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Hundred-Nanometer-Size Crystalline Carbon Tubes from Poly(acrylonitrile) Pore-Filling Anodic Aluminum Oxide Templates via Solvent Annealing

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With a specific pore-filling process, a solvent-annealing process, graphite-like nanotubes can be fabricated from poly(acrylonitrile) (PAN) pore-filling anodic aluminum oxide templates. The molecular orientation of anisotropic PAN chains was induced by solvent annealing due to capillary filling so as to achieve appropriate molecular packing for carbonization. Consequently, hundred-nanometer-sized carbon nanotubes formed after carbonation, as demonstrated by field-emission scanning electron microscopy and transition electron microscopy observations. Importantly, the carbon nanotubes with a graphite-like structure and high crystallinity can be fabricated, as evidenced by selected area electron diffraction, high resolution transmission electron microscopy, and X-ray diffraction results. Notably, these carbon nanotubes cannot be fabricated using the conventional solution-wetting process. The formation of a core−shell cylinder texture was also demonstrated via multiple filling processes.

Introduction

Since Iijima first fabricated carbon nanotubes decades ago,[1] countless nanotube studies have been conducted.[2−4] The various mechanical, electrical, and thermal applications depend on the composition of carbon nanotubes. Notably, carbon nanotubes, which can be utilized as conductors or semiconductors, have extremely high thermal conductivity, and significant mechanical strength.[5−7] For such applications, carbon nanotubes must be templated, uniformly sized, and well aligned. Template techniques have been developed in response to these needs. One highly effective templation method is to use a porous template, such as anodic aluminum oxide (AAO), to synthesize uniformly sized and well-aligned carbon nanotubes.[8−11,35] Nevertheless, controlling the diameter of carbon nanotubes exceeding over hundred-nanometer-size remains challenging.

To obtain polymeric objects with hundred-nanometer size, one can wet porous templates with polymer solution or melt.[12,13] Russell et al. determined that nanotubes with regular voids were fabricated by annealing polymeric nanotubes. Via templation, a wide range of functional polymeric nanotubes, such as poly(tetrafluoroethylene), poly(ether ether ketone), or poly(methylmethacrylate) nanotubes,[14] were obtained for various applications. Russell et al. also developed an effective and convenient approach for fabricating templated carbon nanotubes.[15] They combined polymer solution wetting and poly(acrylonitrile) (PAN) carbonization techniques to generate carbon nanotubes. Notably, PAN is a well-known carbonization precursor. The carbonization procedure has been studied for several decades. One indispensable process for carbonization of PAN is stabilization, a process well-known in the field of carbon fibers, achieved through a specific thermal treatment. The stabilization process of PAN precursor fibers involves low-temperature heating (200−300 °C) under standard atmosphere to transform them into a structure that can be subjected to high-temperature carbonization treatment without melting or fusion of the fibers. The unsaturated side groups

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(nitrile groups) in the linear polymer of PAN undergo a polymerization reaction on heating, and then form a cyclized structure known as a ladder structure, and finally become a cross-linked network. The cyclized structure is stable toward heat, and can be converted to turbostatic carbon on subsequent carbonization at high temperatures (~1000−2000 °C) in inert atmosphere (i.e., in nitrogen atmosphere) or vacuum. Carbonization of PAN precursors can be achieved via stabilization (at 200−300 °C in the presence of air) and carbonization (at 800−1000 °C in an inert environment) in sequence.[16−21] Therefore, uniformly sized and well−aligned carbon nanotubes can be fabricated by pore-filling an AAO template followed by pyrolysis at 600 °C.

Pore-filling templates are typically performed by using such methods as polymer solution-wetting and melt-wetting process. The pore-filling process is achieved by wetting low-viscosity polymer fluids via capillary action. Therefore, during the solution-wetting process, viscosity can be altered by controlling the PAN solution concentration. The thickness of the polymer layer on the pore increases with the concentration of the polymer in the solution.[37] For the melt-wetting process, PAN must be heated to >300 °C to obtain a low viscosity suitable for the induction of wetting process. However, some side reactions occur at such a high temperature, even when the pore-filling process is seconds long. Furthermore, the degree of stretching and molecular orientation of PAN chains is crucial to the successful formation of carbon fibers. Significant PAN chain scission can occur because of the lack of chain orientation, such that randomly oriented PAN precursors are generally vaporized, causing structural defects after carbonization of non-stretching PAN chains (this is called the brittle failure mechanism).[17,22] Anisotropic chain orientation is required to improve the yield and mechanical properties of carbonized PAN. In the conventional carbonization procedure, anisotropic chain orientation is achieved by physical stretching. However, orienting the packing of PAN chains by directly stretching in a nanometer-scale environment is difficult. Thus, an alternative approach is needed. For example, in a self-assembled block copolymer system, chain orientation results from the balance of free energy associated with the interface between microdomains against the energy associated with the chain stretching away from the interface. Consequently, the anisotropic orientation of polymer chains in each block within microphase-separated microdomains should be formed from the interface because of the thermodynamic consideration of the immiscibility between constituted blocks.[23−25] When PAN pore-fills templates, the chain orientation of PAN molecules via capillary force-filling is a transient state. Thus, during the solution-wetting process, excess solvent can cause relaxation of oriented polymer chains, thereby releasing the induction of chain orientation and the polymer chains returning to the intrinsic state as randomly distributed molecular chains. The aim of this study is to fabricate carbon nanotubes with high crystallinity. By taking advantage of a novel pore-filling process, namely, solvent annealing for pore filling, anisotropic chain orientation can be retained by driving PAN chains into an AAO template with less solvent content than the solution-wetting process. Consequently, anisotropic PAN chains parallel to the inner walls of AAO pores can be fabricated by this pore-filling process, such that carbon nanotubes with a graphite-like structure and high crystallinity can be fabricated following carbonization.

