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# Safer Production of Water Dispersible Carbon Nanotubes and Nanotube/Cotton Composite Materials

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Additional information is available at the end of the chapter

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## Abstract

Water-dispersible carbon nanotubes (WD-CNTs) have great importance in the fields of biotechnology, microelectronics, and composite materials. Sidewall functionalization is a popular method of enhancing their dispersibility in a solvent, which is usually achieved by strong acidic treatment. But, treatment under such harsh conditions deviates from green chemistry and degrades the structure and valuable properties of CNTs. Alternative safer and easier plasma method is discussed to produce functionalized CNTs (*f*-CNTs). The *f*-CNTs remain dispersed in water for more than 1 month owing to the attachment of a large number of carboxyl groups onto their surfaces. The WD-CNTs are applied to produce conductive cotton textile for the next generation textile technologies. Nonconducting cotton textile becomes electroconductive by repeatedly dipping into the *f*-CNT-ink and drying in air. The *f*-CNTs uniformly and strongly cover the individual cotton fibers. After several cycle of dipping into the *f*-CNT-ink, the textile becomes conductive enough to be used as wire in lighting up an LED. As a demonstration of practical use, the textile is shown as a conductive textile heater, where the textile can produce uniformly up to *ca.* 80°C within *ca.* 5 min by applying an electric power of *ca.* 0.1 W/cm<sup>2</sup>.

**Keywords:** carbon nanotubes, plasma-functionalization, water dispersibility, electroconductive cotton, nanocomposites

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## 1. Introduction

Carbon nanotubes (CNTs) possess a unique place in nanoscience owing to their exceptional electrical, thermal, and mechanical properties [1]. They have found applications in areas diverse as composite materials, energy storage and conversion, sensors, drug delivery, field emission devices, and nanoscale electronic components [2]. Water-dispersible CNTs (WD-CNTs) have

great importance in the fields of biotechnology, microelectronics, and composite materials [2–5]. However, the stable dispersion of CNTs in solvent without changing their physical properties is a significant challenge and a prerequisite for their applications [6–8]. Sidewall functionalization is a popular method of enhancing the dispersibility of CNTs, which is achieved usually by oxidizing CNTs by strong acids or oxidative gases [6, 9–10]. But, treatment under such harsh conditions deviates from green chemistry, and effect in the change of the CNT structure [9–11], which markedly degrade their basic properties [6, 12]. To overcome these problems, alternative safer and easier functionalization methods should be considered. In this chapter, we will discuss about different functionalization methods, especially, the method we have developed in our laboratory to functionalize the CNTs to enhance their water dispersibility.

Possible applications of WD-CNTs will also be discussed, where we will demonstrate the applications of the WD-CNTs to produce conductive cotton textile for the next generation textile technologies. Integration of electronics is one of the smart applications of the textile, which covers the applications in high-performance sportswear, wearable displays, new classes of portable power, and embedded health monitoring devices [13–20]. Recently, interests on the preparation of lightweight and flexible electrothermal materials have been increased for the aviation and aerospace industries, microreactor technologies, and different kinetic systems [14–20]. Resistive wires made of metal alloys have been used as the heat source in many appliances, but in those cases flexibility is poor, and the heat is localized at the wires [20]. If flexible cotton textile can be used as a heating element, it would offer a spectrum of advantages over these traditional materials [13, 20–23].

## 2. Potential applications of CNTs

The properties of CNTs have caused researchers and companies to consider using them in several fields [2, 24].

### 2.1. In composite technology

Because CNTs have the highest strength to weight ratio of any known material, combining them with other materials into composites can be used to build lightweight spacecraft, windmill blades to increase the amount of electricity generated, stronger bicycle components made by adding CNTs to a matrix of carbon fibers, cables strong enough to be used for the space elevator to drastically reduce the cost of lifting people, and materials into orbit. In addition, new materials combined with nanosensors and nanorobots could improve the performance of spaceships, spacesuits, and the equipment used to explore planets and moons.

### 2.2. In biotechnology

CNTs can easily penetrate membranes such as cell walls [25]. The long and narrow shape makes them look like miniature needles, so it makes sense that they can function like a needle at the cellular level [25]. Medical researchers are using this property by attaching molecules to CNTs that are attracted to cancer cells to deliver drugs directly to the diseased cells. Another

interesting property of CNTs is that their electrical resistance changes significantly when other molecules are attached to the carbon atoms [26]. This property is utilized to develop sensors that can detect chemical vapors such as carbon monoxide or biological molecules [26]. They are also used to improve the healing process for broken bones by providing a CNT scaffold for new bone material to grow on.

### **2.3. In electronics**

CNTs can be used to increase the capabilities of electronics devices while reducing their weight, size, and power consumption, for example display screens on electronics devices or highly dense memory chips with a projected density of one terabyte of memory per square inch or greater. CNT ink is used in inkjet printers for printable electronics devices.

### **2.4. In environmental issue**

CNTs are being used in several applications to improve the environment. These include cleaning up existing pollution, improving manufacturing methods to reduce the generation of new pollution, and making alternative energy sources more cost effective. Inexpensive CNT-based sensor can detect bacteria in drinking water. Because of the small size of CNTs with high surface area, a few gas molecules are sufficient to change the electrical properties of the sensing elements. This allows the detection of a very low concentration of chemical vapors.

### **2.5. In energy**

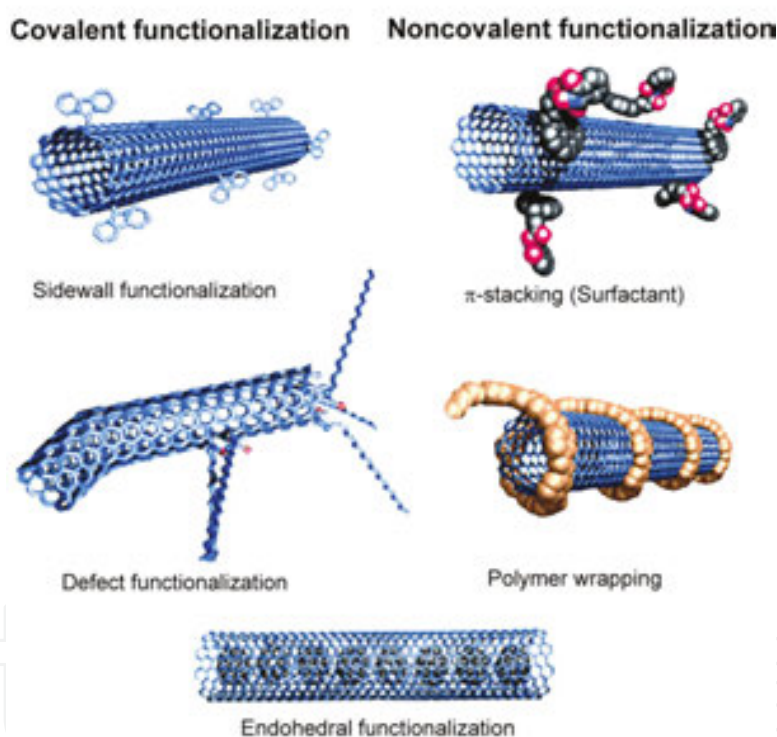
Use of CNT in solar cells can reduce manufacturing costs as a result of using a low temperature process instead of the high temperature vacuum deposition process typically used to produce conventional cells made with crystalline semiconductor material [27]. They can reduce installation costs by producing flexible rolls instead of rigid crystalline panels, and therefore can be installed as a coating on windows or other building materials as integrated photovoltaic [27]. CNTs can decrease the power needed to run reverse osmosis desalination plants because water molecules pass through CNTs more easily than through other types of nanopores. They are used to make current collecting layer for the cathode in batteries and as electrodes in thermocells that generate electricity from waste heat. Combining CNTs with buckyballs and polymers inexpensive solar cells can be produced by simply painting on a surface. CNT-based supercapacitors do even better than batteries in hybrid cars by significantly reducing the weight of the batteries needed to provide adequate power, increasing the available power, and decreasing the time required to recharge a battery.

