

USAGE OF CARBON NANOTECHNOLOGY WITH A REFERENCE OF SUPERCAPACITOR

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ABSTRACT

Carbon-based materials such as graphene, CNTs and activated carbon with macro-, micro-, meso- and nanoporous structures are the essential resources for electrochemical energy storage applications. The first commercialized activated carbon material was used energy storage devices, such as power backup systems in customer electronics, windmills, UPSs, electric and hybrid electric vehicles, airplanes, trains, buses, industrial equipment and telecommunication systems. The innovative porous electrode (cathode/anode types) materials were quickly developed. Numerous resource materials were studied for morphological structures, which are essential for improving supercapacitor performance. Important properties of electro-active materials and increasing surface area with mesoporous/hollow structures control the pore volume/size, electrical conductivity, and stability and surface functionalities. However, until now the predicted supercapacitor performances have not been fully demonstrated i.e. rate capability of charge and discharge time, lower energy density than batteries and their faster self-discharge rate. This study focuses on the importance of materials development with well-defined crystal, hollow crystal and porous crystal structures.

keywords: *supercapacitor , Carbon ,Nanotechnology*

INTRODUCTION

Electrical energy storage is required by a large number of applications that require local storage or generation of electric energy. A storage device must meet all of the criteria for a particular application, including those for energy density (WH) and maximum power (W), as well as those for size, weight, initial cost, and longevity, among other things. Super capacitors bridge the gap between batteries and conventional capacitors by delivering energy and power densities that are several orders of magnitude greater than those of regular capacitors. When it comes to energy storage in portable or remote devices, where batteries and standard capacitors must be over-dimensioned due to a low power to energy ratio, they offer an intriguing alternative. It is anticipated that super capacitors will be utilised in electric, hybrid electric, and fuel cell vehicles as a short-term energy storage device with high power capabilities, allowing for the storage of energy generated by regenerative braking. The number of applications for telecommunications equipment, such as cellular phones and personal entertainment devices, is growing rapidly. Among the multiplicity of challenges that individuals will encounter sooner rather than later, energy-related worries are likely to be the most remarkable. Electric energy storage and change strategies that are more flexible, tough, and productive are required to develop a more manageable society with ample sustainable electricity and less natural pollution. For electric energy storage devices, energy thickness (how long the device can last) and power thickness (how much energy the device can store) are two constraints that may be used to define them (the

amount of that energy can be conveyed from the gadget throughout a specific timeframe). Because of their compactness and comparably high energy thickness, batteries have long been the ideal power storage method for a variety of applications requiring continuous force delivery over an acceptable time period. However, because of their sluggish rate of energy discharge, batteries are unsuitable for many applications that need a tremendous force flood or a rapid force discharge, such as rocket dispatching, because to their high energy density. Even though fresh developments, such as the lithium-particle battery, have been produced to boost force execution (high-rate capability), they are nonetheless dependant on inborn cutoff points that are equivalent to those of the human brain. With their incredibly quick charge-release rates, high-performance super capacitors (also known as ultra capacitors or electrochemical capacitors) are emerging as potential fuel sources for electric vehicles.

SUPER CAPACITORS

Increased diversity, resilience, and effectiveness in the design of electric energy storage and conversion systems are necessary for the development of a more sustainable society with sufficient renewable energy and less pollution. When it comes to electric energy storage devices, energy density (how long the device can last) and power density (how powerful the device is) are two metrics that may be used to differentiate them (how much of that energy can be delivered from the device over a certain period of time). Because of their portability and comparably high energy density, batteries have long been the preferred electricity storage solution for many applications requiring continuous power delivery over an acceptable time period, such as medical devices. Due to their sluggish pace of energy release, batteries are not suitable for some applications that need a huge power surge or quick power release, such as rocket launching, due to their slow rate of energy release. Despite the fact that new technologies, such as the lithium-ion battery, have been created to improve power performance (high-rate capability), they are still subject to the same intrinsic limits as older technologies. The conclusion is that super capacitors (also known as ultra capacitors or electrochemical capacitors) are becoming increasingly popular as feasible energy sources because of their extremely fast charge-discharge rates.

The energy stored by super capacitors is electro statically stored by polarising an electrolytic solution, as opposed to the energy stored by dielectric capacitors, which is stored as separated electrical charge. The design and manufacturing of these devices are similar to batteries in that they consist of two electrodes submerged in an electrolyte with a separator between the two electrodes.

