Novel Avenue for Bio-sensing

Carbon Nanotube Aerogel: Synthesis and Applications

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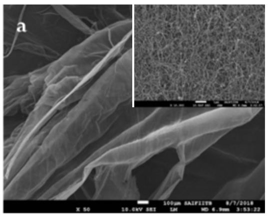

SEM image of Carbon nanotube wool. Inset a large network of isotropically oriented nanotubes

ABSTRACT

Translating the nano-scale properties of individual carbon nanotube (CNT) into a macro-scale is of immense importance for practical utilization of its exotic properties and has been a technological challenge since its discovery. However, carbon nanotube aerogel (CNT aerogel), a self-standing structure of 3-D network of long CNTs, produced by floating catalyst chemical vapour deposition (FC-CVD), could give some hope of retaining large amount of exotic properties of CNTs in macro-scale. In this article our efforts towards synthesis of CNT aerogel have been described. The CNT aerogel has been characterized in detail and further utilized as flexible capacitors, filters for virus and bacteria and in bio-sensing.

KEYWORDS: *Carbon nanotube, Chemical vapour deposition, Microstructure, Sensor*

Introduction

Carbon nanotube (CNT) has been one of the highly researched materials amongst the carbon allotropes due to its extra ordinary strength (>10 GPa), elastic modulus (~1 TPa), electrical conductivity (equivalent to copper) and thermal conductivity (equivalent to diamond). Despite its promising properties, the impact of this material has been limited when it comes to practical mainstream applications. This issue is mainly attributed to the loss of its outstanding properties when scaled-up to macro dimensions. For many years the properties of the CNT were confined to its nano dimension. The initial attempt to scale-up carbon nanotubes into a macro-structure was realized by Bandow *et al.*[2], who made CNT film/ sheets by filtration technique producing Bucky-paper. Even though Bucky-paper was self-standing, a significant loss in properties was witnessed by the researchers[3,4]. Another macrostructure of CNT has become attractive amongst the researchers, named, carbon nanotube aerogel (CNT aerogel)[5]. CNT aerogel is a self-assembled 3D structure of long CNTs that was first envisaged by Li *et al.*[6] using floating catalyst chemical vapor deposition (FC-CVD) from which CNT fiber was drawn by direct spinning. This method was able to retain some of the significant properties of CNTs at macro-scale. CNT fiber produced from CNT aerogel spinning was able to get a strength of 5 GPa and electrical conductivity of 5.6 S/cm^2 [7].

This promising capability of transfer of properties of the CNT into the macro-scale has put it back in the spotlight for practical applications. Some of the established applications of CNT aerogel synthesized through FC-CVD are structural composites, electromagnetic shielding, water purification, ballistics, etc [7,8]. Even though several researchers are working on the production of CNT aerogel through FC-CVD, till now the process mechanism is not very well understood.In this article, the synthesis and applications of CNT aerogel by our group have been discussed.

Synthesis of CNT Aerogel

The synthesis of CNT aerogel was carried out in a horizontal tubular resistance furnace developed in-house (schematic is given in Fig.1). Ethanol (purity ≥ 99.9%, Hayman Ltd, England) was used as the carbon source, ferrocene (purity ≥ 99%, Sigma Aldrich) was used as the catalyst and thiophene (purity ≥ 99%, Sigma Aldrich) was used as the promoter. Hydrogen and argon gases (purity > 99.9%, Six Sigma Gases India Pvt.Ltd) were used as the carrier gases and they provided an inert atmosphere.

Liquid feed (ferrocene and thiophene mixed in ethanol) was pumped to the preheater zone maintained at 200 °C and was allowed to be carried in the main furnace with a carrier flow (mixture of argon and hydrogen) of 1-3 lpm. Reaction took place in the main furnace maintained at a high temperature (1100-1300 °C). CNT aerogel was produced through catalytic cracking of carbon precursor in presence of catalyst. CNT produced in the form of spinnable sock along with other gaseous product was continuously drawn in a harvest box. Snapshot during CNT aerogel formation inside the furnace is shown in Fig.2a. Depending on the requirement, the product