Results and Discussion

Carbon Nanotubes Prepared Using the Solution-Wetting Process. The PAN precursor nanotubes were prepared by solution wetting into an AAO template with 1 or 10 wt % PAN solutions at room temperature. The pore-filled PAN precursors subsequently underwent carbonization via a two-step thermal treatment (a low temperature for stabilization and then a high temperature for carbonization). The stabilization process of PAN precursors was carried out at 230 °C under atmosphere (1 atm) for 20 h to transform the PAN precursors into a cyclized structure, known as a ladder structure, which can be subjected to high-temperature carbonization without melting or fusion. The unsaturated side groups (nitrile groups) in the linear PAN polymer undergo polymerization when heated, and then form a ladder structure, finally becoming a cross-linked network. The cyclized structure is stable when heated and can be converted into turbostatic carbon via subsequent carbonization at 800 °C in an inert atmosphere (i.e., nitrogen atmosphere) or vacuum. Figure 1 shows the transmission electron microscopy (TEM) images of the carbon nanotubes prepared by using the solution-wetting process at room temperature. As demonstrated, the carbon nanotubes prepared from 1 wt % PAN solution were templated by AAO (Figure 1a) such that they have a tubular structure and lots of voids. Similar textures with a preserved tubular structure and voids were observed in the templated carbon nanotubes prepared using 10 wt % PAN solution (Figure 1b). To analyze the molecular structure of these carbon nanotubes, a selected area electron diffraction (SAED) experiment was carried out (insets in Figure 1). A broad ring pattern, corresponding to a disordered carbon structure, was identified via SAED. This analytical result demonstrates that the carbon nanotubes prepared using the solution-wetting process at room temperature have randomly distributed PAN chains, resulting in a disordered carbon structure after high-temperature treatment.[18]

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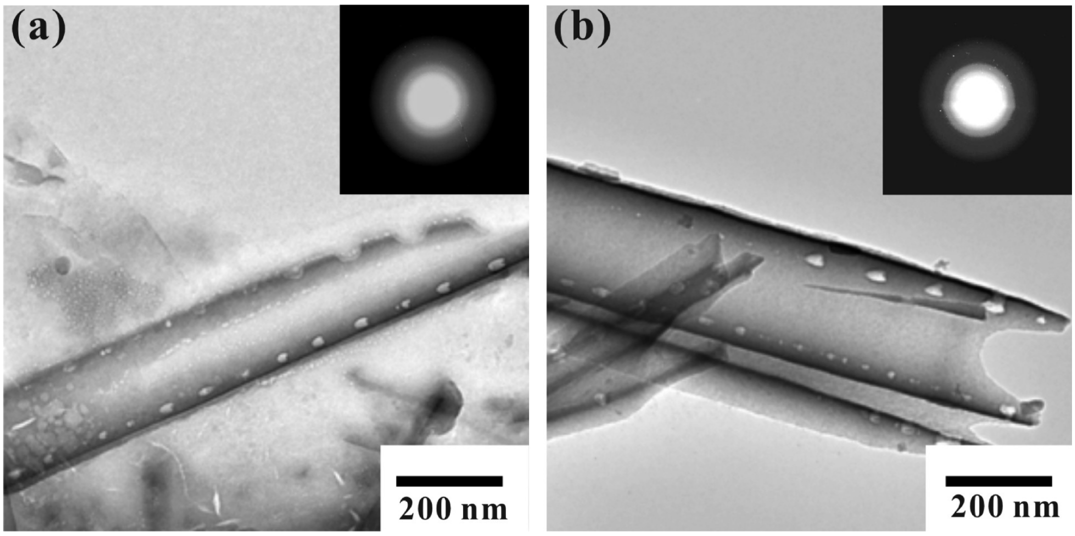


Figure 1. TEM images of the carbon nanotubes prepared by solution-wetting process with (a) 1 wt % and (b) 10 wt % solutions at room temperature. The insets show the corresponding SAED patterns.

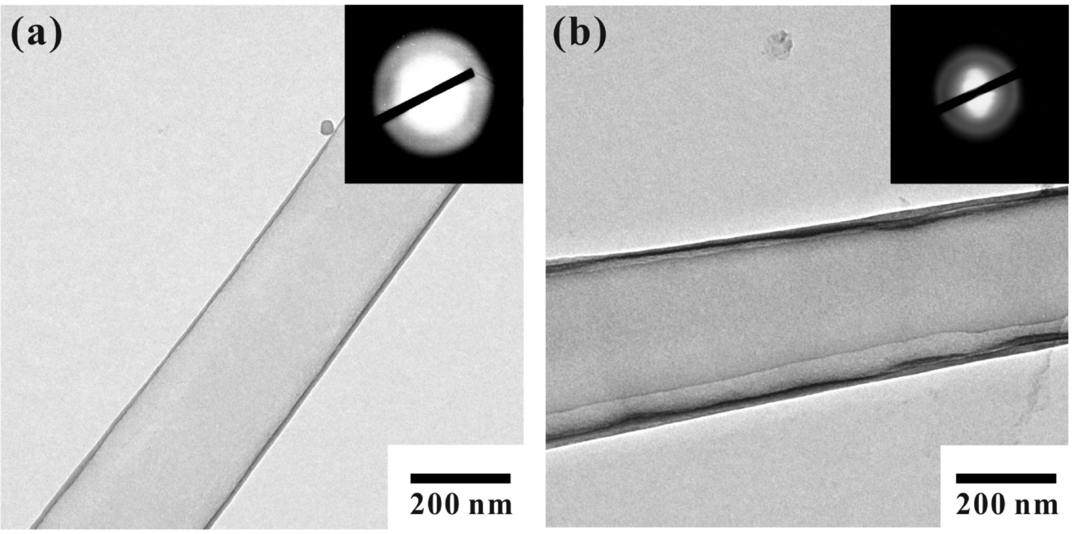
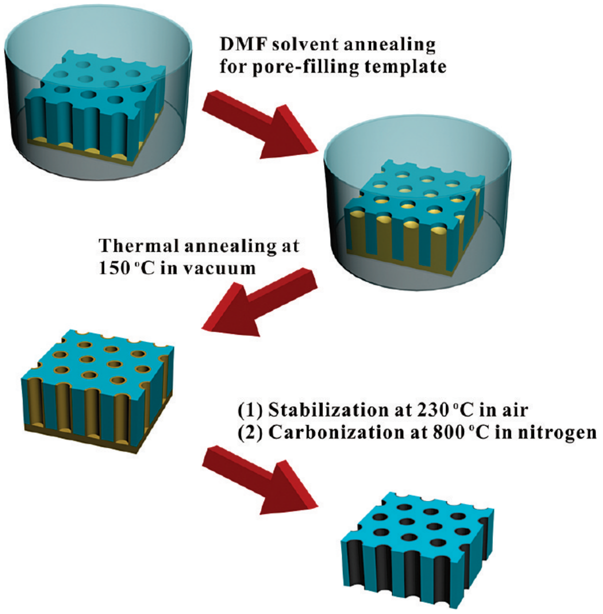


Figure 2. TEM images of the carbon nanotubes prepared by the solution-wetting process with (a) 1 wt % and (b) 10 wt % solutions at 130 °C. The insets show the corresponding ED patterns. The ED pattern of (b) appears as a similar pattern of carbon fiber structure.

Additionally, the formation of voids is attributed to the randomly distributed PAN chains that cause significant chain scission, such that PAN chains vaporize and become defects during high-temperature treatment. The voids of nanotubes can be generated during the treatments at high temperature, and the tubular structure may eventually be destroyed.