2 When a voltage is applied across the positive and negative electrodes of a super capacitor, the ions in the electrolyte are pulled to the electrodes that are oppositely charged to one another. 3 In the microspores of the electrodes, opposing charges are separated across the interface between the solid electrode surface and the liquid electrolyte, resulting in the formation of a very thin "electrochemical double layer" between the solid electrode surface and the liquid electrolyte. As a result, charge separation between the two layers is utilised for the storage of energy.

It is known that the capacitance of traditional planar sheet dielectric capacitors is inversely proportional to the distance between their electrodes. However, the capacitance of a super capacitor is defined by the length of time it takes for charges to transfer from one electrode to another. This distance is significantly shorter than that of a dielectric capacitor and is much smaller than that of a dielectric capacitor. This results in super capacitors having an exceptionally high capacitance as a result of their high capacitance. In terms of capacitance, super capacitors have a capacity that is approximately 100 times more than that of similar

regular dielectric capacitors, and a peak power density that is approximately 100 times greater than that of batteries.

In addition to its high power density, good reversibility, exceptionally long cycle life, and quick mode of operation, super capacitors also have a few more advantages to offer. Their high power density distinguishes them from the competition, making them indispensable for surge-power delivery. Applications for super cathode technology include load-leveling functions for batteries in electric vehicles and hybrid electric vehicles during starting, accelerating, regenerative braking, as well as burst-power generation in electronic devices such as personal computers, cell phones, camcorders, digital cameras, navigational devices, personal data assistants (PDAs), PCMCIA (Personal Computer Memory Card International Association) cards and flash cards, and medical devices.

Super capacitors include electrochemical double layer capacitors (EDLC), such as the ones mentioned above, and pseudocapacitors, which are both sorts of capacitors. EDLC capacitance is based on fast, reversible faradic redox reactions that occur between the oxide and the electrolyte, resulting in a Helmholtz layer; on the other hand, the pseudocapacitor is based on fast, reversible faradic redox reactions that occur between the oxide and the electrolyte, resulting in a so-called pseudocapacitance. Because of the electrochemical redox reaction of the electrode materials, some faradic charge transfer happens in a pseudocapacitor, similar to that which occurs in a battery. As a result, the capacitance of a pseudocapacitor may be significantly greater than that of an EDLC. In contrast, because redox processes are involved, the power performance suffers as a result of this.

Furthermore, because EDLC capacitance is proportional to surface area, electrochemical inert materials with the greatest specific surface area are the most effective electrode materials for producing a double layer containing the greatest number of electrolyte ions in solution. In part, this is due to the huge specific surface areas of carbonaceous materials such as activated carbon, carbon fibres, and carbon aerogels; these materials have been widely studied.

CARBON NANOTECHNOLOGY S

The discovery of carbon nanotechnology (cnt) was made in 1991 by Japanese researcher "sumio Iijima" through the use of a circular segment release vanishing technique. A kind of carbon allotrope known as carbon nanotechnology (CNTs) is characterised by one-dimensional (1D) nanostructures that are spherical and hollow in shape. Fullerene-like pentagon-containing structures are often found at the two ends of these long nanotechnologies, with a width of 1-10nm and a length ranging from a few micrometres (m) to several centimetres (cm). CNTs, in a manner similar to grapheme, lay down the particles in hexagonal patterns.