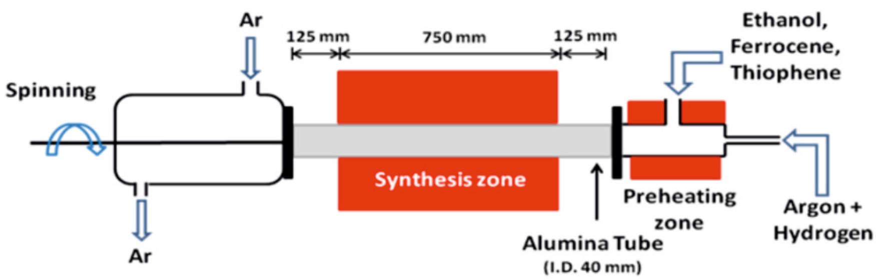

Fig.1: Schematic of the experimental setup for synthesis of CNT aerogel.

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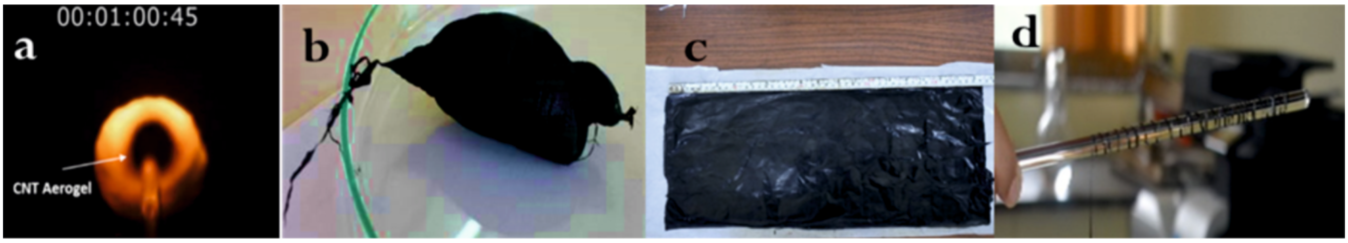

Fig.2: (a) Snapshot of CNT aerogel formation (b) CNT wool (c) CNT sheet (d) CNT fibre.

could be further collected in the form of wool (Fig.2b), sheet (Fig.2c) or fibre (Fig.2d) by varying the process parameters.

Computational Fluid Dynamics

The computational of fluid dynamics (CFD) was carried out using COMSOL Multiphysics software. Weakly compressive fluid flow condition coupled with heat transfer was utilized for determining the flow behavior. Theoretically calculated Reynolds number as per given flow conditions is in the range of 10-30. Hence, a 3-D, steady-state, non-isothermal laminar flow model was used for study. The governing equations utilized in the computation are given in Eqs. (1-4):

$$\frac{d\rho}{dt} + \nabla.(\rho u) = 0 \quad (1)$$

$$\rho\frac{du}{dt} + \rho u.\nabla u = -\nabla.p + \nabla.(u(\nabla u + (\nabla u)^T - \frac{2}{3}\mu(\nabla.u)I) + \rho g \quad (2)$$

$$\rho C_p u.\nabla T + \nabla.q_h = Q_h \quad (3)$$

$$q_h = -k\nabla T \quad (4)$$

Where,

ρ=Density (kg/m^3), μ=Dynamic viscosity (Pa·s), u=Velocity vector (m/s), p=Pressure (Pa), g=Gravitation acceleration (m^2/s), C_p=Specific heat capacity at constant pressure (J/ (kg·K)), T=Absolute temperature (K), q_h=Heat flux vector (W/m^2), k=thermal conductivity (W/(m·K)) Q_h=heat sources (W/m^3).

The reactor was operated at atmospheric pressure condition and at elevated temperature for which the constant wall temperature was used as the boundary condition for heat transfer. The open boundary condition was used at the end ofthe harvest box (outlet to the computation domain).The boundary conditions at the inlet (flow and temperature) are specified in the previous section (synthesis of CNT aerogel). Discretization was carried out usingphysics controlled meshing option available in COMSOL Multiphysics where 1056648 domain elements, 57574 boundary elements, and 2238 edge elements were used for the entire domain (reactor tube and harvest box). Selection of meshing was decided by grid independence test performed over wide range of meshing conditions.