### **2.6. In consumer products**

CNT has already found its way into lots of consumer products such as fabric, sporting goods, cleaning products, food, building materials, and skin care. The composite fabric with CNTs allows improvement of fabric properties without a significant increase in weight, thickness, or stiffness.

### 3. Functionalization of CNTs

CNTs in all their forms are difficult to disperse and dissolve in water or organic media [24, 28]. They are extremely resistant to wetting, which is very important for different applications. A suitable functionalization of the CNTs, i.e., the attachment of chemical functionalities represents a strategy for overcoming these barriers, and thus become an attractive target for synthetic chemists and materials scientists. Functionalization can improve dispersibility [29] and processibility, and will allow combination of the unique properties of CNTs with those of other types of materials. Chemical bonds might be used to tailor the interaction of the CNTs with other entities, such as a solvent, polymer and biopolymer matrices, and other nanotubes. Functionalized CNTs might have mechanical or electrical properties that are different from those of the unfunctionalized CNTs, and thus may be utilized for fine-tuning the chemistry and physics of CNTs.



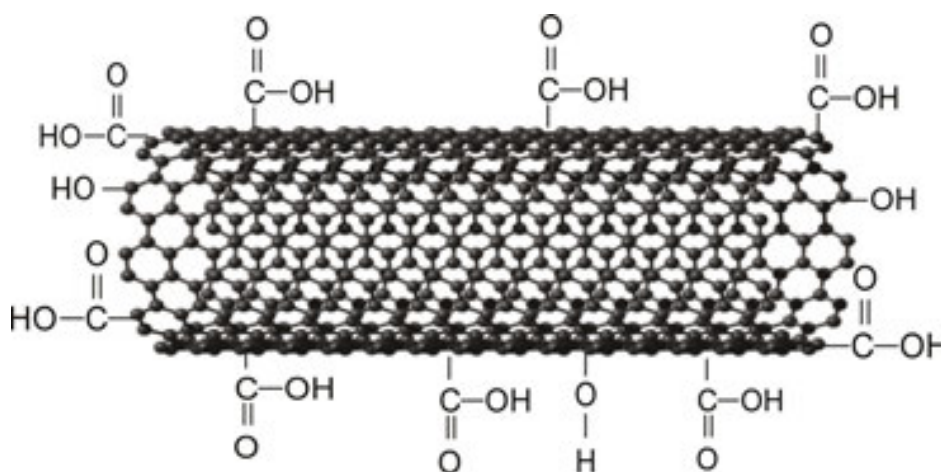
**Figure 1.** Different possibilities of the CNT functionalization. (Reproduced with permission of from ©2002, John Wiley and Sons [30]).

Both covalent and noncovalent functionalizations of CNTs are possible [6, 24, 31]. Different possibilities of these are the sidewall functionalization, defect-group functionalization, noncovalent exohedral functionalization with molecules through  $\pi$ -stacking, noncovalent exohedral functionalization with polymers, and endohedral functionalization as shown in **Figure 1**. Covalent functionalization is based on covalent linkage of functional entities onto the nanotube's carbon scaffold. It can be performed at the termini of the tubes or at their sidewalls. Direct covalent sidewall functionalization is associated with a change of hybridi-



zation from  $sp^2$  to  $sp^3$  and a simultaneous loss of conjugation. Defect functionalization takes advantage of chemical transformations of defect sites already present. Defect sites can be the open ends and holes in the sidewalls, which are terminated by carboxylic groups, and pentagon and heptagon irregularities in the graphene framework. Oxygenated sites, formed through oxidative purification, have also been considered as defects. A noncovalent functionalization is mainly based on supramolecular complexation using various adsorption forces, such as van der Waals' and  $\pi$ -stacking interactions. All these functionalizations are exohedral derivatizations. A special case is the endohedral functionalization of CNTs, i.e., filling of the tubes with atoms or small molecules [6, 32]

### 3.1. Functionalization to increase water dispersibility



**Figure 2.** Section of an oxidized CNT, reflecting terminal and sidewall oxidation.

One of the most common functionalization techniques is the oxidative treatment of CNTs by liquid-phase or gas-phase oxidation, introducing carboxylic ( $-COOH$ ) groups and some other oxygen-bearing functionalities such as hydroxyl, carbonyl, ester, and nitro groups into the tubes. In this process, CNTs are treated by strong acids, such as refluxing in a mixture of sulfuric acid and nitric acid [9, 10], “piranha” solution (sulfuric acid-hydrogen peroxide) [11], boiling in nitric acid [12], or treating with oxidative gases, such as ozone [6, 33]. Upon oxidative treatment the introduction of  $-COOH$  groups and other oxygen-bearing groups at the end of the tubes and at defect sites is promoted, decorating the tubes with a somewhat indeterminate number of oxygenated functionalities. However, mainly because of the large aspect ratio of CNTs, considerable sidewall functionalization takes place (**Figure 2**) [34]. However, treatment under such harsh conditions clearly deviates from green chemistry, and results in the opening of the tube tips [9], shortening of the tubes [11], and fragmentation of the sidewalls [12]. These markedly degrade their basic properties [6, 35]. Since reactivity is a function of curvature [36],

the oxidative stability also depends on the tubes' diameter and on the production process responsible for the tubes' dimensions [37].

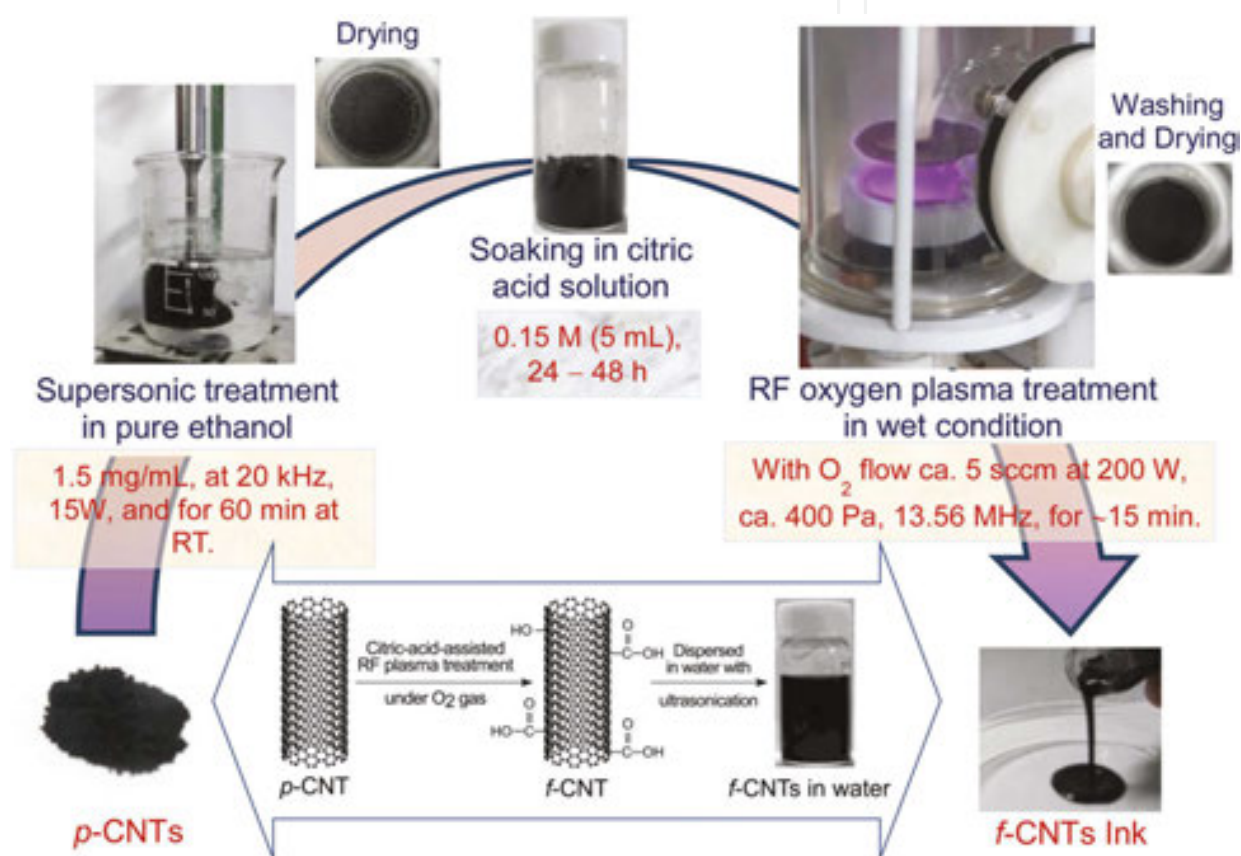
The surface modification of CNTs can be carried out through a wide range of plasma processes, which provide a cost effective and environmentally friendly alternative to other processes, related to environmental issues [38] and biomedical applications [39]. Compared with other chemical modification methods, the plasma-induced functionalization presents interesting properties, is solvent-free and time efficient process. Moreover, this treatment allows the grafting of a wide range of different functional groups depending on the plasma parameters such as power, gas used, duration of treatment, and pressure [40]. In addition, the amount of functional groups can also be tailored. This is important since having saturation of these groups on the surface can alter the electronic conductivity of CNTs. The most common plasma treatment of CNTs is the low pressure RF cold plasma, which is successfully used to bind oxygen [41], hydrogen [42], and fluorine groups [43]. It has been observed that a complete purification of CNTs can also be reached out after their treatment in glow discharges (RF or MW) [44]. However, it was also observed that the average diameter of CNTs decreases with treatment duration. Therefore, the nature of the plasma gas is important, because oxygenated ions or radicals are very reactive in the etching processes. However, destruction of CNT sidewalls is also observed for other less reactive plasma gas such as  $\text{CF}_4$  or Ar [45, 46]. Moreover, it was shown that UV photons promote the defunctionalization of moieties grafted on the CNTs [47]. A probable solution could be the reduction of the power supplied to the plasma or duration of the treatment to limit destruction of the sidewalls. In this work, RF plasma is used to functionalization the CNTs using a parallel plate capacitively coupled reactor.