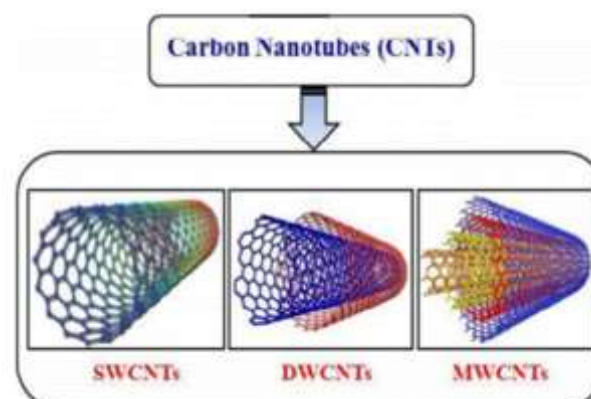


Fig .1 Classification of carbon nanotechnology s for SWCNTs, DWCNTs and MWCNTs

In accordance with the number of concentrically moved up single graphene in each CNT, as illustrated in Fig. 1 CNTs are categorised into four types: sheet single-walled (SWCNT), doubly walled (DWCNT), and multi-walled CNTs (MWCNT) The SWCNT structure is made up of a single nuclear graphene layer of graphene and a few graphene sheets coaxial ones double walled carbon nanotechnology s that are wrapped around one another. DWCNTs are a kind of MWCNT that is distinct in that only two graphene sheets that have been concentrically moved up are accessible. Carbon nanotechnology (CNTs) is comprised of graphene chambers that are closed on one or both sides with pentagonal ring-shaped covers, which are made of carbon. Depending on the configuration, the barrel-shaped CNTs may have ends closed, one end closed, or both closures open; the finishes of some CNTs may be open, while the finishes of others may be closed with entire fullerene coatings. Several factors influence the mechanical, thermal, and electrical properties of CNTs, including their measurement, length, chirality, virtue, and bit (or chirality and virtue).

Carbon nanotechnology, as addressed by Baughman et al. and Popov, is especially intriguing for both business and academic study because of its distinct characteristics. In 1991, Iijima 80 was the first person to identify multi-walled carbon nanotechnology, which he named Iijima 80. (MWNT). In 1993, Iijima and Ichihashi 81 and Bethune et al. 82 revealed the discovery of single wall carbon nanotechnology (SWNT), which was virtually concurrently with each other. Carbon nanotechnology synthesis procedures such as arc discharge, 80,81,82 laser ablation, chemical vapour decomposition (catalytic growth), 84, and high-pressure CO disproportionation are examples of carbon nanotechnology synthesis processes (HiPco).

The mechanical properties of carbon nanotechnology, as well as its electrical conductivity, thermal conductivity, and optical properties, are all exceptional. It is possible for each SWNT to have tensile strengths of 37 GPa^{87,88} and Young's modulus of 640 GPa⁸⁷. 89 At room temperature, the electrical conductivity of SWNT is on the order of 106 S/m, whereas aligned MWNT films along the tube axis exhibit conductivities ranging between 90 and 5000 S/m at room temperature. 91 The superconductivity of some small-diameter SWNTs is seen at low temperatures, such as 1.4-nm-diameter SWNT with a transition temperature of 0.55 K⁹² and 0.5-nm-diameter SWNT synthesised in zeolites with a transition temperature of 5 K⁹³.

MWNT thermal conductivity ($> 3000 \text{ W/m.K}$)⁷⁸ is higher than the thermal conductivity of natural diamond and graphite's basal plane (2000 W/m.K), but lower than the thermal conductivity of isolated SWNT (6600 W/m.K)⁹⁴ at ambient temperature, which is equivalent to the thermal conductivity of a hypothetical isolated graphene monolayer. According to a study of optical absorption, high-resolution electron energy-loss spectroscopy in transmission, and tight-binding calculations, it is possible to accurately determine the mean diameter and diameter distribution in bulk SWNT samples using a combination of optical absorption, high-resolution electron energy-loss spectroscopy in transmission, and tight-binding calculations. It has been determined how much specific surface area individual carbon nanotechnologies and bundles of carbon nanotechnologies have as a function of tube diameter, the number of walls, and the number of carbon nanotechnologies in a bundle. 96 One nanometer in diameter may have a specific surface area of 1315 m² per gramme, whereas bundles with a diameter of 7 nanometers have a specific surface area of 400 m² per gramme, according to the researchers (for SWNT of 1 nm diameter). Due to the properties of carbon nanotechnology, it has a wide range of applications or potential applications, including conductive and high-strength composites, hydrogen storage media, energy storage and conversion devices, field emission displays, and radiation sources, as well as nanometered-sized semiconductor devices, sensors, probes, and

interconnects, field-effect transistors, single electron transistors, rectifying diodes, and nanometered-sized semiconductor devices, sensors, probes, and interconnects, field-effect transistor

CARBON NANOSTRUCTURE MATERIALS

Carbohydrates are one of the most abundant elements on the planet. When it comes to nanostructured carbon allotropes, the graphite and graphene families stand out because of their extraordinary properties that are projected to be used in nanoelectronics, energy disputes, and energy storage applications, among other things. The carbon allotropes feature nuclear orbital hybridization holding states for sp^1 , sp^2 , and sp^3 hybridization, as well as holding states for sp^3 hybridization. The sequence of carbon nanostructures is dictated by the different dimensionalities, starting with zero measurement (0D) structures fullerenes-C60, commonly known as buckyballs, one-dimensional (1D) structures (carbon nanotechnology s), and two-dimensional (2D) structures. The carbon with sp^2 hybridization (graphene) and three-dimensional (3D) structures seen in Fig.2 were made possible by sp^2 hybridization.