As mentioned, the induced orientation of PAN chains via capillary force filling is a transient state. We infer that significant chain relaxation may exist during solvent evaporation, resulting in randomly distributed PAN chains. As a result, the induced molecular chain orientation for carbonization cannot be achieved with templated PAN at various concentrations at room temperature. To maintain the orientation of PAN chains after solution wetting, solution wetting was carried out at a high temperature, 130 °C (DMF vapor pressure: 152 mmHg), to increase the solvent evaporation rate (namely, reduce the relaxation). The carbon nanotubes prepared by the solution-wetting process at 130 °C had a tubular structure templated by AAO (Figure 2). In contrast to the carbon nanotubes prepared by the solution-wetting process at room temperature, the carbon nanotubes prepared at 130 °C have no voids. Furthermore, SAED results (insets in Figure 2) indicate that the carbon nanotubes prepared by solution wetting with 10 wt % solution at 130 °C have an anisotropic molecular packing corresponding to regular carbon fiber packing. Conversely, the carbon nanotubes prepared by the solution-wetting process using 1 wt % solution at 130 °C have a broad ring pattern, similar to the SAED results of carbon nanotubes prepared by solution wetting at room temperature (insets in Figure 1). When the randomly oriented PAN chains were heated to a high temperature, such as 800 °C, the tubular structures hardly remained, and the PAN molecular structure was a disordered carbon structure after carbonization.[18] Conversely, the carbon nanotubes not only have tubular structures of the AAO template but also have a carbon fiber-like

Scheme 1. Experimental Route for the Formation of Graphite-Like Nanotubes Prepared from Carbonization of PAN in AAO Template via Solvent Annealing for Pore Filling



molecular packing for the carbonization of oriented PAN chains. Restated, the morphology and structure of the carbon nanotubes are affected by the solution-wetting condition. Although the PAN chains are simultaneously stretched and oriented by capillary force during the solution-wetting process, anisotropic chain packing can only be retained using a high-polymer-content solution at high temperatures. The chain orientation of PAN can be dynamically controlled; the critical issue is to inhibit the relaxation of oriented chains. Namely, a fast evaporation rate can efficiently reduce the needed evaporation time of the residual solvent, and reducing the solvent content also works. Clearly, the nanotubes prepared using the melt-wetting process have better molecular packing and a higher crystallinity than those prepared using the solution-wetting process, as this process does not require solvent evaporation.[26] Nevertheless, to reach the required low viscosity for driving the PAN into templates during melt wetting, a side reaction caused by high-temperature treatment exists.

To eliminate this side reaction, this study controls the polymer concentration and solvent evaporation rate using a novel process, a solvent-annealing process. When using this solvent-annealing process, the amount of solvent required driving PAN into the AAO template is low; moreover, vapor pressure can be altered by temperature. Consequently, PAN chains can be oriented using capillary force, and the resulting carbon nanotubes can have high crystallinity.

Carbon Nanotubes Prepared Using the Solvent-Annealing Process. The AAO template was placed on a solution-cast, dried PAN film in a closed system with dimethylformamide (DMF) solvent vapor (Scheme 1). The composite was introduced into a controlled chamber with saturated DMF vapor at different temperatures to control DMF vapor pressure. As the PAN films were solvent-annealed by DMF vapor, the PAN films can be filled into the AAO templates via capillary forces. After the removal of residual DMF solvent, PAN adhered to the inner walls of AAO pores. The pore-filled PAN precursors then underwent carbonization. After carbonization of PAN precursors, the AAO templates were dissolved in a dilute HCl or NaOH solution to obtain a pristine or carbonized template, and then rinsed several times with distilled water.

The pristine PAN nanotubes were obtained by dissolving AAO templates in dilute HCl(aq) solution; this did not affect the tubular structure of pristine PAN.[27] The resulting PAN nanotubes were observed by field-emission scanning electron microscopy (FESEM) (Figure 3). Because of the polydispersity AAO template pore size, PAN nanotubes with diameters of 150−400 nm were generated. To complete the carbonization process, pore-filling samples were treated by low-temperature stabilization and high-temperature carbonization as described, and then the AAO templates were removed by dissolving them in an NaOH solution, which has a faster etching rate than the HCl solution. The nanotubes were successfully carbonized, and the dimensions of the AAO template were preserved (Figures 3c and d).

To demonstrate the effect of the solvent-annealing process, the conventional approach, the solution-wetting process, was applied for comparison. The nanotubes were prepared using the solution-wetting process using 10 wt % DMF solution for pore-filling the AAO templates at room temperature. The PAN nanotubes were formed by both processes because of the templation of AAO (Figure 4). Nevertheless, the PAN nanotubes obtained by the solvent-annealing process have thicker walls (Figure 4b) than those prepared by the solution-wetting process (Figure 4a). We infer that templated thickness depends upon the solution concentration for pore filling. Consequently, the solvent-annealing process generates higher solid PAN content for pore filling than the solution-wetting process.[31] Following carbonization, the carbon nanotubes retain their tubular structure, but wall thickness decreases (Figures 1b and 4c). The reduction in wall thickness during carbonization is attributed to the removal of residual atoms, such as nitrogen, hydrogen, oxygen, and so forth, leading to the densification of molecular packing. As a result, the PAN volume should decline, and the packing of each carbon layer should gradually reduce.

As mentioned, the degree of PAN chain orientation is crucial to generate the carbonized PAN graphite-like structure with high crystallinity during carbonization. To examine the molecular packing of the carbonized nanotubes, a SAED experiment was conducted. The ED patterns of the nanotubes prepared by the solution-wetting process and treated at high temperature have broad ring

