Research Article

Fabrication of Vertically Aligned CNT Composite for Membrane Applications Using Chemical Vapor Deposition through *In Situ* Polymerization

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We report the fabrication of vertically aligned carbon nanotubes (CNT) composite using thermal chemical vapor deposition (CVD). A forest of vertically aligned CNTs was grown using catalytic CVD. Fluorocarbon polymer, films were deposited in the spaces between vertically aligned MWCNTs using thermal CVD apparatus developed in-house. The excessive polymer top layer was etched by exposing the sample to water plasma. Infrared spectroscopy confirmed the attachment of functional groups to CNTs. Alignment of CNTs, deposition of polymer and postetched specimens were analyzed by field emission scanning electron microscope (FE-SEM). Uniform distribution of monomodel vertically aligned CNTs embedded in the deposited polymer matrix was observed in the micrograph. Observed uniform distribution otherwise is not possible using conventional techniques such as spin coating.

1. Introduction

The unique physical properties (electrical, thermal, mechanical, and magnetic) of carbon nanotubes (CNTs) and their high aspect ratio make them attractive candidates for the fabrication of the nanostructures. Anisotropic properties of CNTs require their alignment or patterning in a manner that these properties can be efficiently exploited for a variety of applications like nanoelectromechanical systems (NEMS), microelectromechanical systems (MEMS), and CNT-membranes [1–3].

Various methods using electrophoresis deposition (EPD) [4] and magnetic [5] as well as electric fields [6, 7] have been successfully employed for aligning and patterning of the CNTs. Besides the fabrication of CNT membranes, the aligned CNTs are required to fabricate nanostructures like electron field emitters. But for fabrication of isoporous CNT membranes a perfect vertical alignment of CNTs is key requirement. Thus, a forest of vertically aligned CNTs grown by catalytic CVD was used for desired composite fabrication.

For fabricating the isoporous CNT membrane, a polymer is deposited in the spaces between the vertically aligned CNTs. These membranes have the potential to separate the challenging liquid-liquid and gaseous mixtures [8]. A main challenge for the fabrication of these nanomembranes is the efficient deposition of polymer in the spaces between vertically aligned CNTs. Conformal, pinholes-free and uniform polymer films are required for an efficient and durable sealing of spaces between aligned CNTs. To date spin coating is among the most common techniques used to deposit polymer for fabrication of isoporous CNT membrane. However, major drawbacks of spin coating are that (1) drying of solvent

causes porosity in the deposited films and (2) nonuniform wetting and surface tension effects result in poor quality of the deposited film on nonplaner surfaces. Vapor phase polymer deposition methods like plasma enhanced CVD and thermal CVD have potential to address these problems. To deposit good quality polymer films with minimum bond defects, thermal CVD is usually preferred [9].

The present study describes the fabrication of isoporous CNT composite for membrane application by depositing the polymer in the spaces between vertically aligned CNTs using CVD.

2. Experimental Section

2.1. Materials. Hexaflouropropylene oxide (C_3F_6O) and methyl viologen dichloride hydrate (98%) were supplied by Sigma-Aldrich Chemicals (UK). Multiwalled carbon nanotubes (MWCNTs) forest was grown at University of Surrey, UK.

2.2. Growth of Vertically Aligned MWNTs. Vertically aligned multiwalled carbon nanotubes of 1 micron length with an inner diameter of nearly 9.5 nm were grown using temperature catalytic CVD. A nickel layer of 5 nm was sputtered on n-type silicon substrate. This nickel layer was then plasma-activated to form nickel catalyst particles. Catalytic CVD reactor was evacuated to 10^{-6} Torr and heated to 1023 K. Ammonia at a rate of 100 standard cubic centimeters per minute (sccm) was purged in CVD system. Subsequently, acetylene gas at a rate of 25 sccm is introduced to the reactor for a duration of 10 minutes. The grown and vertically aligned CNTs forest was finally subjected to fluorocarbon polymer deposition by TCVD method.

2.3. Thermal Chemical Vapor Deposition (TCVD). A forest of 1 micron long MWCNTs was subjected to fluorocarbon polymer deposition by TCVD. Deposition of fluorocarbon polymer by TCVD involves (i) decomposition of the precursor gas by heating. (ii) transport of the decomposition species towards substrate held at room temperature (iii) initiation of polymerization of the decomposed species.