The CFD model in this work has been used to predict the flow field inside the reactor. Fig.3 shows the velocity profile of the gas phase as predicted by the CFD simulation. It can be observed that the aerogel formation takes place at the upper half of the furnace tube. This is due to the backflow of the gas from the harvest box into the furnace tube through the bottom half of the furnace tube. The backflow occurs as a result of the low carrier flow rate utilized to maintain laminar flow to prevent flow instability. The rotation of the collection rod ensured that the collected CNT aerogel was symmetrical in shape and the collection was continuous. Detailed CFD analysis can be found in another BARC newsletter article[9].

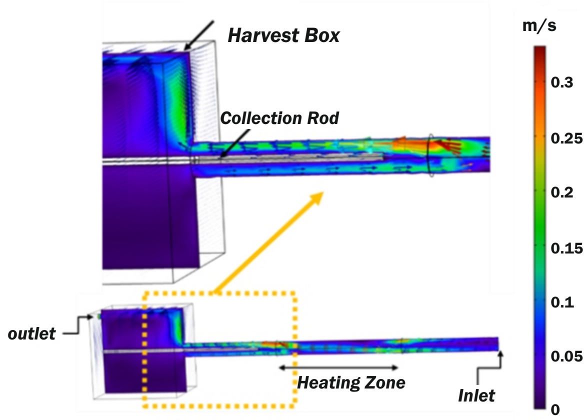

Fig.3: Velocity profile of the gas phase predicted by CFD.

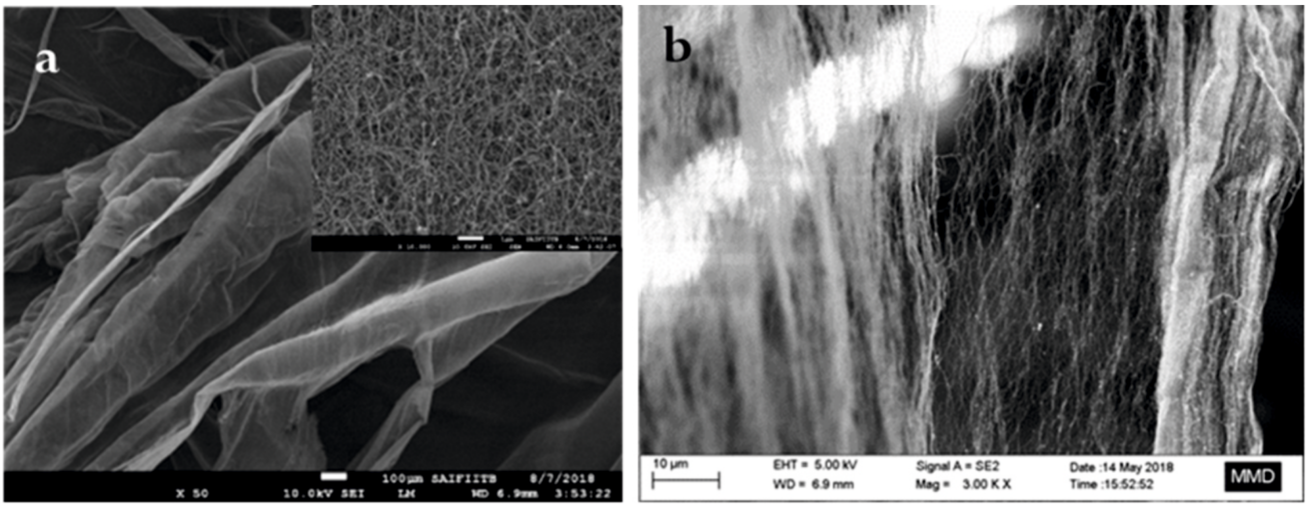

Fig.4: SEM images of (a) CNT wool and (b) CNT sheet.