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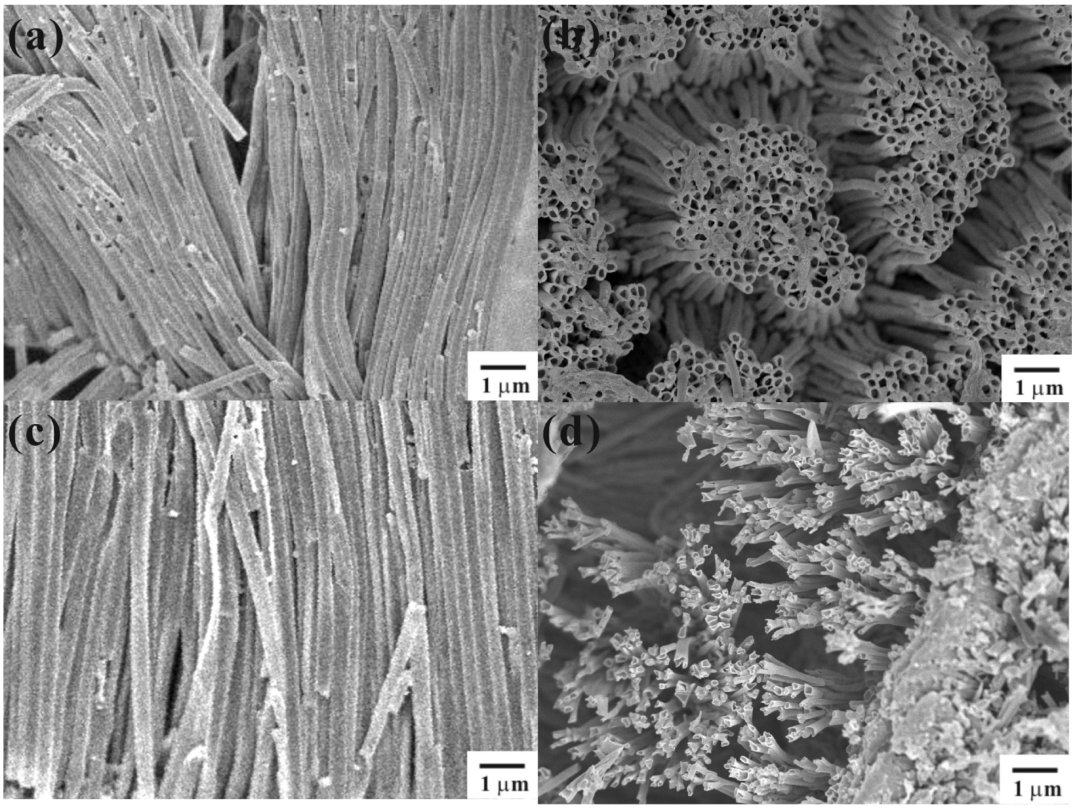

Figure 3. FESEM images of PAN nanotubes prepared by the solvent-annealing process at 130 °C: (a) side-view and (b) top-view images of the pristine PAN nanotubes; (c) side-view and (d) top-view images of the carbon nanotubes prepared from carbonization of PAN.

reflections that corresponds to the disordered carbon structure (insets in Figure 1). By contrast, the ED pattern of the carbon nanotubes prepared using the DMF solvent-annealing process (Figure 5b) have arc-like reflections at Bragg spacings of 0.35 and 0.21 nm. These spacings corresponds to the interplanar and intraplanar spacings of the hexagonal stacking of graphite layers, and are identified as spacings of (002) and (100) reflections for a graphitic carbon structure, respectively.[28,29] The arc reflections of (002) suggest that the packing direction of carbon sheets is parallel to the inner walls of AAO pores. Moreover, the (100) reflection should have an intense distribution on the axis normal to the reflections of (002). It is noteworthy that the normal of the planes of carbon sheets is parallel to the normal of the inner walls of AAO pores. Consequently, the non-uniform intensity distribution resulted from the contribution of the [100] direction rotating along the induced direction of capillary force. Restated, the intensity of reflections from the axis of rotational symmetry is weaker than that on the rotating axis. Thus, the intense reflection of 2-fold symmetry is diffuse, and the weak reflection of 4-fold symmetry merged with the reflection of 2-fold symmetry because of the slight mis-orientation of molecular packing resulting from carbonization. However, the TEM images and ED results are inadequate to demonstrate the formation of the multilayer structures and the high crystallinity of the carbon nanotubes. Therefore, high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) experiments were carried out to further confirm the existence of multilayer and crystalline structure in the carbon nanotubes prepared by the solvent-annealing process. The HRTEM image (Figure 6a) shows that the carbon nanotubes have multilayer structures, and the growth direction of layers aligns along the axis of AAO pores. The anisotropic packing results are consistent to the suggestion from SAED patterns (Figure 5b). The distance between two neighboring layers is 0.36 nm, corresponding to the interplanar spacing of graphite layers. The induced orientation is referred to the capillary force-driven behavior regardless of the confinement effect by considering the dimension of mesoscopic AAO as compared to the size of PAN chains. Shin and co-workers suggested that, as the polymers were induced into the nanopores (less than 15 nm in diameter) via thermal annealing process, the polymer chains can be disentangled but not stretched in the direction of flow. As described, the polymer chains are compressed in a direction orthogonal to the flow because of confinement.[38] Note that the radius gyration of a polymer chain is equivalent to the size of nanopores. Accordingly, the confinement effect is of thermodynamic origin because of the geometric constraints. It is very different to our experimental results at which anisotropic orientation of polymer chains can be found after solvent annealing as evidenced by SAED. The anisotropic results are

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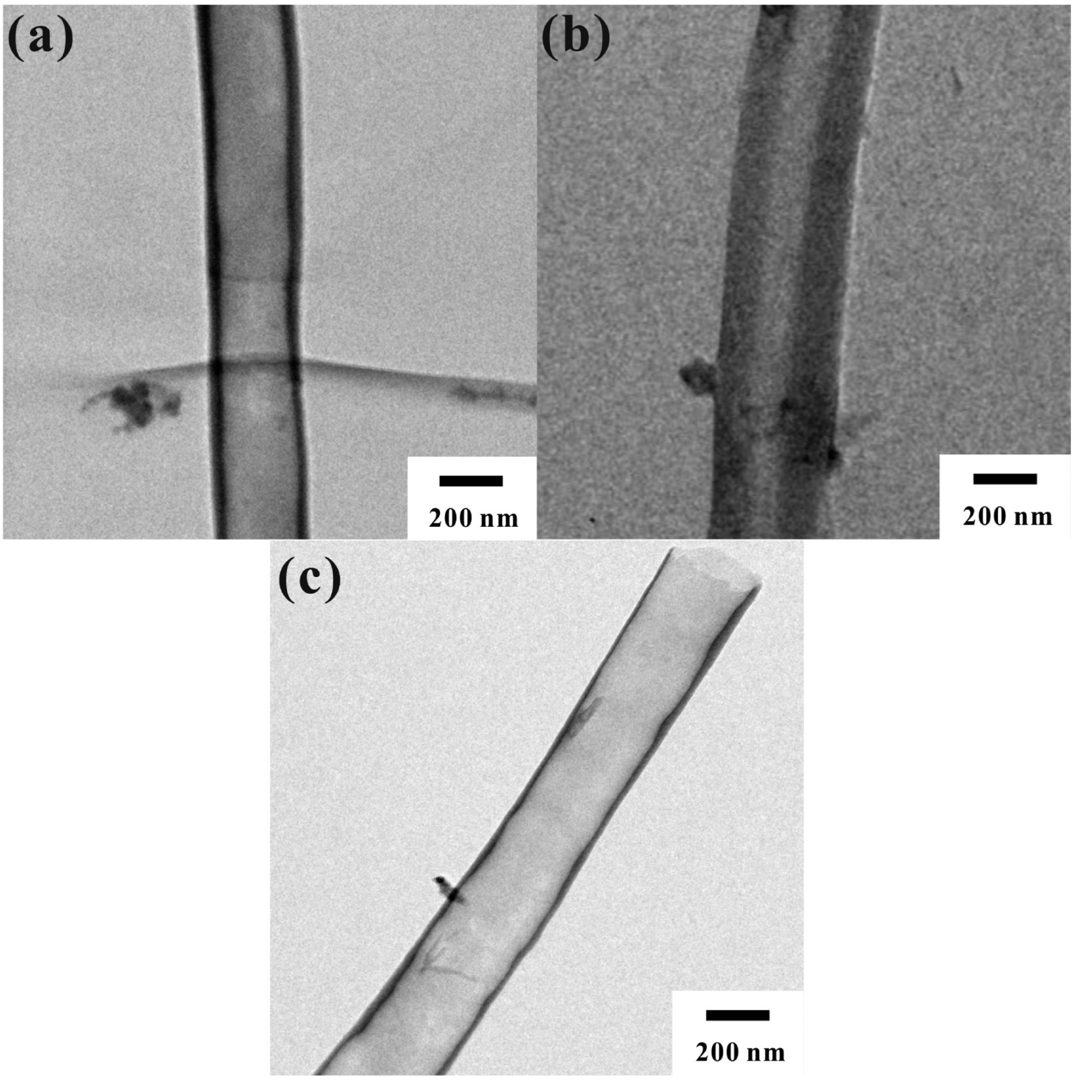