Thermal CVD apparatus was developed in-house using quartz tubular reactor equipped with nichrome coil as a heating source according to the scheme given in Figure 1.

Precursor gas was introduced through a nozzle at one end of the reactor while silicon substrate was placed at the opposite end. Flow rate of precursor was measured and controlled by a mass flow controller. Temperature of the substrate having aligned CNTs was maintained at 298 K by back face water cooling.

Hexaflouropropylene oxide (C_3F_6O) was used as a precursor to deposit the fluorocarbon polymer films. TCVD system equipped with nichrome coil was first evacuated, and then dry nitrogen was purged thoroughly into the reactor to make it oxygen free. Forest of aligned carbon nanotubes grown by CVD was placed in the TCVD system and kept at ambient temperature.

Nichrome coil was heated to 723 K. C_3F_6O gas was purged into TCVD reactor from inlet port in such a manner that the whole gas had a contact with the coil. The precursor gas flow was maintained at a rate of 15 standard cubic centimeters per minute (sccm). The pressure of TCVD reactor was maintained at 100 mTorr. After a process time of 40 min, carbon nanotubes were completely masked by a white layer of polymer. Thereafter, precursor gas flow was cutoff and heating terminated. Reactor was again evacuated, and the nitrogen was purged until the system approached near to atmospheric pressure [9].

2.4. Etching. Silicon substrate was etched by dipping the sample in 20% KOH solution for 2 h at 80°C. The excessive polymer was etched by exposing the sample to water plasma under a vapor pressure of 0.3–0.5 Torr for 80 min. The power needed for the plasma was supplied by a radio frequency at 250 kHz.

3. Characterization

Alignment of functionalized SWCNTs was analyzed by Field-Emission Scanning Electron Microscope (FE-SEM) Quanta-200. FTIR was used to analyze the functional groups at the surface of SWCNTs. The FTIR spectrum was taken using Perkin Elmer Spectru-100 series instrument.

4. Results and Discussion

4.1. SEM Image of Grown Vertically Aligned MWCNTs. Figures 2(a) and 2(b) show the cross-sectional and top view SEM micrographs of vertically aligned MWCNTs grown by catalytic CVD. A forest of vertically aligned CNTs is visible.

4.2. FTIR Analysis of PTFE Deposited CNTs. Fourier transform infrared spectroscopy (FTIR) confirms that deposited PTFE is identical to bulk PTFE (Figure 3). The spectrum of the grown carbon nanotube forest indicates no distinctive FTIR peaks. The spectrum of the PTFE-coated forest in contrast shows strong absorptions of the symmetric and asymmetric CF2 stretches in the 1149–1250 cm^{-1} region, characteristic of bulk PTFE. Other methods like PECVD or laser ablation may also be used for thin fluorocarbon coatings that can cover the entire length of the nanotubes, but these coatings, unlike TCVD, suffer from the poor compositional resemblance to bulk PTFE.

The polymerization mechanism for the said process is given by Limb et al. [9]. The decomposition mechanism proposed by these authors is given below in the following:

$$C_3F_6O \longrightarrow CF_3-CF=O + CF_2 \qquad (1)$$
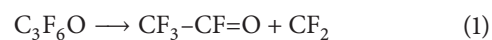
CF_2 is highly reactive; it polymerizes readily and also bonds chemically to CNTs [11, 12]. As oxygen is tied up in relatively stable fluorinated ketone ($CF_3-CF=O$) decomposition product, little oxygen is incorporated in the deposited films, which results in a good quality of the fabricated films.
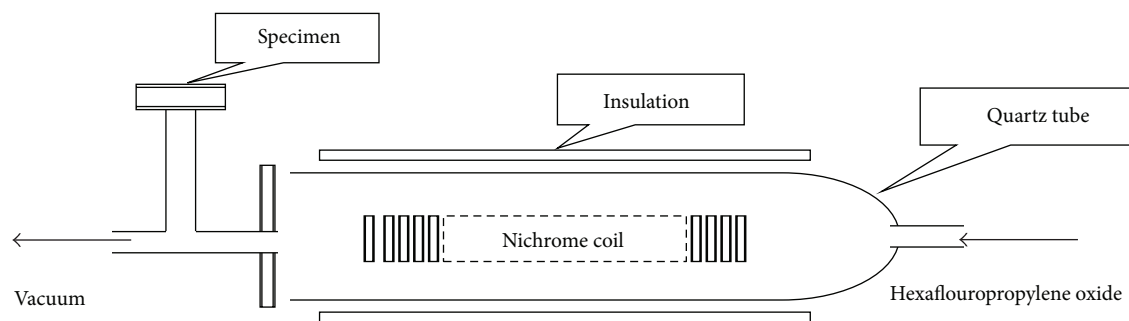
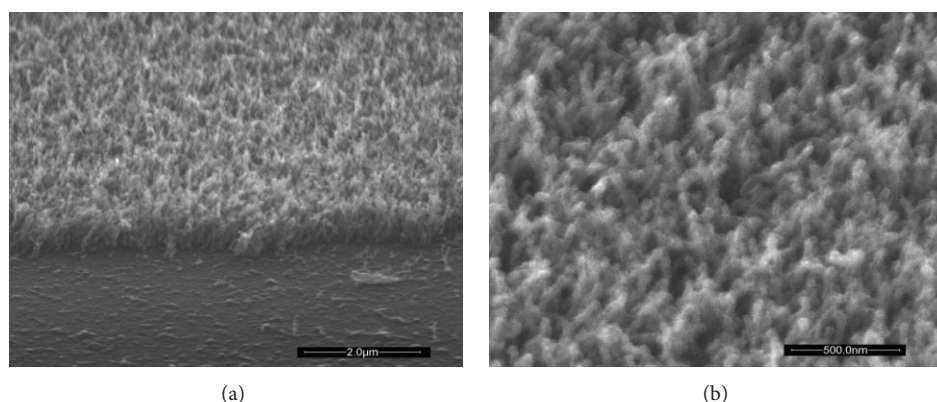FIGURE 1: Schematic of CVD apparatus developed in-house.

(a)

(b)

FIGURE 2: (a) Cross-sectional SEM image of vertically grown MWCNTs. (b) Top view of grown vertically aligned MWCNTs.
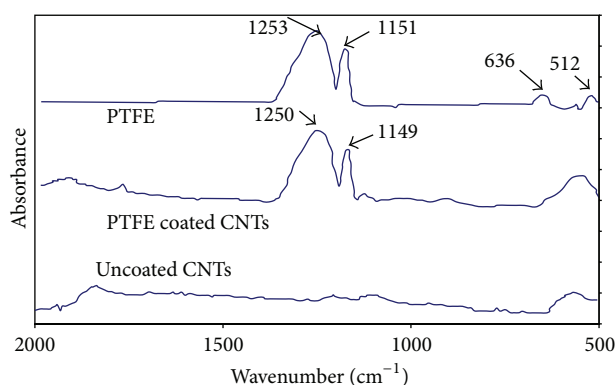

FIGURE 3: FTIR spectrum of (i) PTFE and (ii) PTFE coated CNTs.

4.3. Morphology of Deposited Polymer by SEM. Figures 4(a) and 4(b) show the SEM images of the deposited fluorocarbon polymer films.

After 15 min of the deposition process, the black colour of sample turned to whitish. Gaps between vertically aligned MWCNT were observed after 15 min of deposition. MWCNTs are also still visible, but their blackish surface turned whitish (Figure 4(a)), confirming the deposition of polymer. It is also evident from Figure 4(a) that the polymer is deposited on the surface of the walls of MWCNTs without affecting the alignment. After 40 min of deposition, 1 micron long carbon nanotubes completely disappeared. Figure 4(b) shows the cross-sectional view of a sample after the deposition. It confirms the deposition of polymer in the spaces between MWCNTs without affecting their alignment.

4.4. Morphology of Etched Membrane. Figure 5 shows the SEM image of the top surface of membrane after water plasma etching. Uniformly distributed pores of about 40 nm diameters were visible after 80 min water plasma etching indicating the removal of excessive polymer and the caps of MWCNTs. The plasma leads to a high concentration of atomic oxygen. The atomic oxygen can oxidize top-end of fabricated specimen in a controlled fashion. As a result, caps at top-end of nanotubes were removed, and opened top-end CNTs were obtained. No defect is visible between the spaces of MWCNTs ensuring the uniform and efficient deposition of PTFE.