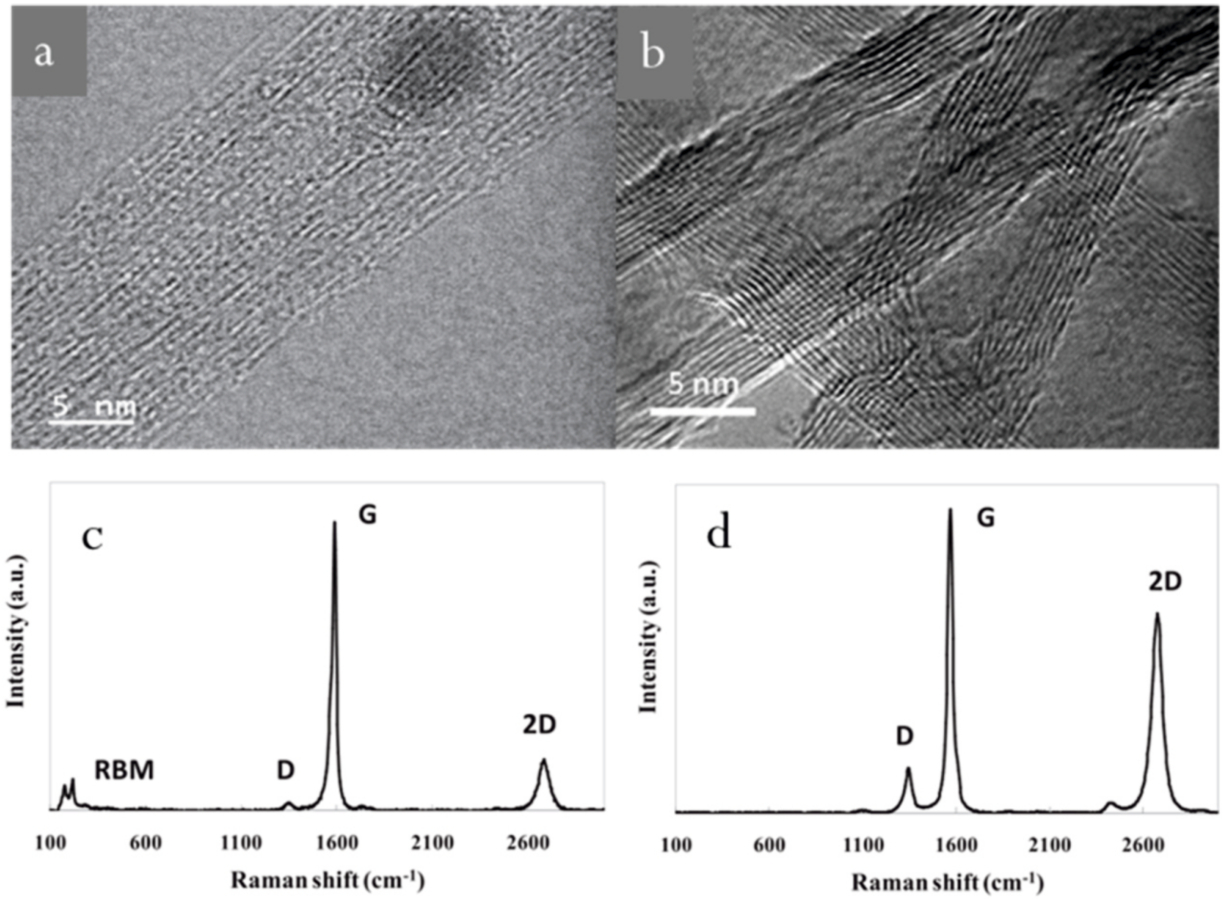

Fig.5: (a) TEM image of SWCNT bundles (b) TEM image of MWCNT (c) Raman spectrum of SWCNT (d) Raman spectra of MWCNT.

Microstructural Characterization

Typical scanning electron micrograph (SEM) of a CNT wool is shown in Fig.4(a). The inset image depicts a large network of isotropically oriented CNTs. However, in the CNT sheet the CNTs are relatively aligned, as shown in Fig.4(b).

Depending on the processing conditions the CNTs may be either single-walled (Fig.5a) or multi-walled (Fig.5b), which can be understood from the transmission electron micrographs (TEM). It can also be understood from the Raman spectra[10]. Single-walled CNT produces RBM peak along with sharp G peak, prominent 2D peak and negligible D peak (Fig.5c). The RBM peak is missing and the D peak is prominent in the case of multi-walled CNT (Fig.5d).