Figure 4. TEM images of the pristine PAN nanotubes prepared by (a) solution-wetting process with 10 wt % solution at room temperature and (b) solvent-annealing process at 130 °C; (c) the carbon nanotube prepared by solvent-annealing process at 130 °C after carbonization.

dependent upon the competition between capillary force-induced orientation and polymer chain relaxation resulting from solvent residue. The solvent-annealing process dependent upon the control of solvent evaporation rate is of a kinetic origin; unlike the confinement effect, the viscosity of the pore-filled system examined here is critical for the evolution of final morphologies.

To further confirm the structure of CNTs, we collected the powder of CNTs and performed an XRD experiment. The XRD profile (Figure 6b) shows the reflections are located at $2\theta = 26.1°$ and 41.9°, corresponding to (002) and (100) planes of carbonized PAN having Bragg spacings of 0.34 and 0.22 nm, respectively.[30] The reflections are identical with the SAED results and indicate the formation of high crystallinity of the carbon nanotubes. Moreover, the characteristic reflection of pristine PAN precursor (i.e., at $2\theta = 16.7°$) was absent because of the achievement of carbonization. These results indicate that the carbon nanotubes prepared by the solvent-annealing process have a crystalline and graphite-like structure, in which the planes of carbon sheets are parallel to the inner walls of AAO pores and the rotating axis of the carbon sheet is parallel to the central axis of AAO pores because of the specific PAN chain orientation driven by the capillary-filling process.

Mechanism of Chain Orientation Induced by Solvent Annealing. In contrast to nanotubes prepared by the solution-wetting process, the anisotropic chain orientation of PAN can be induced by the solvent-annealing process as it uses less solvent than in the solution-wetting process. The mechanism of induced chain orientation for nanotubes prepared by solvent annealing was examined by controlling the experimental temperature, namely, DMF vapor pressure. The pristine nanotubes prepared by solvent annealing at room temperature have a tubular structure templated from the AAO templates (Figure 7a). Additionally, in contrast to the pristine nanotubes prepared at high temperatures (Figure 4b), the walls of nanotubes prepared at low temperatures are thick. Since solvent vapor pressure and solubility are strongly dependent upon experimental temperature, the polymer

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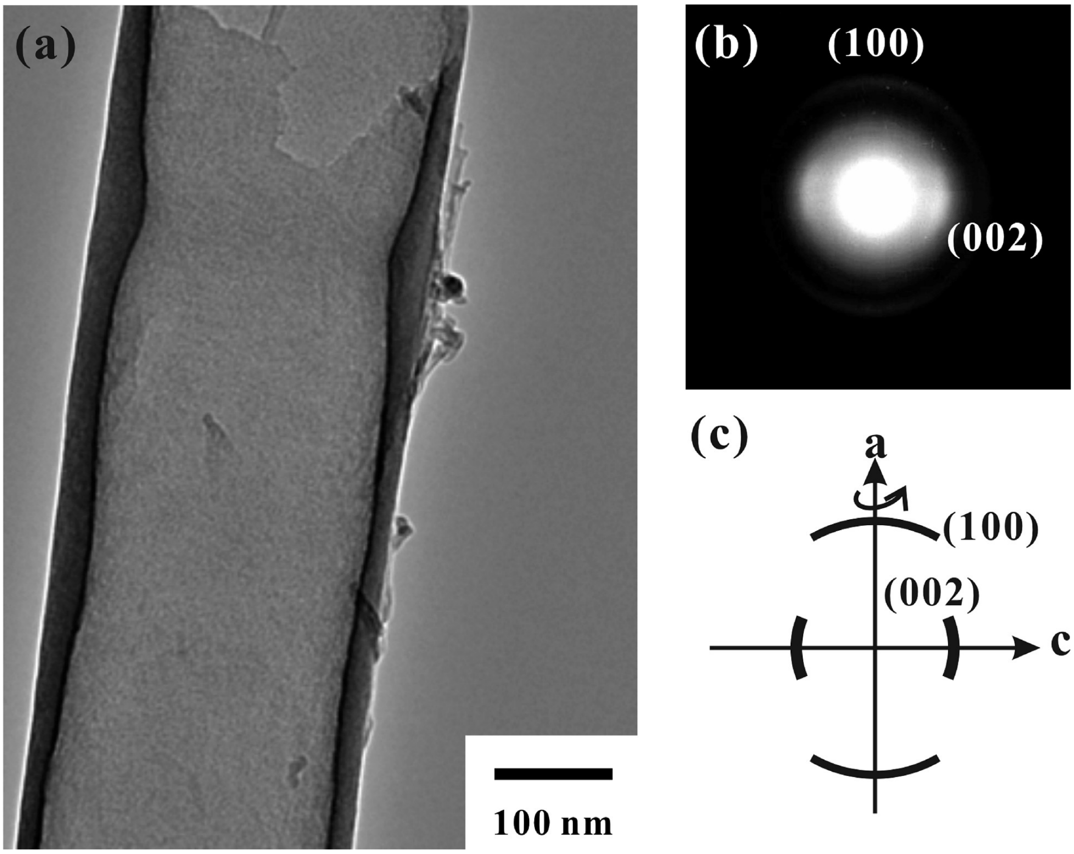

Figure 5. (a) TEM image and (b) corresponding ED pattern of the graphite-like nanotube prepared using the solvent-annealing process. (c) Illustration of the corresponding ED patterns of the graphite-like nanotubes. The ED pattern appears a similar pattern to that of graphite structure.