#### 4. Methodology of the research

Here, an environmentally friendly approach to functionalizing CNTs has been described, which is developed to attach  $-\text{COOH}$  groups onto their surfaces, and carried out under a wet condition using citric acid solution in RF (13.56 MHz) oxygen plasma [48, 49]. CNTs are first pretreated supersonically in ethanol. Then they are wetted with citric acid solution and subsequently treated using oxygen plasma including citric acid and water. This method is safer than the methods available in the literature, as no hazardous reagents are used here. The surfaces of the CNTs are chemically functionalized with  $-\text{COOH}$  groups, and they can be easily dispersed in water. To achieve the main objective of avoiding the destruction of the structure, which could change the valuable properties of CNTs, the functionalize conditions are optimized in each step. The functionalized CNTs can be used as a multifunctional coating material in improved electronic applications [3], in energy storage devices [50], as well as in the pharmaceutical industry, particularly in the area of drug delivery or as components of biosensors [4, 51]. They are also highly suitable as a filler component for water-soluble polymer composites [4].

#### 4.1. Functionalization of CNTs

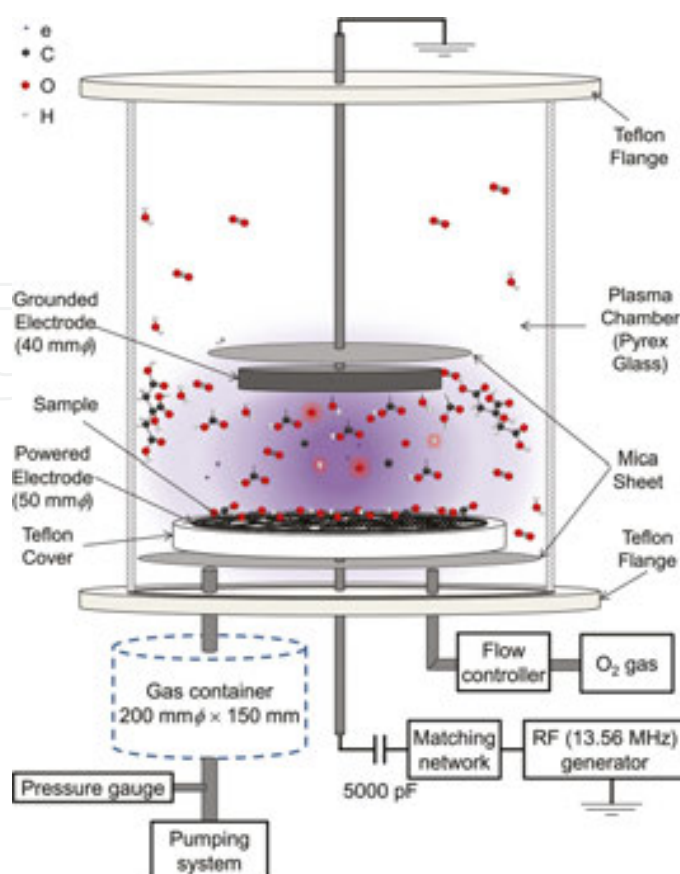
A flow chart of the functionalization process is shown in **Figure 3** and the setup of the plasma reactor, indicating the dissociation of oxygen, water, and citric acid molecules is shown schematically in **Figure 4**. 20–30 mg of CNT powder (Sigma-Aldrich, outer diameter = 10–30 nm, inner diameter = 3–10 nm, length = 1–10  $\mu\text{m}$ , purity >90%) is added to 20 mL of pure ethanol (Wako Pure Chemicals Co., purity >95%) and sonicated at room temperature using a supersonic homogenizer (Sonics Vibra cell, VC 130, Sonic & Materials Inc.,  $f = 20\text{ kHz}$ , 6.0 mm  $\phi$  probe) at an input power of 15 W for 60 min.



**Figure 3.** The flow chart of the functionalization process with the optimum treatment conditions and the schematic of the functional group attachment.

The suspension is dried under reduced pressure and soaked in 0.15 mole (5 ml) of citric acid (Wako Pure Chemicals Co., assay >98%) solution for more than 24 h. The CNTs in the solution are then placed on the lower electrode (SUS, 50 mm $\phi$ ) of a plasma reactor as shown in **Figure 4**, which is evacuated to ca. 400 Pa using a rotary pump at a very slow rate. When the wet phase starts to disappear, oxygen gas is introduced into the reactor at a rate of 5 sccm and the background chamber pressure is kept at about 400 Pa. Though the water molecules, and part of the citric acid molecules evaporate, it is considered that they remain inside the chamber and in the gas container connected to the chamber, and contribute to the functionalization process. Then the plasma reaction is carried out for about 15 min by an RF input power of  $P_{\text{rf}} = 200\text{ W}$ ,





**Figure 4.** Schematic diagram of the plasma reactor.

$f = 13.56$  MHz. The reflected RF power is minimized ( $< 20$  W) by controlling the matching network during the plasma reaction. It is noted that when the samples become fully dried before starting the plasma reaction, they are less reactive for the oxygen plasma. However, when the plasma started in the wet phase, the water molecules and part of the citric acid molecules evaporate with the processing time, and considered to remain inside the chamber and in the gas container connected to the chamber, contributing to the functionalization process. After the treatment, the CNTs are washed at least three times using pure water (Wako Pure Chemicals Co., distilled water) and dried under reduced pressure at room temperature. It is observed that approximately 13% of the CNTs are lost by the oxygen plasma, which is measured from the mass difference of the samples before placing in the citric acid and after the final washing process.

