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Formation of Large Area Conducting Paper of Carbon Nanotubes for Electrode Applications

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Abstract
In present work we report simple and scalable method for the formation of multiwalled carbon nanotubes (MWCNTs) based large area conducting paper for electrode applications. The MWCNTs based paper have been successfully fabricated with well dispersed catalytically grown high quality MWCNTs followed by simple vacuum filtration technique. Our study demonstrated that these MWCNTs based paper have great advantage as large area, conducting and binder free electrode material for flexible and portable devices.

Keywords: CNTs, XRD, SEM, TEM, RAMAN.

Introduction
In recent years carbon nanotubes (CNTs) have been attracted a great attention due to their unique combination of thermal, mechanical and electrical properties [1-2] such as high thermal and electrical conductivity, high specific surface area, high mechanical strength, high charge transport capability etc. [3-6] make them more promising and multifunctional material for portable electronic devices.
Now it is necessary to design inexpensive, light weight, foldable and wearable electronic devices. Thus we need to developed new versatile, flexible and highly conducting electrode as an alternative to the electrode material used in conventional energy storage devices such as batteries and supercapacitors [7-9]. However the performances improved with advanced carbon materials such as activated carbon (AC), graphene, carbide derived carbon and their composite/hybrids combined with conducting polymers or metal oxides. [10-11]. The most widely used advanced carbon material for commercial applications are AC, is low cost electrode material with high surface area, but AC is still difficult to handle in powder form for an electrode material. Thus we need conductive agents and binder for the fabrication of flexible electrode materials.[12]. Moreover for the commercial applications, the large scale production of inexpensive, light weight, flexible and binder free electrode materials are still remains a great challenge.
In this work we report the simple and scalable method for preparation of large area conducting CNTs paper (bucky paper) for electrode applications in portable devices. CNTs based paper are produced by self-assembly of CNTs, dispersed in an appropriate solvent and filtered through membrane leaving the laminar structure with network of intertwined CNTs held together by van der Waals forces at tube-tube junctions. These large area, conducting, and binder free papers become an important candidate in CNTs research, the intrinsic properties these papers make them very useful in industrial and commercial applications such as filtration, actuators, capacitors and battery electrode [13-14].

Methods
Ferrocene ($C_{10}H_{10}Fe$) purchased from Otto whereas toluene (C_7H_8) and acetone (C_3H_6O) were purchased from Molychem India.

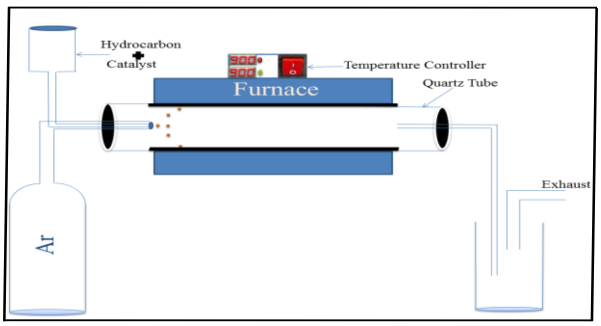

Figure 1: Schematic of experimental setup used for MWCNTs synthesis.

For the growth of MWCNTs we have prepare the homogeneous solution of ferrocene (catalyst) and toluene (source of carbon), using spray pyrolysis technique the prepared solution injected into a tube furnace which maintained at 850° C.[15-16]. The product deposited on the wall of the tube was collected. The good alignments of CNTs were obtained after purification by acid treatment [17-18].

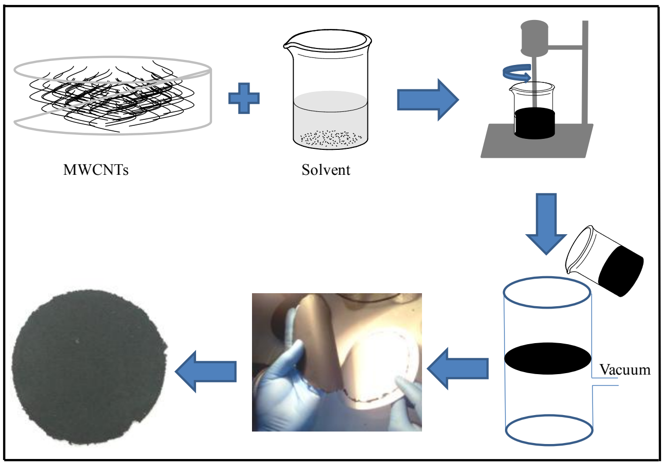

Figure 2: Schematic of MWCNTs paper preparation.

0.4 gm MWCNTs was dispersed in acetone using high speed homogenizer (Remi Motor, Elektrotechnik Ltd. Vasai- India) @ 8000 rpm for 10 min. The dispersed CNTs were filtered by specially designed vacuum filtration unit using whatman qualitative filter paper, grade 1 of diameter 150 mm and pore size 8 μm. The prepared CNTs film was easily recovered from filter paper after drying over 10 min at 45° C.