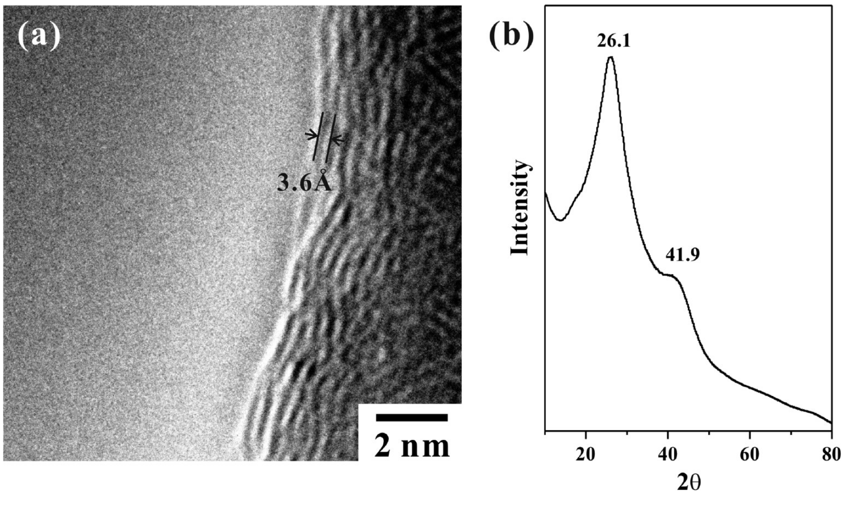

Figure 6. (a) HRTEM image and (b) XRD profile of the graphite-like nanotube prepared using the solvent-annealing process.

content of nanotubes prepared by solvent annealing at room temperature is higher than that of nanotubes prepared by solvent annealing at high temperatures. Therefore, the thick-wall structure of pristine nanotubes is attributed to the high solvent content and the prolonged evaporation time. In addition, the inner walls of nanotubes have a specific undulated morphology. This morphology is driven by Rayleigh instability and similar to that of nanotubes thermally annealed for a prolonged time.[31,36] Since this undulated morphology is found in nanotubes prepared by the solvent-annealing process at room temperature, this undulated morphology does not exist for prolonged thermal annealing. In Rayleigh instability, the fluid breaks into smaller packets with the same volume but less surface area to compensate for excess surface free energy. When the polymer is moistened by solvent vapor to achieve a higher chain mobility than thermal annealing can provide, undulation develops from the polymer surface and is driven by the reduction in surface area or total surface energy. Nevertheless, the final stage, the hole-containing morphology reported by Russell et al., was not observed.[31] We speculate that the

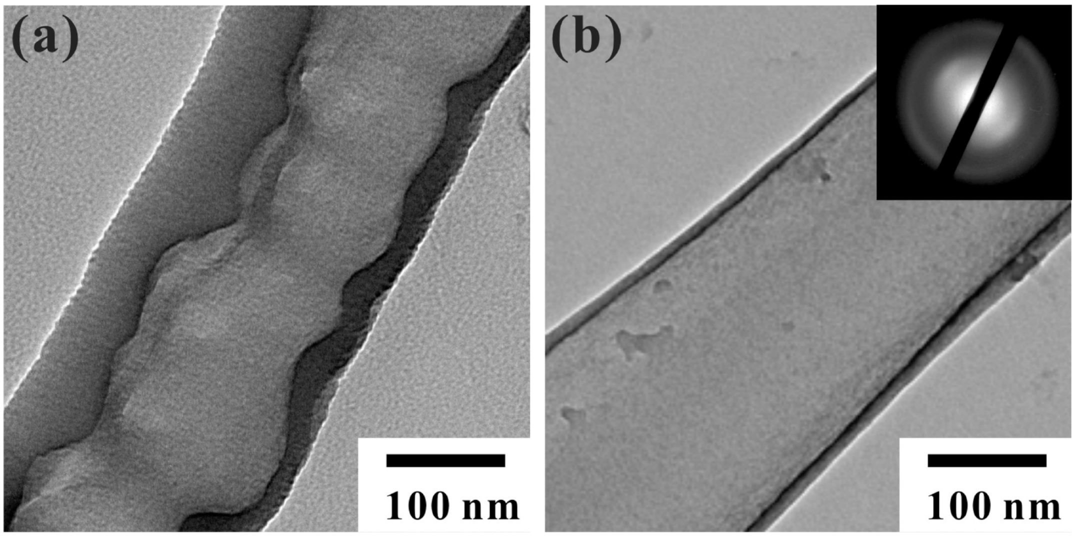

Figure 7. TEM images of (a) the pristine and (b) the carbonized PAN nanotube prepared using the solvent-annealing process at room temperature. The inset of (b) shows the corresponding ED pattern. The ED pattern has a similar pattern to that of graphite structure.

hole-containing morphology may occur after solvent annealing at a lower temperature for a long time. Figure 7b shows the TEM image and corresponding SAED pattern of the carbon nanotubes following carbonization. The tubular structure of carbon nanotubes was observed, and the graphite-like structure was identified by the SAED result. However, the reduction in wall thickness of nanotubes prepared by the solvent-annealing process at room temperature is greater than that at high temperatures. This reduction resulted from densification of molecular packing during carbonization. Since the solvent evaporation rate is slower at room temperature than at high temperatures, the capillary force-induced chain orientation is likely disturbed. Namely, the nanotubes prepared by the solvent-annealing process at room temperature have disoriented polymer chains causing disoriented molecular packing. The disoriented molecular packing layers generate an undulated morphology. We speculate that as solvent-annealing time increases, the undulated morphology would move closer to the inner walls of the AAO pores because of Rayleigh instability. During the final stage of Rayleigh instability, the hole-containing tubular structures may have an entirely disordered carbon structure. This disordered carbon structure would be vaporized during the carbonization process. Nevertheless, oriented molecules induced by capillary force near the inner walls of AAO pores may remain. The carbon nanotubes after the carbonization process exhibit graphite-like structures, as demonstrated by SAED results. As a result, carbon nanotubes with a crystalline and graphite-like structure can be generated using the solvent-annealing process. Furthermore, the morphology of carbon nanotubes can be controlled by varying the solvent-annealing process conditions.