## 4.2. Characterizations

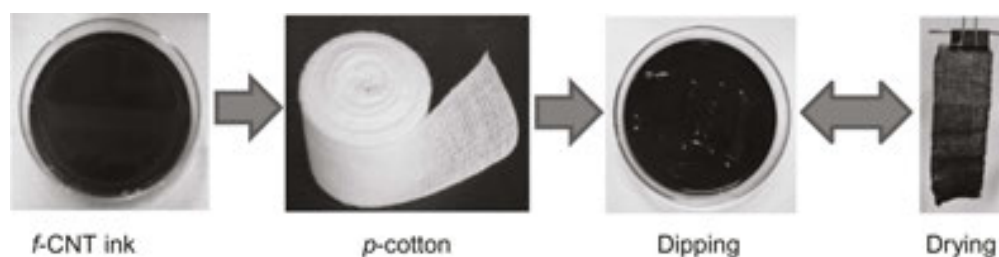
The dispersibility and dispersion stability of CNTs are primarily observed by mixing 20 mg of CNTs in 10 mL of pure water with bath sonication for 2 min, then keeping the mixture undisturbed for more than 20 days. To confirm the dispersion stability of the pristine, and plasma-treated CNTs (hereinafter denoted as *p*-CNTs and *f*-CNTs, respectively ca. 1.0 mg of the dried sample is mixed with 8.0 mL of pure water with brief sonication for 2 min in a bath

sonicator (Iuchi Japan, US-1, 110 W, 38 kHz) so that they are dispersed homogeneously. Then the sample is placed in a quartz cuvette ( $1.0 \times 1.0 \times 4.5 \text{ cm}^3$ ) and the change in the absorbance ( $Abs$ ) at a wavelength of 250 nm is observed for 4 h using a UV-visible spectrometer (JASCO V-630). Here, the wavelength is chosen corresponding to the maximum absorbance region of the UV-visible spectra, because according to Beer's law, the relationship between the absorbance and the concentration of the absorbing particles remain linear up to higher concentration in this region as compared to other region [52].

FT-IR spectroscopy is used to identify the chemical groups attached onto the CNTs. Approximately 0.5 mg of the dried sample is dispersed in 1.0 mL of propanol, and the mixture is uniformly coated on a  $\text{CaF}_2$  substrate (Sigma Koki Co., 20 mm diameter and 1 mm thickness), dried, and measured using an FT-IR spectrometer (Shimadzu Co., 8700, 100 scans averaged). The spectra in this thesis are presented after baseline correction.

The dispersibility of the CNTs is also observed by a TEM (JEOL JEM-1400 Plus, acceleration voltage of 120 kV), and their structural quality is measured by a Raman spectrometer (JASCO Co., NR-1800,  $\lambda = 532 \text{ nm}$ ). For thermal analyses a thermogravimetric analyzer (Rigaku Thermo plus TG8120) is used, which is operated under air ambient at a heating rate of 10 K/min from room temperature to 973 K [48].

#### 4.3. Preparation of the cotton nano-composites



**Figure 5.** Coating scheme of the *f*-CNTs/cotton textile.

To obtain the cotton composite, *f*-CNTs are dispersed into water to produce stable [49]. A piece of 100% cotton (*p*-cotton) textile of ca. 24 mesh/inch with thread diameter of ca. 0.25 mm is repeatedly dipped into the 0.25–1.0 wt% of the *f*-CNT ink and dried at room temperature. The steps of the *f*-CNT loading process in the cotton textile are shown in **Figure 5**. The textile sheet is dipped and dried repeatedly until the electrical resistance becomes of the order of several  $\text{k}\Omega$  for an area of  $5 \times 5 \text{ cm}^2$ . To calculate the amount of the loaded *f*-CNTs ( $W_{\text{nt}}$ ), the cotton textile is weighed before dipping in the *f*-CNT ink and after drying it sufficiently.

#### 4.4. Measurements

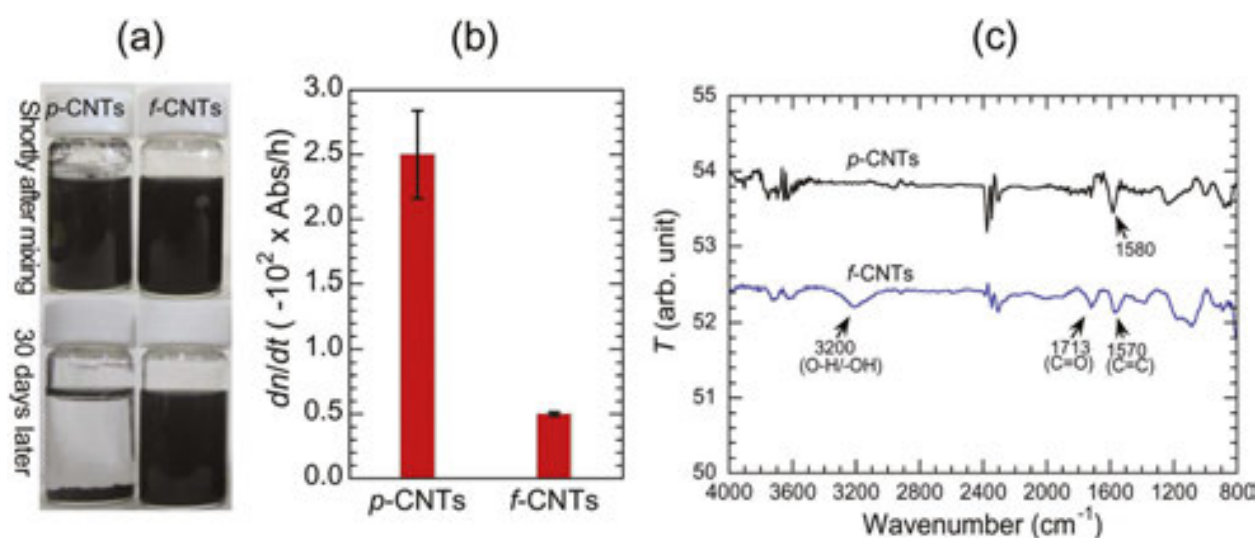
Electrical resistance,  $R = V/I$ , of the textile is obtained from the current,  $I$ , in the circuit, and potential drop,  $V$ , across the sample measured by a digital multimeter (Iwatsu VOAC 87, Japan). A dc voltage,  $V_{\text{inv}}$ , is applied by a regulated power supply (Kikusui Electronics PAB 350–0.2, Japan) between two Nickel electrodes (thickness of 0.15 mm, 40 mesh, Nilaco Co.,

Japan) of width  $D$  placed on the coated cotton textile at a distance  $L$ . The sheet resistance ( $R_s$ ) of the textile is then calculated using the formula:  $R_s = R/(D \times L)$ . The coating uniformity of CNT on the cotton fibers is confirmed by the SEM images taken by a JEOL JSM 6510LV SEM at an operating voltage of 20 kV, and the thermal stability of the textile is observed by a TG/DTA (Rigaku Thermo Plus TG 8120). The temperature of the  $f$ -CNTs/cotton textile is measured using a thermometer (ASONE TM-301) and an infrared camera (FLIR i3, emissivity 0.95, focus length = 6.8 mm). A standard washing test is also performed on the coated textile using a standard launder meter to study the toughness of the  $f$ -CNTs on the cotton fibers.