Application as a Flexible Capacitor

CNT aerogel derived films were cut into circular shapes (diameter =2.5 cm). Copper strips were connected to the CNT films using silver paste. The copper strips were insulated using polyimide and epoxy layer. The solid-state electrolyte was prepared from polyvinyl alcohol (PVA: Sigma Aldrich) and KOH. Both the electrodes were covered with PVC sheets from backside. The two CNT aerogel circular films were placed over each other in such a way that a symmetrical capacitor was formed. The gist is given in Fig.6.

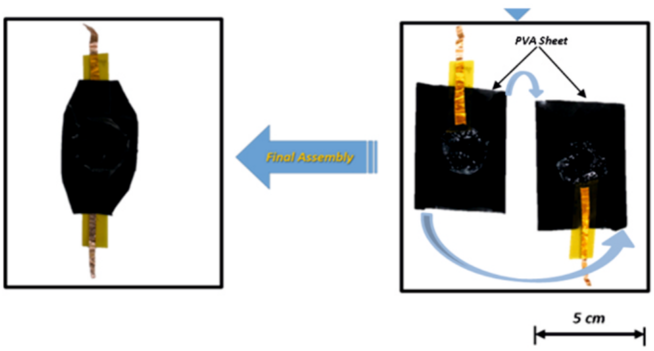

Fig.6: Preparation of a flexible capacitor.

The effect of bending on the flexible capacitor is shown in Fig.7. Very low (less than 1%) change in capacitance was observed even after a full 180° bend.

Application as a Filter against Virus

Filters have been prepared from the CNT wool (Fig.8a) for trapping nanoparticles, virus and bacteria. The average pore-size of the CNT-wool is below 100 nm. The efficacy of CNT-wool based filter was tested against bacterophage P1, which is a virus that infects bacteria. The phage P1 has a large icosahedral head of approximately 55–85 nm diameter attached to a characteristic long tail of 200-300nm. CNT wool filters were autoclaved (121°C and 15 Psi, 15 min) for sterilization and then used for checking filtration efficiency for P1 phage using the millipore filter assembly using standard procedure. The CNT wool filter could trap the bacteriophage with an efficiency comparable to a commercial N95 mask. The image of the trapped virus in the filter is shown in Fig.8b.

Application in Bio-sensing

An ultrasensitive label-free biosensor has been prepared from CNT aerogel, which is capable of detecting DNA hybridization very rapidly[11]. The multi-directional CNT embedding into the CNT aerogel electrode demonstrated linear ohmic and near isotropic electrical properties, therefore

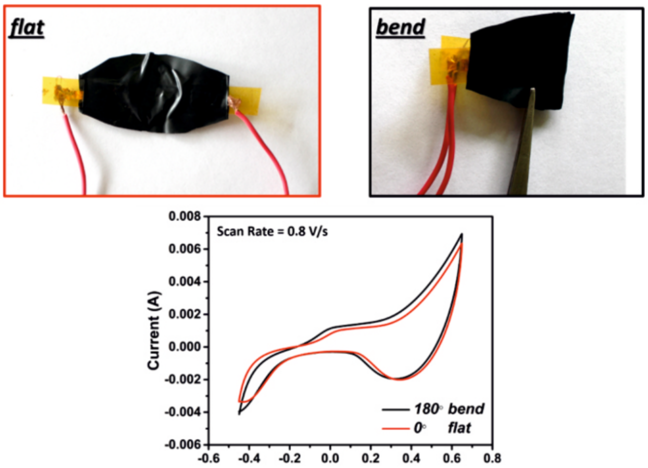

Fig.7: Variation of CV with bending of the flexible capacitor at a scan rate of 0.8 V/s.

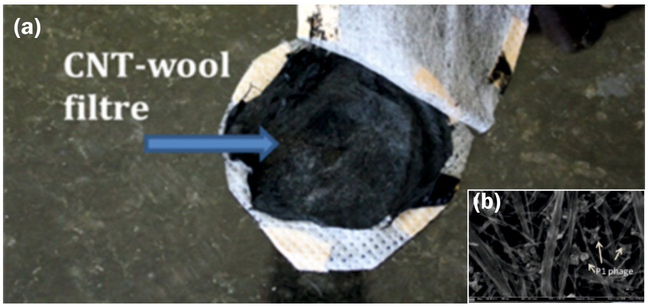

Fig.8: (a) Filter made from CNT wool (b) SEM image (inset) showing the P1 phage trapped in the filter.