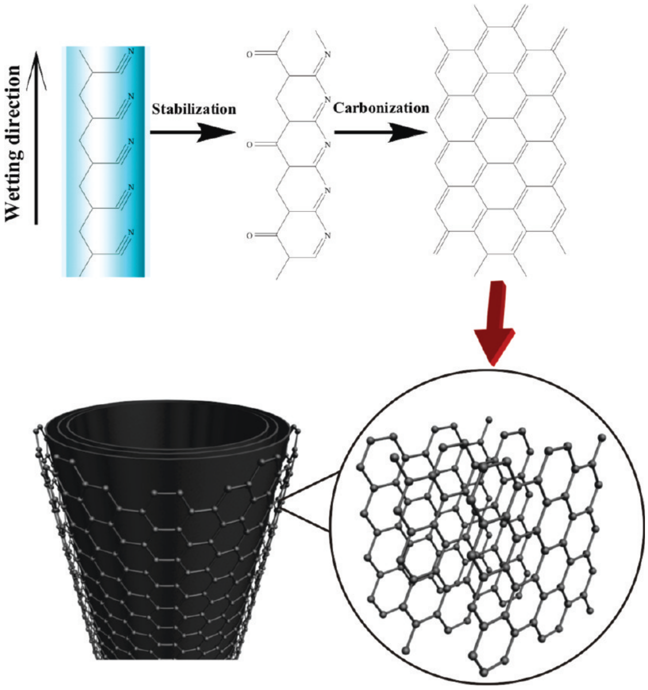

Figure 8. Illustration of the anisotropic chain orientation of molecular packing in a graphite-like nanotube prepared from PAN pore-filling AAO template via solvent-annealing process.

Herein we propose a mechanism for the formation of graphite-like nanotubes prepared by templation (Figure 8). As PAN chains are solvent annealed by DMF vapor, the chain mobility is enhanced by introducing solvent vapor molecules into the PAN matrix and PAN chains are gradually pore-filled the AAO templates via capillary force. The polymer chains moistened by solvent are directionally driven into the pores of the AAO template, and polymer chains are stretched by capillary force.[32,33] Therefore, all carbon nanotubes prepared by capillary filling should have an anisotropic molecular packing structure and high crystallinity induced by capillary force. However, this speculation does not apply to morphological

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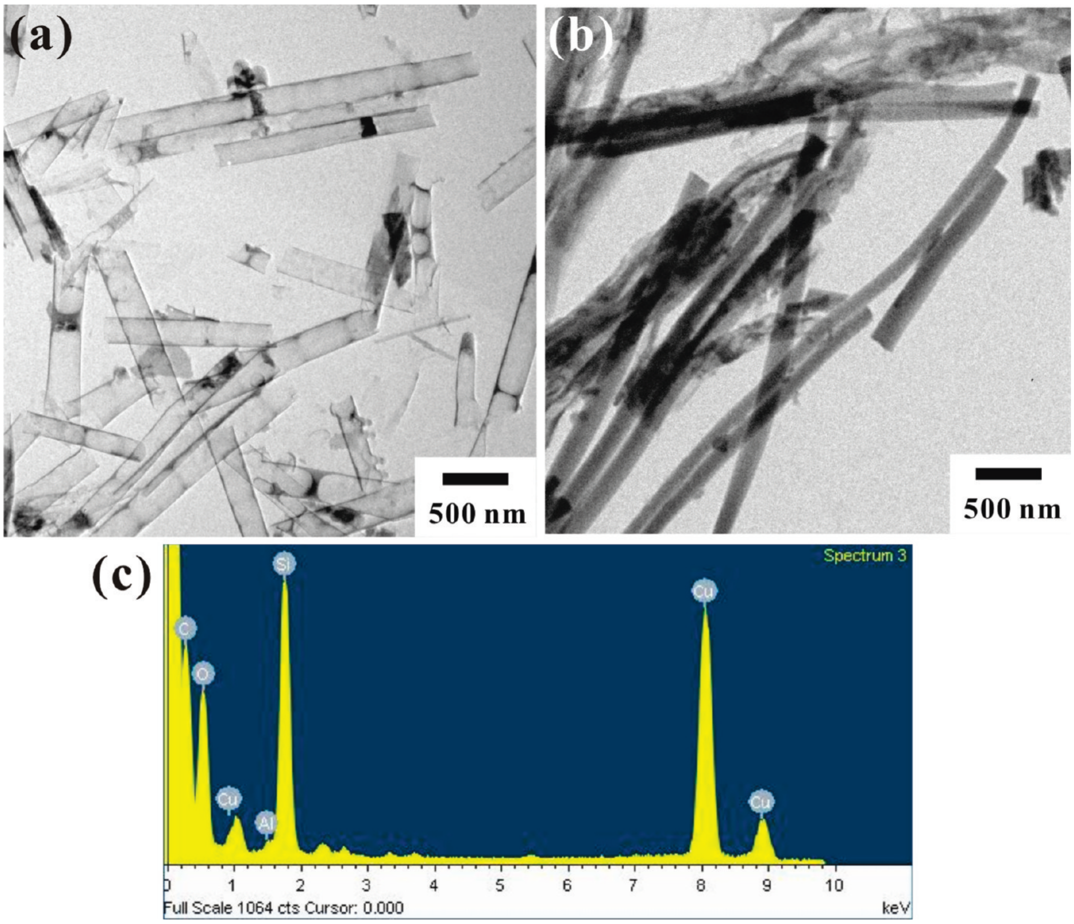

Figure 9. TEM images of (a) the tubular structure of stabilized PAN nanotube prepared by solvent annealing at 130 °C; (b) the rod structure of SiO_2 sol−gel filled core−shell cylinder. (c) EDX results of the SiO_2/carbon core−shell cylinders.

development after releasing solvent molecules. In early stage of the capillary force-filling process, polymer chains are introduced into the AAO template and appear as oriented chains as a result of the capillary force direction. Subsequent solvent evaporation and elastic recovery of oriented chains, namely, the relaxation of oriented chains, may occur simultaneously. The slow solvent evaporation or high solvent fraction would reduce the aligned conformation and eventually transform the aligned chains into a random coil-like conformation. During the solution-wetting process, the amount of solvent is much higher than that in the solvent-annealing process. As a result, the capillary force-induced orientation of chain packing cannot be preserved during the solution-wetting process. However, the chain orientation in the solvent-annealing process can be preserved after evaporation, transforming the PAN molecules into the graphite-like structure after carbonization. Notably, the graphite-like structure was not observed during solution wetting at room temperature. Consequently, a novel approach to fabricate hundred-nanometer-size carbon nanotubes with regular arrays and graphite-like structures was applied.

