deformation of multibranched carbon nanotubes synthesized by CVD in the AAO template. J Phys Chem B 2001;105(8):1523–7.

[12] Jeong SH, Lee KH. Fabrication of the aligned and patterned carbon nanotube field emitters using the anodic aluminum oxide nano-template on a Si wafer. Synth Met 2003;139(2):385–90.

[13] Yu GJ, Wang S, Gong JL, Zhu DZ, He SX, Li YL, et al. Synthesis of carbon nanotube arrays using ethanol in porous anodic aluminum oxide template. Chin Sci Bull 2005;50(11):1097–100.

[14] Lin C-T, Chen T-H, Chin T-S, Lee C-Y, Chiu H-T. Quasi two-dimensional carbon nanobelts synthesized using a template method. Carbon 2008;46(5):741–6.

[15] Wurtz A. Ueber eince neue Klasse organischer Radicale. Justus Liebigs Ann Chem 1855;96(3):364–75.

[16] Wang LS, Lee CY, Chiu HT. New nanotube synthesis strategy – application of sodium nanotubes formed inside anodic aluminum oxide as a reactive template. Chem Commun 2003;15(15):1964–5.

[17] Huang CH, Chang YH, Wang HW, Cheng S, Lee CY, Chiu HT. Formation of porous carbon materials with in situ generated NaF nanotemplate. J Phys Chem B 2006;110(24):11818–22.

[18] Kim TW, Park IS, Ryoo R. A synthetic route to ordered mesoporous carbon materials with graphitic pore walls. Angew Chem Int Ed 2003;42(36):4375–9.

[19] Zhi LJ, Wu JS, Li JX, Kolb U, Müllen K. Carbonization of disclike molecules in porous alumina membranes: toward carbon nanotubes with controlled graphene-layer orientation. Angew Chem Int Ed 2005;44(14):2120–3.

[20] Jian K, Yan A, Kulaots I, Crawford GP, Hurt RH. Reconstruction and hydrophobicity of nanocarbon surfaces composed solely of graphene edges. Carbon 2006;44(10):2102–6.

[21] Jian KQ, Hurt RH, Sheldon BW, Crawford GP. Visualization of liquid crystal director fields within carbon nanotube cavities. Appl Phys Lett 2006;88(16):163110.

[22] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. Phys Rev B 2000;61(20):14095–107.

[23] McCulloch DG, Prawer S, Hoffman A. Structural investigation of xenon-ion-beam-irradiated glassy carbon. Phys Rev B 1994;50(9):5905–17.

[24] McCulloch DG, Prawer S. The effect of annealing and implantation temperature on the structure of C ion-beam-irradiated glassy carbon. J Appl Phys 1995;78(5):3040–7.

[25] Nakazawa H, Mikami T, Enta Y, Suemitsu M, Mashita M. Structure chemical bonding and these thermal stabilities of diamond-like carbon (DLC) films by RF magnetron sputtering. Jpn J Appl Phys 2003;42(6B):676–9.

[26] Tamor MA, Vassell WC. Raman "fingerprinting" of amorphous carbon films. J Appl Phys 1994;76(6):3823–30.

[27] Wang Y, Serrano S, Santiago-Aviles JJ. Raman characterization of carbon nanofibers prepared using electrospinning. Synth Met 2003;138(3):423–7.

[28] Trouvat B, Bourrat X, Naslain R. Interest of adding a carbon interphase on mechanical properties of C/C microstructures. EuroCarbon 98 1998;2:651–2.

[29] Dwivedi H, Mathur RB, Dhami TL, Bahl OP, Monthioux M, Sharma SP. Evidence for the benefit of adding a carbon interphase in an all-carbon composite. Carbon 2006;44(4):699–709.