Although the thrust of the paper resides in fabrication of a composite membrane by embedding vertically aligned CNTs in a polymer using in situ polymerization, however, preliminary evaluation reveals some characteristics related to diffusion parameters of the fabricated membrane as reflected in Table 1. The probe molecules of methyl viologen dichloride hydrate $[MV^{+2}]$ are used for diffusion experiments. Results confirm the efficient deposition of PTFE.

The core diameter of CNTs inferred from these data works out to be ~8.9 nm which favourably compares with actual core diameter of ~9.5 nm of CNTs grown by catalytic CVD.

TABLE 1: Membrane parameters and formulae used for calculation.

Membrane parameters	Values	Method
Molar flux of MV^{+2}, J, (moles/S)	166.02×10^{-11}	Determined experimentally
Diffusivity of MV^{+2}, D, (m^2/s)	7.74×10^{-10}	Reference [10]
Concentration, ΔC, (moles/m^3)	5	Concentration of feed solution
Membrane thickness, Δl, (m)	10^{-6}	From cross section of SEM
Pore area, A_p, (m^2)	4.29×10^{-7}	$A_p = J \times \Delta l / D \times \Delta C$
Membrane area exposed to solution, A_m, (m^2)	3×10^{-5}	Exposed area of membrane to solution.
Porosity of membrane, ε_p	1.43%	$E = (A_p / A_m) \, 100$
Permeable pore density, (no. of CNTs/m^2)	2.3×10^{14}	Calculated from top view of SEM.
Calculated core diameter of CNTs, d, (nm)	8.9	Permeable pore density = $(A_p / A_m) / (\pi d^2 / 4)$
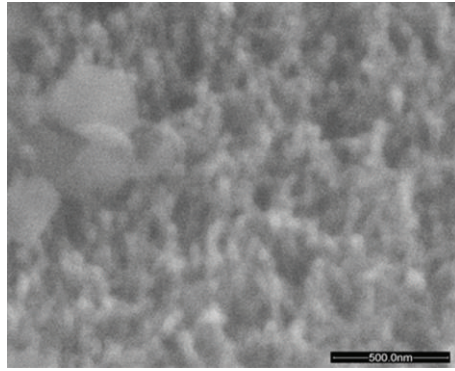
(a)
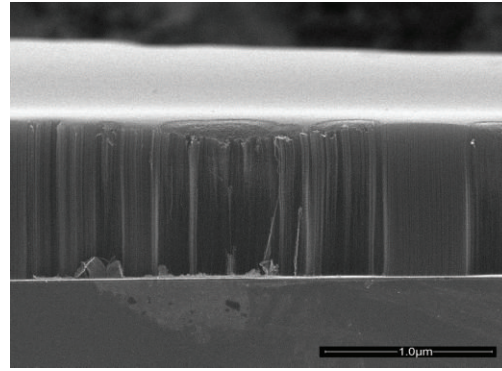
(b)

FIGURE 4: (a) Surface morphology of a sample after deposition of polymer by thermal CVD (after 15 minutes). (b) Cross-sectional view of deposited fluorocarbon polymer between vertically aligned MWCNTs (after 40 minutes).
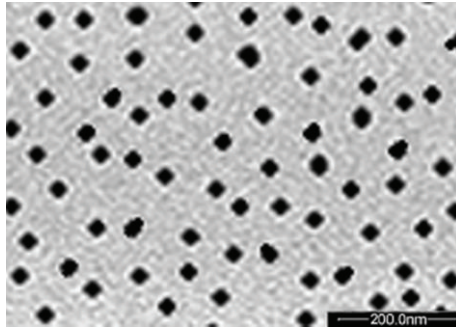

FIGURE 5: Surface morphology of Etched membrane.

Further diffusion experiments are planned, and the result will be reported in a companion paper.

5. Conclusion

The thermal CVD is an effective technique to deposit fluorocarbon polymer between intertube gaps of vertically aligned CNTs to fabricate CNT membranes using relevant precursor. It is a more efficient and convenient method compared to the spin coating. Defect-free deposition without affecting the alignment of carbon nanotubes is achieved. The contention is adequately supported by far field and high resolution SEM cross-sectional images of the fabricated and etched membranes. FTIR analysis indicates the attachment of CF_2 groups with host CNT membrane walls. These films are anticipated to have superior properties quite akin to bulk PTFE.

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