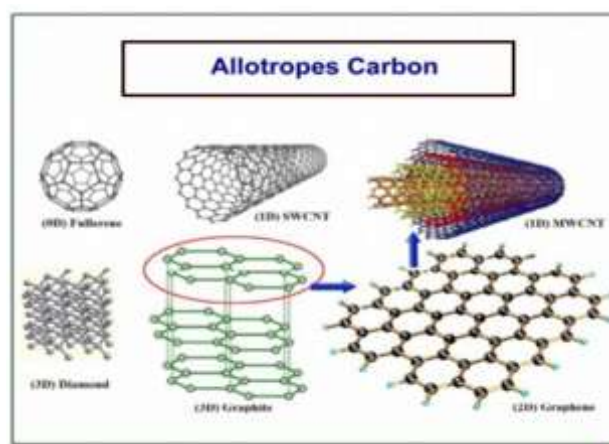


Fig.2 Different types of allotrope of carbon nanostructure materials

SYNTHESIS TECHNIQUES OF CNTS

Manufacturing CNTs was accomplished by a variety of technologies such as arc discharge, laser ablation, and Chemical Vapour Deposition (CVD). As may be seen in Fig.3, the different strategies are well explained.

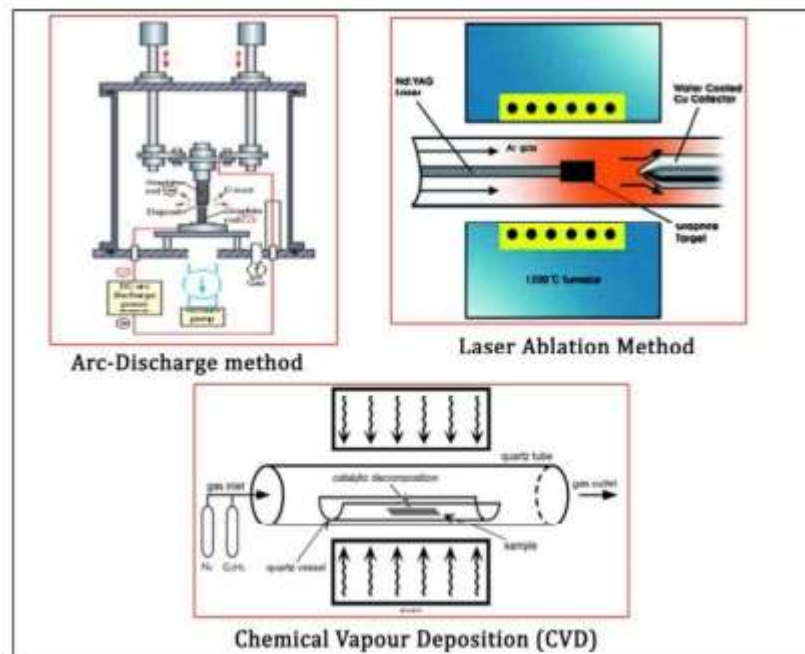


Fig 3 there are three types of CNT synthesis processes that are illustrated in the diagram: arc discharge, laser ablation, and chemical vapour deposition (CVD).