SiO_2/Carbon Nanotubes Core−shell Cylinder Structure. By taking advantage of the hundred-nanometer-size tubular structures combined with template wetting and sol−gel chemistry, SiO_2/carbon nanocomposites can be prepared by the tetraethoxysilane (TEOS)/HCl sol−gel synthesis. To increase PAN resistance to HCl, the PAN nanotubes prepared by the solvent-annealing process were stabilized, and then utilized as templates for TEOS/HCl solution wetting, followed by the sol−gel reaction process. The tubular structure of the stabilized nanotubes and rod-like structure of the SiO_2/carbon core−shell cylinder were clearly identified by TEM (Figures 9a and b). To further examine the SiO_2/carbon core−shell cylinder, energy dispersive X-ray spectroscopy (EDX) analyses were performed on individual nanotubes. From the EDX spectrum (Figure 9c), and ignoring the trace amount of residual alumina from the AAO template and copper from the copper grid, the nanotubes are mainly composed of C and Si from carbon nanotubes and SiO_2, respectively, indicating successful preparation of SiO_2/carbon core−shell cylinders.[34]

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Conclusions

The hundred-nanometer-size carbon nanotubes with high crystallinity were obtained via the combination of a novel wetting process, the solvent-annealing process, for pore-filling templates, and the well-known carbonization process. The nanotubes prepared from the conventional solution-wetting process had an amorphous carbon structure after carbonization. Conversely, the carbon nanotubes prepared using the solvent-annealing process had the graphite-like tubular structures, as demonstrated by TEM and SAED results. During the carbonization process, the chain orientation of PAN markedly affected the properties and yields of carbonized nanotubes. The decline in yield was due to vaporization resulting from the random-coiled conformations of PAN during carbonization. Achieving anisotropic chain orientation of PAN is crucial to overcome this problem. In a macro-scale environment, anisotropic chain orientation can be attributed to polymer chain stretching by applying a simple force. In a microscale environment, polymer chain stretching must be accomplished by specific approaches, such as stretching induced by the incompatibility between two immiscible blocks in a block copolymer system or the capillary force-induced chain orientation, as described herein. When the PAN chains were driven into the template by capillary force, anisotropic conformation aligned with the pore direction of AAO. The PAN nanotubes then turned into carbon nanotubes with high crystallinity following carbonization. However, the capillary-filling action is a kinetic behavior, and the capillary force-induced chain orientation is transient. The residual solvent provides the polymer chain with mobility, and the anisotropic chain orientation is reduced. Thus, the nanotubes prepared using the solvent-annealing process can retain their anisotropic conformation, in contrast to nanotubes prepared using the solution-wetting process. Because of their tubular structure and high crystallinity, these carbon nanotubes have potential for applications on the conductors or the field-emission devices. Moreover, the tubular structures can be filled with functional materials, such as SiO_2 or metal nanoparticles, to prepare a growth ring-like core−shell cylinder structure by controlling the pore-filling conditions for various nanotechnology applications.

Experimental Section

Materials. The PAN homopolymer was obtained from Material and Chemical Research Laboratories, Industrial Technology Research Institute, Taiwan. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 1140 and 1330 kg/mol, respectively. The AAO templates were purchased from Whatman Ltd.; the template with thickness was roughly 60 μm and pore diameter was 150−400 nm.

Carbon Nanotubes Preparations. Nanotubes for the solution-wetting process were prepared at two concentrations, 1 and 10 wt % PAN in DMF solvent. The solutions were preheated at various temperatures, room temperature and 130 °C, and dropped onto a glass slide. The AAO membranes were immediately placed onto the drop at each experimental temperature. After the solution evaporated, the PAN solution-wetted AAO templates were annealed at 150 °C overnight. As shown in Scheme 1, to prepare the solvent-annealed nanotubes, PAN films were first prepared by solution casting onto glass glides. The AAO templates were then placed onto PAN films under a closed system with saturated DMF vapor at room temperature or 130 °C for 12 h. Subsequently, the PAN/AAO composites were dried at 150 °C in vacuum for 12 h. The carbonization process was simplified as a two-step process comprising stabilization and carbonization. Stabilization was conducted under atmosphere at 230 °C for 20 h. To complete carbonization, stabilized samples were heated to 800 °C with 10 °C/min heating rate under nitrogen. To remove the AAO templates, the pristine PAN/AAO and carbonized PAN/AAO composites were immersed in 0.1 M HCl(aq) for 4 h and 5 wt % NaOH(aq) for 2 h, respectively. The nanotubes were then washed several times with deionized water for the following characterizations.

SiO_2/Carbon Composites. Before sol−gel solution wetting, the PAN polymer thin layers remaining on the top and bottom surface of AAO templates were carefully removed using a razor blade. A silica precursor mixture was introduced into the stabilized PAN/AAO composites by immersing the templates in TEOS/HCl(aq.)-(0.1M) mixture (weight fraction of TEOS/HCl(aq.)(0.1M) = 10/1) at room temperature for 24 h, and then treated under controlled humidity at room temperature for 48 h. After drying, the SiO_2/stabilized PAN/AAO nanocomposite samples were prepared. However, the SiO_2 from the sol−gel process without calcination is amorphous. To complete the carbonization and get crystalline SiO_2, calcinations of the nanocomposites at high temperature (more than 800 °C) are necessary. Consequently, the amorphous SiO_2 was transformed to crystalline SiO_2. To remove the AAO template, this composite was immersed into 5 wt % NaOH(aq) for 2 h. The nanocomposites were then washed several times with deionized water.

Structure Analysis and Characterizations. The FESEM experiments were performed on a JEOL JSM-7401F using an accelerating voltage of 5 keV. Bright-field and high resolution TEM was conducted with the JEOL JEM-2100(HT) operating at an accelerating voltage of 200 keV. The EDX data were obtained on an attached Oxford INCA ED spectrometer. For TEM observations, samples were sonicated in ethanol/deionized water (1/1) solution for 2 h and placed onto carbon-coated grids. Bright-field TEM images were directly obtained using the mass−thickness contrast. The SAED experiments for thin films were also conducted. ED spacing was calibrated using TlCl in a *d*-spacing < 0.384 nm, that is, the largest spacing for TlCl. Spacing values exceeding 0.384 nm were calibrated by doubling the *d*-spacing of those diffractions based on their first-order diffractions. The XRD experiment was recorded on an X-ray diffractometer with Siemens D5000 1.2 kW tube generator (Cu Kα radiation) for XRD powder experiments. The scanning 2θ angle ranged between 5° and 80° with a step scanning of 0.05° for 3 s. The diffraction peak positions and widths observed from XRD experiments were carefully calibrated with silicon crystals with known crystal size.

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