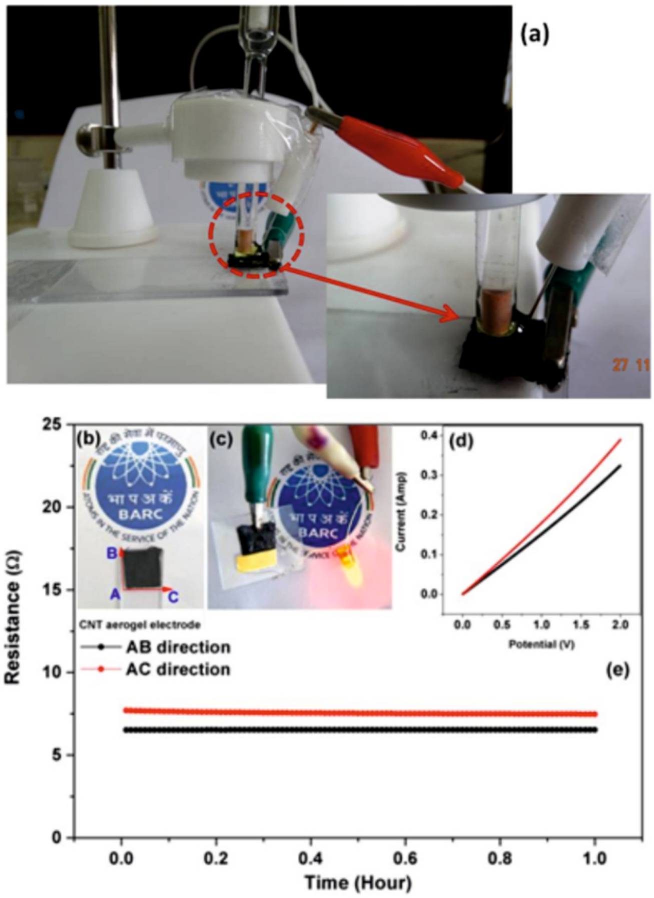

Fig.9: (a) Electrochemical impedance system for bio sensing and (b) CNT aerogel electrode (c) conductivity test (d) IV curve (e) chronoamperometry test of CNT aerogel electrode.

providing ultra-high sensitivity and specificity toward bio molecules (Fig.9(a-e)).

Using this device, the target DNA hybridization was detected by a quantifiable change in the electrochemical impedance, with a distinct response to the single-stranded probe alone or double-stranded target-probe complex. The target DNA was specifically detected with limit of detection (LoD) of 1 pM with a turnaround time of less than 20 minute (Fig.10(a-c)). Moreover, this system is able to differentiate between the closely related target sequencesby the distinct impedance response rendering it highly specific. The detection mechanism of CNT aerogel electrode works on the principle of π-π interactions between negatively charged single stranded DNA and CNT.

Fig.10(a) The detailed sequence of the probe and target DNA oligonucleotides; Agarose gel electrophoresis showingthe fluorescent bands corresponding to the perfect match (PM)-dsDNA and mismatch (MM)-dsDNA and Nyquist plot of all bio-samples in (b) hybridization buffer (c) stringent hybridization buffer (with 8% formamide). This is the first study in the literature, where fabricated standalone bare CNT electrode without any substrate support, coupled with electrochemical impedance spectroscopy, has been used for the detection of DNA hybridization. Altogether, the results show that our system is fast, sensitive and specific forlabel free rapid direct DNAdetection, promising a novel avenue for bio-sensing.

Conclusion

CNT aerogel is an exotic material where long CNTs are self-assembled to form a self-standing 3-D structure. This material has been produced by FC-CVD process and shaped into wool, sheet and fibre forms. The flow and the temperature profiles of the reactor have been simulated using COMSOL Multiphysics. The CNT aerogel has been characterized by electron microscopy and Raman spectroscopy. The aerogels have been used to make (1) flexible energy storage devices, (2) filters for trapping viruses and (3) bio-sensors with low LoD and rapid detection time. This wide range of applications is possible by tuning the structures and the properties of the CNTs in the aerogel.

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