APPLICATION OF CARBON NANOTECHNOLOGY S IN SUPER CAPACITORS

The primary function of super capacitors is to provide a large amount of capacitance in a small package. The maximal extreme force thickness of a super capacitor is defined as $16 P_{max} = V_i^2 / 4R$ (where V_i is the underlying voltage and R is the identical arrangement opposition (ESR)), where P_{max} is the underlying voltage divided by four. ¹⁷ Therefore, a high force thickness is required to ensure that the actual terminal is not electrically blocked as well as that the contact between the cathodes and flow gatherers is not electrically obstructed by a high force thickness. Because of its amazing explicit surface area and electric conductivity, carbon nanotechnology has unquestionably a significant role to play. The exceptional structure of carbon nanotechnology is also an advantage over typical carbon materials in terms of performance. A strong and permeable carbon nanotechnology structure will typically be formed as a result of the majority of carbon nanotechnology structures having a viewpoint percentage of greater than 1000. As a result of the permeable structure created by open spaces between imprisoned nanotechnology particles and little opposition of the actual terminal, electrolyte particles have relatively easy access to the cathode/electrolyte interface, which is crucial for charging an electric double layer. Furthermore, the strength of the nanotechnology skeleton mandates the use of only a few or no fasteners, which is rare for carbon-based materials of traditional construction.

Niu and colleagues, who built super capacitor cathodes out of unconnected mats of MWNTs, were the first to employ carbon nanotechnology in the construction of double layer super capacitors. ¹⁸ Other forms of carbon terminals that feature micropores, such as the cut and impasse pores, are not linked together; however the pores in the carbon nanotechnology anode are gaps inside the snared nanotechnology organisation and are thus connected together. In contrast to conventional nanotechnology terminals, they are open designs that enable the electrolyte to reach practically every surface zone. Only roughly a third of the surface zone of an initial carbon anode with a surface area of 1000 m²/g is available for the creation of an

ionic double layer, despite the fact that the surface area is 1000 m²/g. 19 This allowed the nanotechnology cathodes to attain a force thickness of more than 8 kW/kg, which was unprecedented.

With the remarkable electrochemical performance of carbon nanotechnology anodes, there has been an explosion of interest in the field. Frackowiak and colleagues undertook an organised investigation to evaluate the electrochemical characteristics of super capacitors constructed from different types of MWNTs and SWNTs and to link these qualities with the microtexture and critical architecture of super capacitors. 20 It has been discovered that, despite the presence of mesopores framed by carbon nanotechnology trapping, the focal canals of the cylinders contribute to the easy availability of particles charging the electrical double layer, according to the findings. As a result of their enormous surface area, it appears that SWNTs have a higher explicit capacitance than other materials after everything is said and done. The researchers observed that MWNTs can have capacitance twice as high as SWNTs when specific circumstances are met, according to Frackowiak et al. 21 Their hypothesis was that the higher capacitance of MWNTs observed in their study was due to the presence of mesopores caused by the open focal trench and open organisation of entrapped nanotechnology s, implying that assisting in the transportation of particles from a solution for the Capacitance execution of carbon nanotechnology s is also influenced by the surface state of the nanotechnology s Carbon nanotechnology that has been synthetically modified by solid corrosive oxidation has showed a well-characterized pseudo capacitance conduct due to the Faradaic redox reactions of their vast surface functionality. The capacitance, on the other hand, must be steadily lowered over the course of a long cycling cycle. Regardless of whether the estimation of a specific capacitance increased primarily as a result of an increase in by and large pseudo capacitance (an increase from 80 to 137F/g in one study and from 56 F/g in another study), the blurring of a portion of the capacitance has extremely limited reasonable significance in this context. As a result, this type of super capacitor is practically the same as an EDLC in terms of performance. According to the authors, similar pseudo capacitance conduct demonstrated by expansive redox reactions has also been observed in SWNT cathodes, though it is unclear whether this was due to the presence of oxygen-containing practical gatherings connected to the outside of the nanotechnology or to the debasements held after purging in nitric acid was responsible for the phenomenon. Using high-temperature reinforcement to strengthen the material, these redox reactions can be avoided.

OBJECTIVE OF THE STUDY

1. To test device performance with doped and undoped CNTs and graphene electrodes in super capacitor applications.
2. To use three electrode systems to undertake electrochemical evaluation of un-doped and hetero atoms doped CNTs for super capacitor applications..

MATERIALS AND EXPERIMENT

Functionalized SWNT Film Preparation

Dr James M. Tour's lab at Rice University has functionalized SWNT with arylchloride, sodium sulfonate, arylchloride and 4,4'-methylenedianiline, and bis(3,5 -di-tert-butylphenyl)-5-aminobenzene-1,3-dioate using the previously described technique. As demonstrated in Table 1 and Figure 4, the functionalized SWNTs have different compositions as well as different structural configurations.