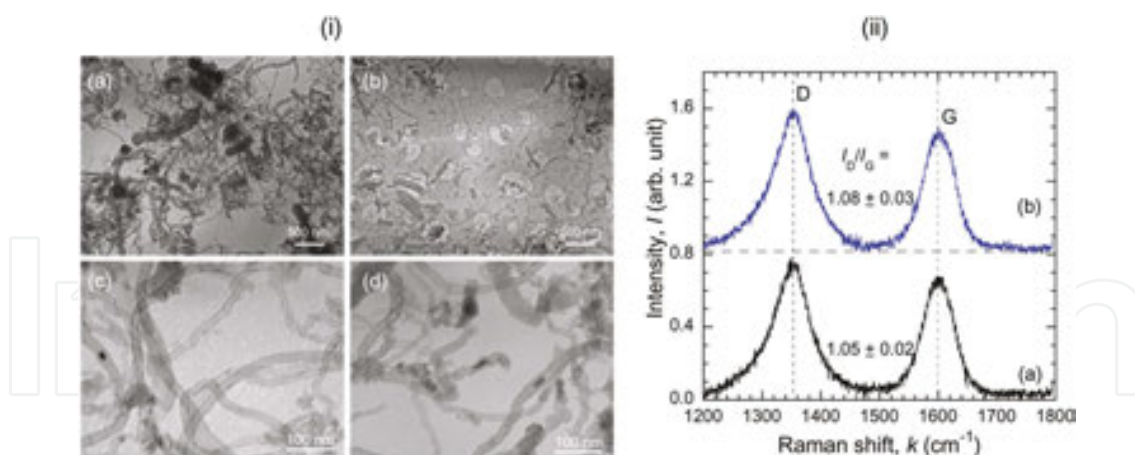
## 5. Results and discussions

### 5.1. Functionalization of CNTs

The enhancement of dispersion stability is confirmed from visual observation of the mixer of CNTs in pure water and measuring the settling speed for a dispersion using the absorbance data of the UV-visible spectroscopy as shown in Figures 6(a) and (b), respectively [48]. Attachment of the functional groups onto the CNTs is studied by a Fourier transform infrared (FT-IR) spectrometer (Shimadzu Co., 8700, 100 scans averaged). The FT-IR spectra of the  $p$ -CNTs and  $f$ -CNTs are presented in **Figure 6(c)** after the base line correction. The  $f$ -CNT spectrum shows additional peak compared to that of the  $p$ -CNTs at *ca.*  $1713\text{ cm}^{-1}$ , which corresponds to the C=O stretching bonds, and the broad band at *ca.*  $3200\text{ cm}^{-1}$  corresponding to the O-H/-OH bonds [48]. Therefore, carboxyl groups are considered to be attached on the CNTs after functionalization.



**Figure 6.** (a) Photographs of the dispersion of 20 mg of  $p$ -CNTs and  $f$ -CNTs in 10 mL of pure water using 2 min of bath sonication. (b) Settling speed,  $dn/dt$ , calculated from the  $Abs$  (250 nm) versus *time* graphs for the  $p$ -CNTs and  $f$ -CNTs. (c) FT-IR spectra of the  $p$ -CNTs and  $f$ -CNTs.

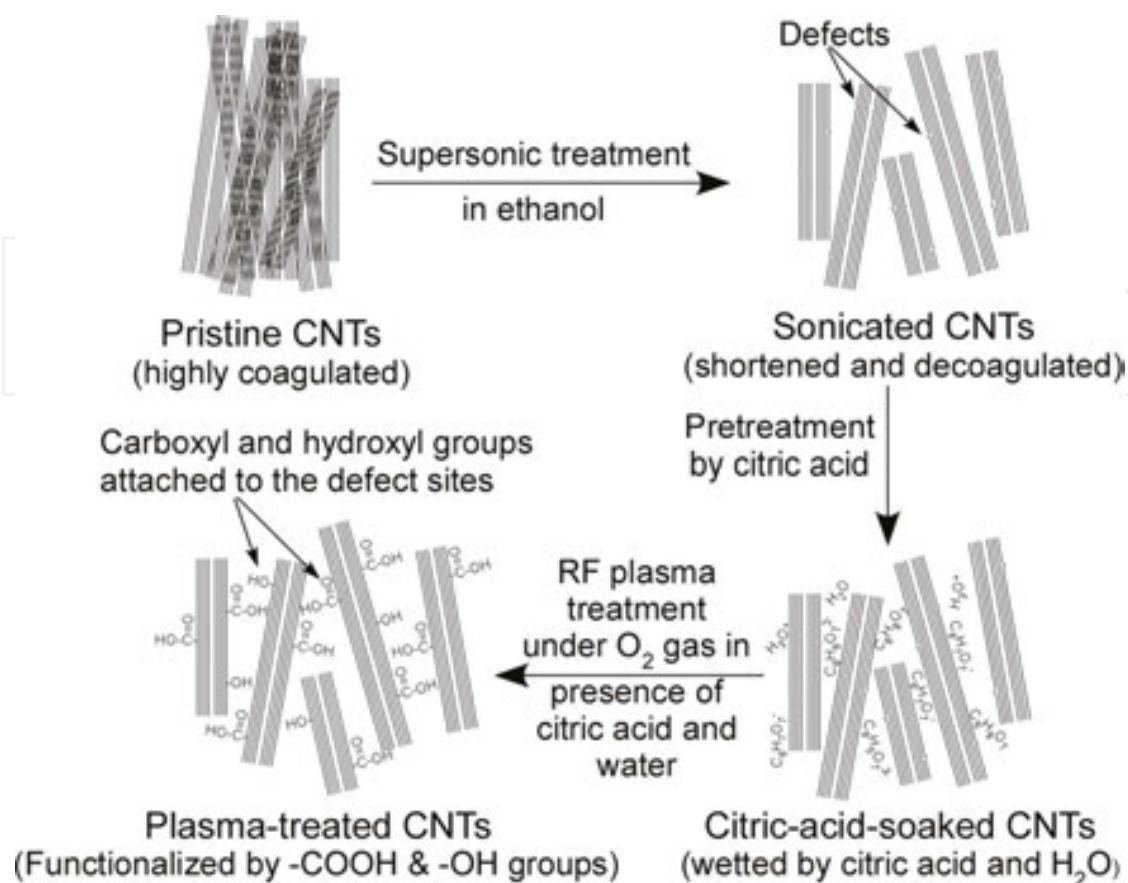


**Figure 7.** (i) TEM images of the (a, c) *p*-CNTs, and (b, d) *f*-CNTs in two different magnifications. (ii) Raman spectra of the (a) *p*-CNTs, and (c) *f*-CNTs.

The improved dispersion of the *f*-CNTs is further confirmed from the transmission electron microscope (TEM; HITACHI High Technology Co., H-7500, acceleration voltage of 100 kV) images as shown in **Figure 7(i)**. Compared to the *p*-CNTs, the dispersibility of the *f*-CNTs is enhanced clearly as shown in **Figure 3(a) and 3(b)**. In the higher magnification images, it is observed that the structural quality of the CNTs remain similar after the citric-acid-assisted RF plasma functionalization, which is also confirmed from the Raman spectroscopy as shown in **Figure 7(ii)**, which are normalized and bodily shifted in the intensity axis. [48]. Because, Raman spectrum is considered to be an important tool to study the CNT structure [53, 54] and is widely used to assess the amount of defects [55, 56]. The defect-induced D band appears at ca. 1350 cm<sup>-1</sup>, which indicates the amount of disordered carbon in the CNT structure, and its intensity,  $I_D$ , corresponds to the degree of disorderness. The G band ca. 1600 cm<sup>-1</sup> corresponds to the graphitic (ordered) carbon, and its intensity,  $I_G$ , corresponds to the amount of ordered carbon. Therefore, the ratio,  $I_D/I_G$ , is used to estimate the change in structural quality of CNTs after functionalization in different processes. Defect density corresponding to  $I_D/I_G$  for the *p*-CNTs and *f*-CNTs are observed to be  $1.05 \pm 0.02$ , and  $1.08 \pm 0.03$ , respectively. The changes are very small, and also no distinct changes are observed in terms of the Raman shift. These suggest that the CNT structure and the chemical composition of the interior of the CNTs are almost unaffected by the ultrasonic and plasma treatments.