Results

The structural and morphological analysis of as synthesized MWCNTs was determined by X-ray powder diffraction (PANalytical, UK) using Cu Kα radiation and scanning electron microscope (ZEISS, Germany) respectively. Raman analysis (Renishaw,UK) was carried out for crystallinity of MWCNTs as well as identifying D band and G band at room temperature with an excitation wavelength 532 nm.

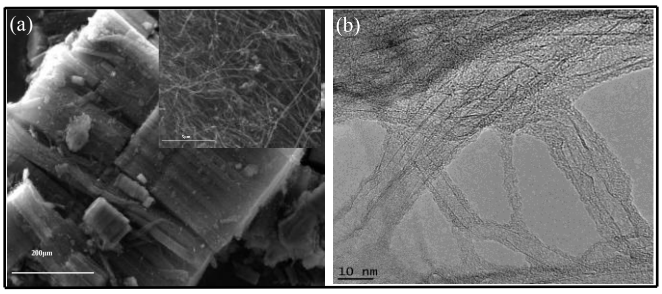

Figure 3: (a) SEM micrographs of as produced MWCNTs, the inserts image show the SEM micrographs of bucky paper. (b) HRTEM image of bucky paper showing individual MWCNTs.

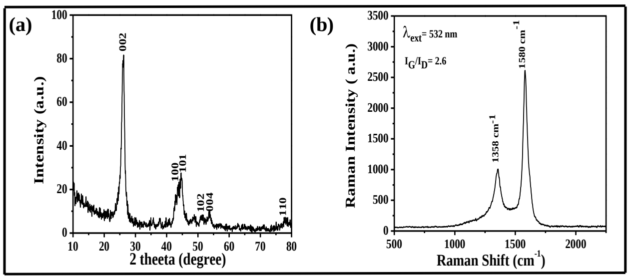

Figure 4: (a) XRD pattern of as synthesized MWCNTs. (b) Raman spectra of as produced bucky paper.

Discussion

Figure 3(a) is the SEM image of CNTs, which shows the bundle of CNT having average diameter 50 nm with amorphous carbonaceous impurities. The effect of homogenization is also visible in the inserts image of figure the figure in which CNT- CNT entanglement improved and figure 3(b) is the HRTEM image of as prepared bucky paper which shows the individual MWCNTs with average diameter about 20 nm. Whereas figure 4(a) shows the XRD pattern of purified MWCNTs. All the peaks obtained in XRD spectra were well and perfectly matches with the XRD pattern of JCPDS file no . 75-1621. The most intense peaks at $2\theta \approx 26°$ which corresponds to (002) plane and also the peaks at 42°, 44°, 53° and 77° corresponds to plane (100), (101), (004) and (110) respectively. This confirms that as synthesized material to be pure hexagonal structure.

Raman spectroscopy is an extremely important technique that is generally used for quick and nondestructive characterization for all type of carbons; figure 4(b) shows Raman spectra of as prepared MWCNTs paper. This spectra consists D band at about 1358 cm^{-1} due to the presence of amorphous carbon and double resonance in sp^2 carbon and G band at about 1580 cm^{-1}, is due to the tangential vibration of graphitic carbon atom [19-20]. The intensities of this G peak depend strongly on the metallicity of the nanotubes and the intensity ratio of the G and D peaks (I_G/I_D) determines the level of crystallinity [21]. In the case of bucky paper this value is ~2.6 represent the lowest defect within the bucky paper. Figure (5) shows the digital images of as prepared conducting, highly flexible and large geometrical area (~ 18 cm^2) bucky paper which can easily fold without any damage.

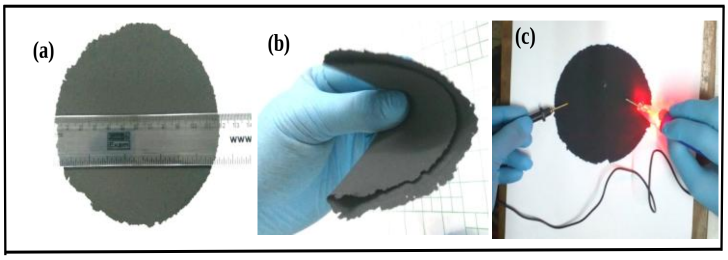

Figure 5: Shows the digital images of bucky paper. (a) Large area circular bucky paper with diameter ~ 12 cm. (b) Shows the flexibility of the bucky paper. (c) Shows as prepared bucky paper is conducting and continuous.

Conclusion

Light weight, binder free, freestanding and large area thin (~200 µm), conducting MWCNTs paper was prepared by using a simple and novel dispersion technique. This can be used as an electrode in flexible and portable devices for commercial applications. Moreover the method can also employed to fabricate different kind of CNT- based composites/hybrids paper with different properties in order to meet our requirements for the applications in devices such as flexible lithium ion batteries, supercapacitors and solar cells etc.

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