Contact Angle Measurement

The contact angle was measured on VCA Optima contact angle analysis system (AST Products, Inc.). Other experimental procedures are described in paper.

Table 1. Composition of functionalized SWNT electrodes

	Functional groups	Functionalized Percentage (%)
Bucky paper		0
JLH-67	Arylchloride	3.5
JLH-100		4.0
JLH-111		5.9
JLH-103	Sodium sulfonate	----
CDD-I-26	Arylchloride and 4,4'-methylenedianiline	----
CDD-I-76	Bis(3,5 -di-tert-butylphenyl)-5-aminobenzene-1,3-dioate	----

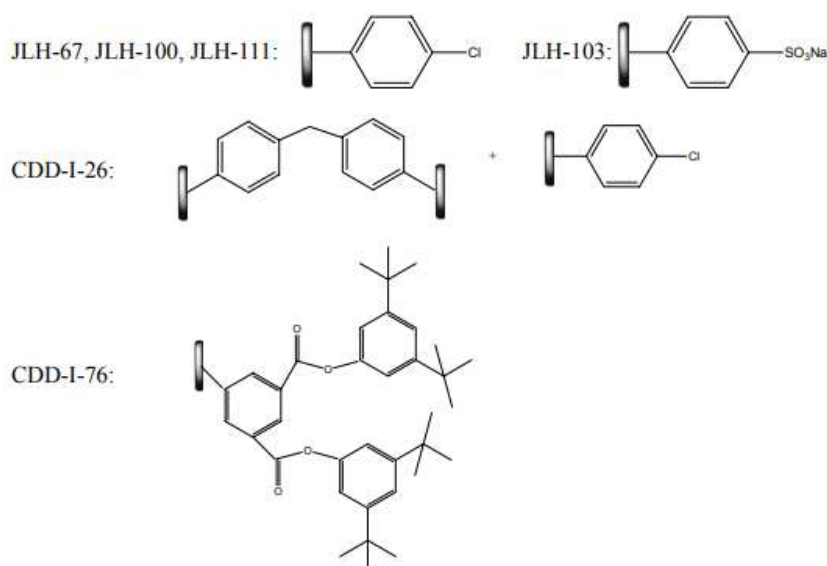


Figure 4. The structures of variously functionalized SWNTs

RESULTS AND DISCUSSION

Morphology Characterization for Arylchloride Functionalized SWNT

The morphology of the bucky paper and functionalized SWNTs was investigated using scanning electron microscopy (SEM). The rough surface of the control bucky paper is seen in Figure 5a. The sizes of the SWNT bundles are approximately 48 x 16 nm. While loosely packed thicker bundles are detected in the arylchloride membrane JLH-67, thicker bundles are observed in the arylchloride membrane JLH-67 (Figure5b). According to the results of this study, JLH-111 (Figure 6d) with a higher degree of arylchloride functionality displays a significantly more compact structural pattern, with bundles having a significantly smaller diameter than those of the control bucky paper and JLH-67, while the JLH-100 (Figure 5) with an intermediate degree of arylchloride functionality exhibits the presence of both small and large bundles. This result suggests that the functionalization may cause some CNTs to be damaged and some amorphous carbon to be formed.