On the basis of the above results, the basic functionalization scheme of the CNTs by the citric-acid-assisted oxygen plasma treatment is summarized in **Figure 8**. CNTs are long, web-like, and remain strongly aggregated. When they are dispersed in ethanol by the supersonic treatment, ethanol molecules enter the aggregated parts of the CNTs and weaken the attractive forces between them. When the sonicated CNTs are placed in the citric acid solution, the citrate and hydronium ions attack their weak parts. During the plasma reaction, oxygen, water, and citric acid molecules or ions are fragmented to generate oxygen containing ions, radicals, and CO or CO<sub>2</sub>, which react with the defect sites [56–58]. The CO and CO<sub>2</sub> are oxidized to form –COOH groups and attach to the CNT surfaces [59]. Also, the attached –OH groups are further oxidized to form –COOH groups [58, 60]. These functional groups enable the CNTs to readily





**Figure 8.** A model of the functionalization process of CNTs [48].

disperse in water due to hydrogen bonds formed between the carboxylic acid groups and water molecules [61]. The negatively charged surfaces of the CNTs repel each other and prevent them from coagulating. The polar interactions of the functional groups with the water molecules reduce the settling speed of the *f*-CNTs [56].

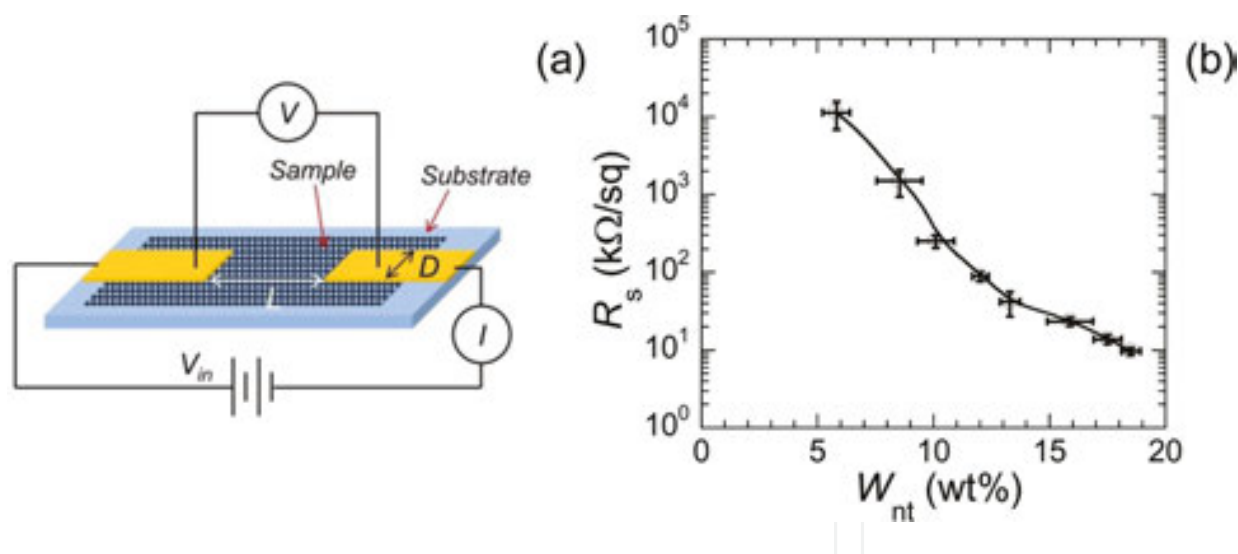
Hussain et al. functionalized CNTs by  $H_2O$  plasma treatment under controlled environment. Through the controlled functionalization process the electrochemical properties of the CNTs were modified, expanding the range of potential applications of the *f*-CNTs in the field of energy and environment [62]. The different oxygen containing groups attached on to the surfaces of the nanotubes change the physicochemical properties of the CNTs. After the plasma treatment, the specific capacitance of the CNTs increased from 23 up to 68  $Fg^{-1}$ . Hordy et al. [63] functionalized the grown CNTs via an  $Ar/O_2/C_2H_6$  capacitively coupled RF plasma discharge. CNTs are grown directly from a stainless steel mesh and are subsequently plasma functionalized in the same reactor. The functionalized CNTs removed from the substrate are found to remain stable for extended periods of time. But in this case acidic pre-treatment step were followed and the process needed some complicated steps. Chen et al. [56] worked on attaching functional groups other than oxygen containing groups on to the CNTs, such as amine groups by using a microwave-excited  $NH_3/Ar$  surface-wave plasma. This functional



group improved the hydrophilicity of CNTs, though the atomic composition and structural properties of the *f*-CNTs were compromised.

## 5.2. Properties of the cotton nanocomposites

When the *p*-cotton textile is dipped into the *f*-CNT ink it becomes easily coated with the *f*-CNTs. After sufficient amount of loading ( $>5.0$  wt%), the coated textile shows measurable resistance,  $R$ . The schematic setup of the resistance measurement is shown in **Figure 9(a)**. This is owing to the formation of conducting path on the cotton fibers.  $R$  values of the coated textile are observed to vary linearly with  $L$ . As  $W_{nt}$  increases with the dipping-drying cycles,  $R_s$  of the *f*-CNTs/cotton textile decreases gradually as shown in **Figure 9(b)**. The *f*-CNTs/cotton textile becomes conductive with  $R_s$  *ca.*  $9.65 \text{ k}\Omega/\text{sq}$ , when  $W_{nt}$  is *ca.*  $18.5$  wt%. After first and second dipping cycles, only parts of the textile become poorly conductive. However, after 5-6 cycles of dipping, the variation of  $R_s$  along the width or length becomes very small indicating the homogenous coating of the cotton textile. Comparing the  $R_s$  of the *f*-CNTs/cotton textiles (*ca.*  $10^2 \text{ k}\Omega/\text{sq}$ ) with those of the *p*-CNTs/cotton textiles (*ca.*  $10^5 \text{ k}\Omega/\text{sq}$ ) for the same  $W_{nt}$ , it is realized that homogenous dispersion of the CNTs is very important in the coating process. When thickness of the *f*-CNTs/cotton textile is,  $b \approx 0.5 \text{ mm}$ , the bulk resistivity,  $\rho = [R (D \times b)]/L$ , is calculated to be *ca.*  $2.3 \text{ k}\Omega\cdot\text{m}$ , and the conductivity,  $\sigma = 1/\rho$ , is *ca.*  $0.43 \text{ S/m}$ .



**Figure 9.** (a) Schematic setup of the sheet resistance ( $R_s$ ) measurement. (b) The  $R_s$  versus the loaded *f*-CNTs,  $W_{nt}$ , in the cotton textile [49].

SEM images of the *p*-cotton and *f*-CNTs/cotton textiles at different magnifications are presented in **Figure 10**. It is observed that the *f*-CNTs coat the cotton fibers uniformly, and are firmly attached to them as shown in the cross sectional view of the fiber in **Figure 10(c)**. Cotton has hydroxyl groups in the cellulose fibers [13, 22, 64], which enable the *f*-CNTs to form strong hydrogen bonds with the surfaces of the fibers, resulting in the high density network coating [13, 65, 66].