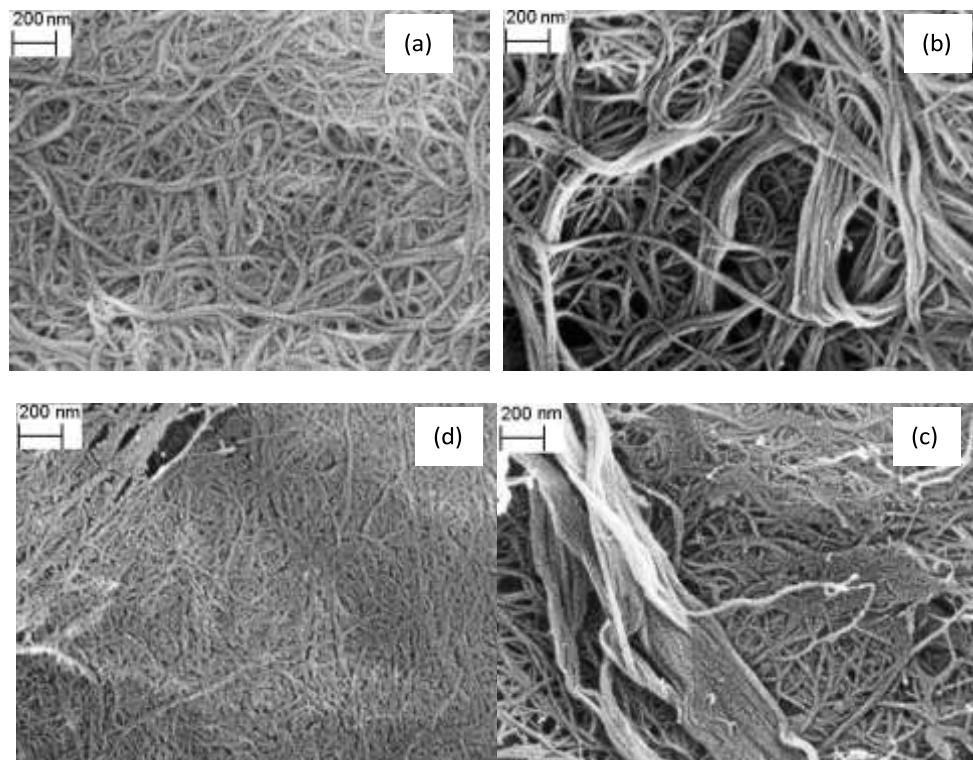


Figure 5. Scanning electron micrographs of control bucky paper and functionalized SWNT films. (a) Bucky paper; (b) JLH-67; (c) JLH-100; (d) JLH-111.

CHARACTERIZATION OF SURFACE AREA AND PORE SIZE DISTRIBUTION FOR ARYLCHLORIDE FUNCTIONALIZED SWNT

JLH-67 and JLH-100 exhibit isothermal type IV activity, indicating that these membranes have relatively big pores, but JLH-111 exhibits isothermal type V behaviour, indicating that the adsorptive molecules have a stronger affinity for one another than for the functionalized SWNT membranes (Figure 6).

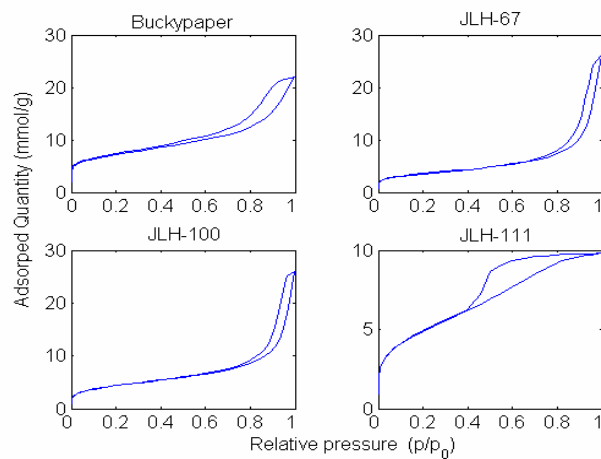


Figure 6. Adsorbed N_2 quantity vs. relative pressure of isothermal N_2 adsorption (77 K) for arylchloride functionalized SWNT electrodes with different degree of functionalization.

According to the DFT approach, the control SWNT and functionalized SWNT have pore sizes and pore size distributions that are depicted in Figures 7, respectively. In this study, it appears that the functioning impacts not just the pore size but also the pore size distribution. JLH-67 and JLH-100 contain very big holes and a wider pore size distribution, ranging from 1 to 300 nm, but JLH-111 has comparatively tiny pores, with some pores measuring less than 10 nm in diameter. According to the available evidence, the amorphous carbon formed via fictionalisation is responsible for the narrow pore size distribution of JLH-111. The production of amorphous carbon can be increased since a high fictionalisation degree can result in the destruction of additional SWNTs.

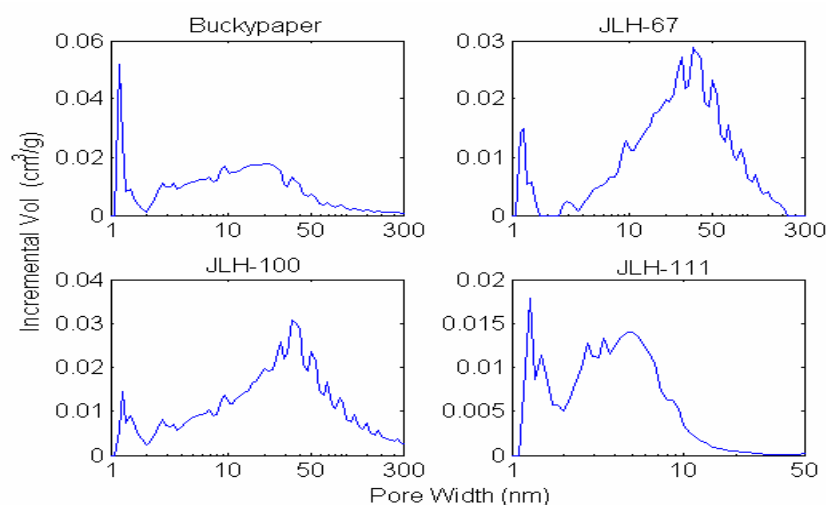


Figure 7. Pore size distribution determined by DFT model for arylchloride functionalized SWNT electrodes.

The pore volume of these samples is comparable among them (approximately $0.76 \times 0.90 \text{ cm}^3/\text{g}$ for bucky paper, JLH-67, and JLH-100), while the pore volume of the JLH-111 is more than twice as large as that of the bucky paper. The widening of interstitial pores caused by the intercalation of arylchloride may be responsible for the increased pore size. At least 20% more surface area is present on the control bucky paper when compared to the functionalized samples (Table 2). Various porosity parameters for functionalized SWNTs are listed in Table 2, as well as capacitance and other characteristics.

Table 2 Capacitance, surface area, and various porosity parameters of arylchloride functionalized SWNTs

Discharge current 1 mA		Bucky paper	JLH-67	JLH-100	JLH-111
Capacitance (F/g)	0.1 V	55	93	74	33
	0.7 V	41	47	38	6
	mean	49	74	53	20
BET surface area (m ² /g)		546	277	343	392
Total Pore Volume (cm ³ /g)		0.76	0.9	0.9	0.34
DFT surface area (m ² /g)	Total	297	182	189	206
	Micro	167	67	76	98
	Meso	128	75	109	107
	Macro	1.2	40	4	1
DFT Pore Volume (cm ³ /g)	Total	0.69	0.70	0.85	0.30
	Micro	0.11	0.04	0.05	0.07
	Meso	0.52	0.52	0.6	0.23
	Macro	0.06	0.14	0.2	0
C _{dl} (μF/cm ²) (0.1V capacitance)	BET	10	34	21	8
	DFT-Total	19	51	39	16
	DFT-Meso&Macro	43	81	65	30
Average Pore Size (nm)		5.6	13.0	10.5	3.5

* Micro, meso and macro pore refers respectively the pore size of < 2 nm, 2 nm – 50 nm, and > 50nm.

CONCLUSIONS

Producing meso porous SWNT/carbon composites by the stabilisation and carbonization of a ternary composite film consisting of PAN, SAN, and SWNT is a viable method of producing these composites.

The addition of single wall carbon nanotubes in the PAN/SAN blend affects the shape of the mixture. When it comes to membranes, the pore size of carbonised PAN/SWNT/SAN membranes is in the 5–200nm range, whereas the pore size of carbonised PAN/SAN mix film is in the 2–10m range. In 6 M KOH, the specific capacitance of carbonised PAN/SWNT/SAN composite film electrodes is higher than 100 F/g, indicating that they are highly capacitance. The presence of surface functional groups on the carbonised PAN/SWNT/SAN has resulted in an extremely high electrical double layer capacity (205 F/cm²), which has been attributed to the presence of the surface functional groups. According to the manufacturer's datasheet, the double layer capacity of activated carbon is in the region of 10 - 50 F/cm². Compared to aqueous electrolytes, carbonised PAN/SWNT/SAN films show lower capacitance in ionic liquid than they do in aqueous electrolytes, despite the fact that they have better affinity in ionic liquid than in 6 M KOH. SWNT membranes coated with pyrrole exhibit high specific capacitance (350 F/g) and double layer capacity (154 F/cm²), indicating that they have a high double layer capacity. Particularly, the specific capacitance of pyrrole treated SWNT membranes rose monotonically with increasing macro surface area, indicating that macro pores (pores larger than 50 nm in diameter) are critical for generating high capacitance.

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