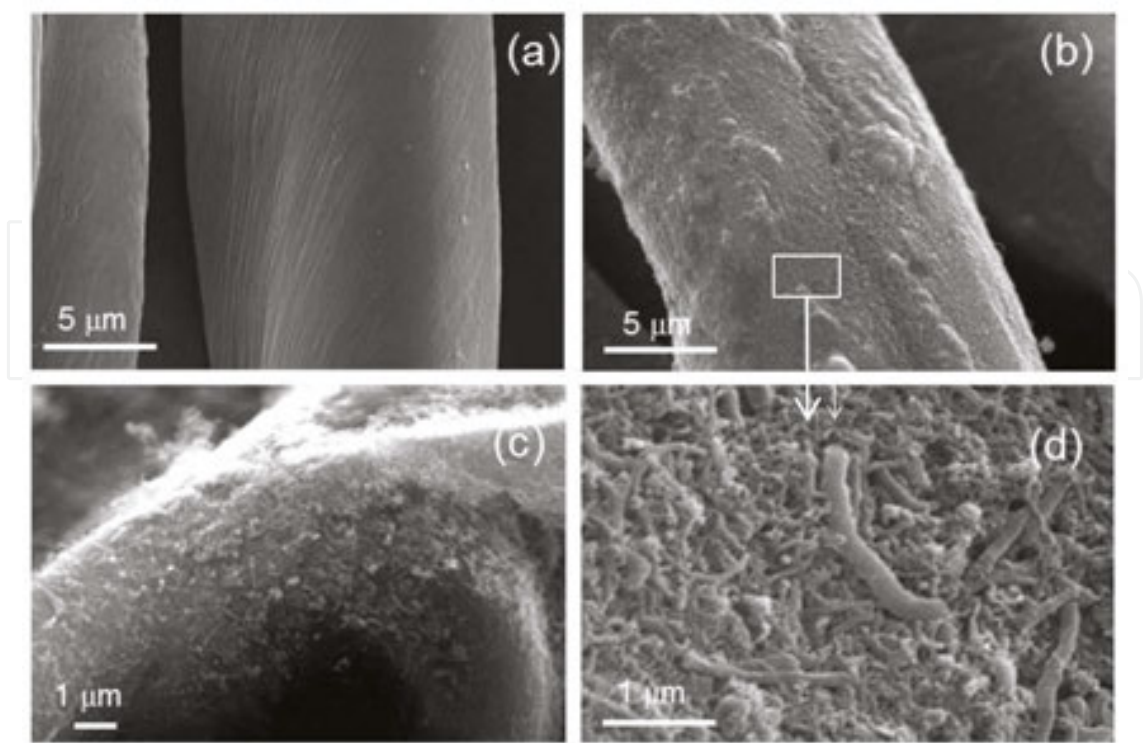


Figure 10. SEM images of the (a) *p*-cotton, (b–d) *f*-CNTs/cotton textile.

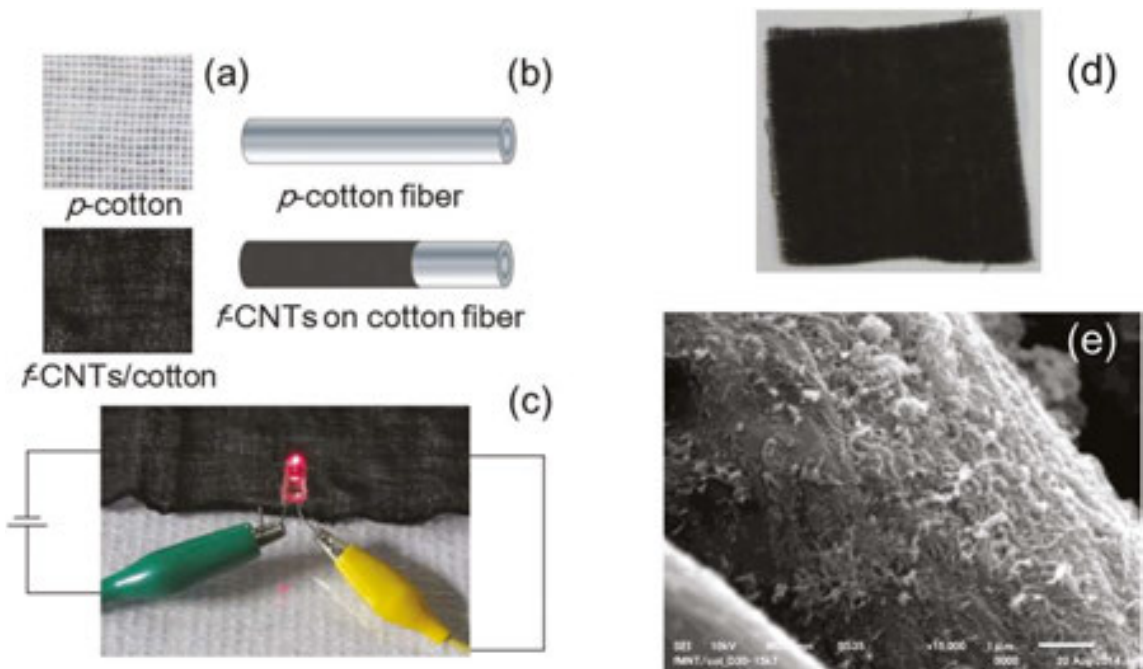


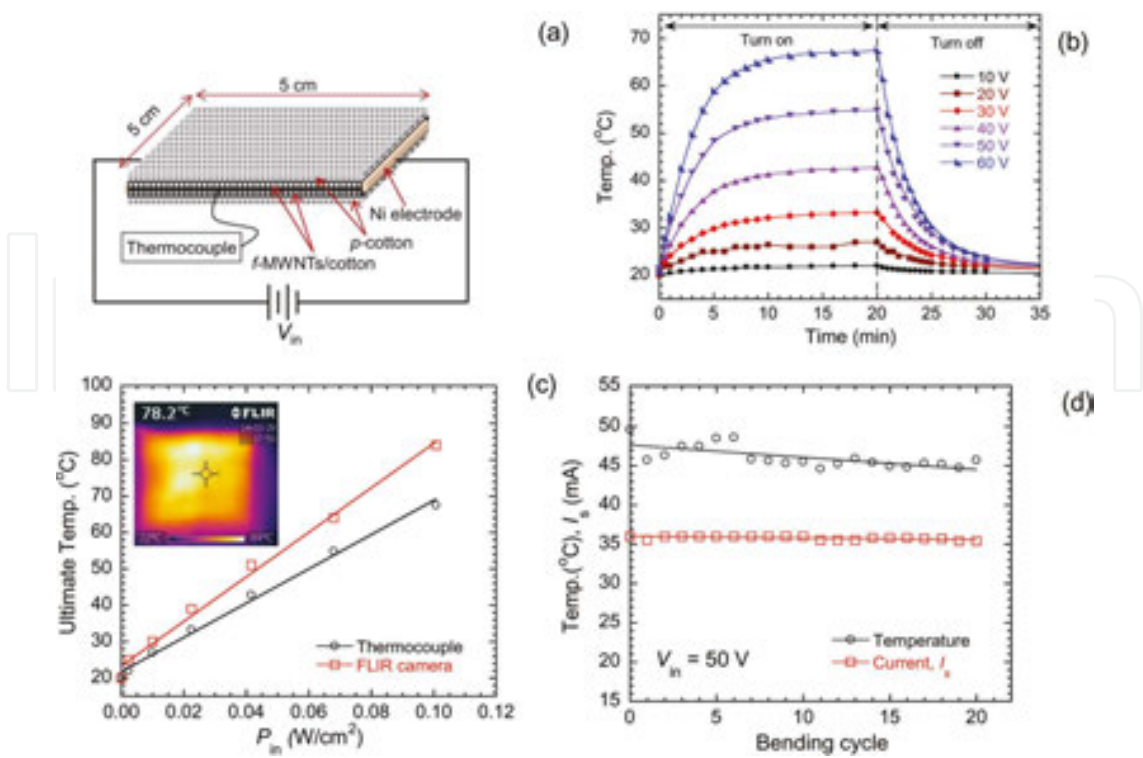
Figure 11. (a) Comparison between the *p*-cotton (upper) and *f*-CNTs/cotton (lower) textiles. (b) Schematic of the fiber coating. (c) The *f*-CNTs/cotton textile acting as a conducting path in the emission of an LED. (d) The textile after a standard washing test for 30 min, (e) SEM image of the cotton fiber after the washing test.

After dipping in the *f*-CNT ink, the *p*-cotton textile becomes black as shown in **Figure 11(a)**, which is owing to the formation of CNT network armor on each cotton fiber as shown schematically in **Figure 11(b)**. After 10 cycles of dipping in 0.5 wt% *f*-CNT ink, the resulting *f*-CNTs/cotton textile becomes conductive with  $\sigma$  more than *ca.* 0.20 S/m. As a demonstration of the conductivity, an LED device connected to a dc source can be easily powered through the prepared conducting textile as shown in **Figure 11(c)**. It is observed that the *f*-CNTs cannot be removed from the coated textile after normal washing, and the *f*-CNTs/cotton textile remain as black as it is just coated. To study the toughness of the *f*-CNTs on the cotton fiber, a piece of *f*-CNTs/cotton textile is washed in a standard launder meter with detergent/DI water (0.5 g/L) at a temperature of  $40 \pm 2^\circ\text{C}$  with a revolution rate of 0.67 Hz for 30 min. It is observed that only a very little portion of the loaded *f*-CNTs are removed from the textile and lots of CNTs still remain on the fiber as shown in **Figure 11(d) and (e)**, suggesting the high level of toughness of the *f*-CNTs on the textile.

Thermal conductivity of the *f*-CNTs/cotton textile is observed to be *ca.* 0.045 W/mK, which suggests *ca.* 70% improvement. It is conjectured that strong bonding between the *f*-CNTs and the cotton fibers ensure better heat transfer in the textile [22, 66]. From the thermogravimetric study, it is observed that the final combustion of the *f*-CNTs/cotton textile is delayed by *ca.* 100°C as compared to *p*-cotton, signifying the improved thermal stability of the textile. This improvement in thermal stability is due to the uniform coating of the cotton fibers by the *f*-CNTs, because thermal stable CNTs act as armor for the cotton fibers protecting them from burning in a relatively lower temperature. The combustion processes of the *p*-cotton and *f*-CNTs/cotton textiles are studied by hanging them on a metal supporter, and then igniting simultaneously by a gas flame. It is observed that the *p*-cotton textile catches fire immediately and burns quickly to ashes completely. However, the *f*-CNTs/cotton textile becomes charred only, which provides direct evidence of improved flame retardancy.

### 5.2.1 The textile as a low powered flexible heater

The above results strongly suggest that the *f*-CNTs/cotton textile can be used as an electro-thermal heating element. The electric heating behavior of the patterned textiles is evaluated by measuring the changes in the resistance and temperature under  $V_{\text{in}} = 10 \times 60 \text{ V}$ . When few layers of such *f*-CNTs/ cotton textiles ( $5 \times 5 \text{ cm}^2$ ) is stacked together, the resultant R values become low enough to produce heat applying small voltages based on the Joule heating from electric power [67, 68]. When  $V_{\text{in}}$  is applied through a four layered such textile of  $R_s$  *ca.* 1.67 k $\Omega$ /sq as shown schematically in **Figure 12(a)**, it is observed that heat starts to radiate from the textile indicating the increase in temperature with time as presented in **Figure 12(b)**. The little difference between the thermocouple-based and infrared-based measurements shown in **Figure 12(c)** validates the data obtained from the measurement, which is because of the slow response of the thermocouple owing to the slow heat propagation [69]. Temperature of the *f*-CNTs/cotton textile can be increased above 60°C within 5 min depending on the applied voltage.



**Figure 12.** Heating and cooling temperatures of the *f*-CNTs/ cotton textile of  $R_s = 1.67 \text{ k}\Omega/\text{sq}$  using a dc power supply. (a) Schematic of the heat measurement setup. (b) Heating and cooling temperatures at the center of the textile with time measured by a thermocouple. (c) The increase in ultimate temperature of the *f*-CNTs/cotton textile with input power (inset: thermal image at  $V_{in} = 60 \text{ V}$  showing the uniform heating of the textile). (d) Changes in the temperature and current after repeated bending.

When an electric power of approximately  $0.1 \text{ W/cm}^2$  is applied to the textile its temperature increases uniformly to ca.  $84^\circ\text{C}$ , which is shown in the IR image of **Figure 12(c)**. The white color indicates the area over which the temperature reaches more than 90% of the maximum temperature. Temperature homogeneity of this textile as heating element is better than those made with only stainless steel yarns, because in the latter case, heat is produced and localized only at the conductive yarns [21, 70]. Uniform distribution and dissipation of heat allow the heating element to be located in close proximity to the heated area in order to maximize warmth/heat production/output, to minimize response time, and to eliminate hot spots. The samples with four layers show a temperature increase of ca.  $40^\circ\text{C}$  (ca.  $0.1 \text{ W/cm}^2$ ) within 0.5 min. The heat releasing ability is also high for the coated textile, which is observed from the exponential decrease of the temperature to the room temperature within few minutes. The temperature of the water could be raised more than  $80^\circ\text{C}$  inserting the textile heater into it.

The flexibility of the textile as heating element is studied by measuring the changes in the temperatures within 20 cycles of bending over a time frame of 80 min. It is observed that with repeated bending, the current conducting through the heating textile does not change significantly, and the decrease in temperature is very small as shown in **Figure 12(d)**. These indicate that the flexibility of the textile is high, which along with the temperature homogeneity suggests the use of the *f*-CNTs/cotton textile as a flexible heating element. These lightweight



textiles can be configured and cut into any size or any shape, and are useful for portable heating system. For heating up to ca. 90°C, a power of 0.1 W/cm<sup>2</sup> is required, which is much lower than that of the conventional wired heater (ca. 0.3 W/cm<sup>2</sup>) [71]. This allows more efficient heating with less energy, which will find potential applications in garments and in transportation to improve thermal comfort.

Mattana et al. [72] employed nanoscale modification of natural cotton fibers with conformal coatings of gold nanoparticles, deposition of thin layers of the conductive polymer poly(3,4-ethylenedioxythiophene) and a combination of these two processes to obtain conductive cotton from plain cotton yarns. The electrical and mechanical properties of these yarns are improved to be successfully used as conductors, in order to bias electronic devices. They demonstrated the possibility of realizing a fully textile circuit, including passive and active elements, and paves the way for a future complete integration between electronics and textiles. Kotov groups in their communication showed the coating of cotton yarn with CNTs and polyelectrolytes [19]. Their method provides a fast, simple, robust, low-cost, and readily scalable process for making e-textiles. Even though the cotton yarn became slightly harder after being coated with SWNTs, it is still very flexible and soft, both of which are important for the wearability of electronic fabric.

It was informed that CNTs have toxic effects. Isolated CNTs in human body would make damage to the organic cells. In order to avoid these effects the textile can be covered with some additional fabric or by other means before using it in different applications, by which direct contact to the human body or diffusion into the air could be avoided.

## 6. Summary

Functionalization of CNTs is very important to realize their applications in modern technological advancements. A safe method has been developed to functionalize CNTs. In the sequence of treatments, CNTs are pretreated in pure ethanol using a supersonic homogenizer, wetted using citric acid solution, and plasma treated using RF oxygen plasma. By the plasma reaction in the presence of water vapor, O<sub>2</sub> and citric acid, plasma species interact with them to create many kinds of ions and radicals. They attack the CNT surfaces and activate a large number of sites to enhance the attachment of –COOH groups onto their surfaces. These attached groups significantly enhance the dispersion stability of the CNTs in water. Therefore, we are able to produce highly stable dispersed *f*-CNT ink, where the structural integrity of the *f*-CNTs is conjectured to be preserved, which is verified by the Raman and TEM measurements.

Nonconducting cotton textile becomes electroconductive by repeatedly dipping into the stable *f*-CNT ink and drying in air. The *f*-CNTs uniformly and strongly cover the individual cotton fibers, which remain attached even after 30 min of standard washing. After several cycle of dipping into *f*-CNT ink, the textile becomes conductive enough to be used as wire in lighting up an LED, and its conductivity becomes more than 0.20 S/m depending on the loaded content of *f*-CNTs in it. The thermal conductivity of the textile is enhanced by ca. 70%, and the thermal stability and flame retardancy are also improved. As a demonstration of practical use, the



textile is shown as a conductive textile heater designed with parallel electrodes. The temperature of the *f*-CNTs/cotton textile can be increased homogeneously to *ca.* 80°C within *ca.* 5 min by applying an electric power of *ca.* 0.1 W/cm<sup>2</sup>, which is much less than the power required for conventional wired heater. In our process, the dispersion of the CNTs are achieved by functionalizing them with a safe and surfactant-free method of plasma treatment, which helps to avoid impurities as well as to preserve the properties of the CNTs to be incorporated in the cotton fibers.

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