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# Production of Water Dispersible Carbon Nanotubes and Nanotube/Cellulose Composite

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Kazi Hanium Maria and Tetsu Mieno

Additional information is available at the end of the chapter

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## Abstract

Polymer wrapping methods have been used to disperse carbon nanotube (CNT) by using gelatin, an environment-friendly and easily decomposable biopolymer. The amino acid chain of gelatin becomes immobilized by the physical adsorption in the side wall of the CNTs through hydrophobic-hydrophobic interaction and results in the untangling of the CNT bundles. The dispersed solution remains stable for more than a month. Furthermore, this technique does not affect the physical properties of CNTs while enabling their dispersion in aqueous solutions. In addition, gelatin can be easily removed from the nanotubes after the dispersion of nanotubes by heating in water and filtration. Gelatin-dispersed CNTs are homogeneously mixed with the cellulose suspension and dried at room temperature to produce CNT/cellulose composite paper sheet. Adding multiwalled carbon nanotubes (MWNTs) in composite improves the mechanical, thermal, and electrical properties of cellulose. SEM investigation confirms the homogeneous distribution of MWNTs in the cellulose, which can be attributed to the improvement of its characteristics. Both sides of the CNT/cellulose sheet show uniform electrical conductivity, which is enhanced by increasing the MWNTs' content. IR image of the sheet clearly shows the temperature homogeneity of the surface. Thermal stability and the flame retardancy of the sheet are also found to be improved. The sheet has also strong absorbing of electromagnetic waves, which make them important for microwave technology applications.

**Keywords:** carbon nanotube, polymer wrapping, water dispersibility, gelatin, CNT/cellulose composite

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## 1. Introduction

Carbon nanotubes (CNTs) are realized to have a tremendous potential in many fields of applications because of their associated admirable chemical and physical properties [1, 2]. These molecular-scale

tubes of graphitic carbon are among the stiffest and strongest fibers known and have remarkable optical, electronic, and mechanical properties and many other unique characteristics [3]. For these reasons, there are already many studies using CNTs for electronic devices, including the use of CNTs as transistor channels, electrical wiring for lighting solutions industries (LSIs), and electron emitters [4–8]. Nevertheless, the as-produced material is extremely difficult to process. CNTs have a tendency to aggregate owing to the van der Waals attractive interaction between their sidewalls [9]. This tube-to-tube contact results in the hydrophobic nature of CNTs, which is responsible for their poor solubility in water and also incompatibility with a majority of solvents [10]. As a result, CNTs are precipitated in solvent. This lack of solubility and the difficulty of manipulating them in solvents limit the development of CNT-based devices or composites of interest for new applications. In order to obtain fine dispersion in the selected solutions, especially water, it is important to break the cohesion of aggregated CNTs. Development of efficient processes and chemical treatments that are able to control the quality of the CNT samples and to induce both their dispersion and partial or complete de-bundling remains highly challenging. Chemical modifications are the well-established method up to now, though this method modifies the desirable properties of CNTs [11]. On the other hand, polymer wrapping methods can preserve the intrinsic properties of CNTs. Usually, polymers and surfactants wrap the nanotube surface to enable the CNT dispersion in aqueous solutions [12, 13]. Also, this method produces impurity in the sample because wrapped polymers and surfactants become stuck in the sample after dispersion. Therefore, to overcome this problem, easily decomposable polymer should be considered for the dispersion of the CNTs. Here, in this chapter, various dispersion methods will be reviewed and an efficient procedure for the water dispersion will be reported by using gelatin, an environment-friendly material to wrap the surface of single walled carbon nanotubes (SWNTs) enabling their dispersion in water.

Next-generation computer devices, consumer electronics, wireless LAN devices, wireless antenna systems, cellular phone systems, high-performance sportswear, wearable displays, new classes of portable power, and embedded health monitoring devices are few portable device applications that have attracted a large interest in the scientific community because of their remarkable utilities [4–8]. The design of soft portable electronic equipment requires the development of a new class of materials with an array of novel functionalities, such as flexibility, stretch ability, and light-weight. Generally, this new class of material is termed as composites, which allow for many applications and designs previously impossible with traditional electronics technology. Nowadays, composites based on carbon nanotubes (CNTs) are very promising for the continuous growth of telecommunication market due to their many unique chemical and physical properties. Here, we introduced a convenient production method for the CNT composite, where cellulose is employing with multiwalled carbon nanotube (MWNTs) to enlarge the cellulose functionalities. This approach is illustrated by the blending of CNT with cellulose and characterization studies show that CNTs enable them to show outstanding electrical properties and thermal stabilities.

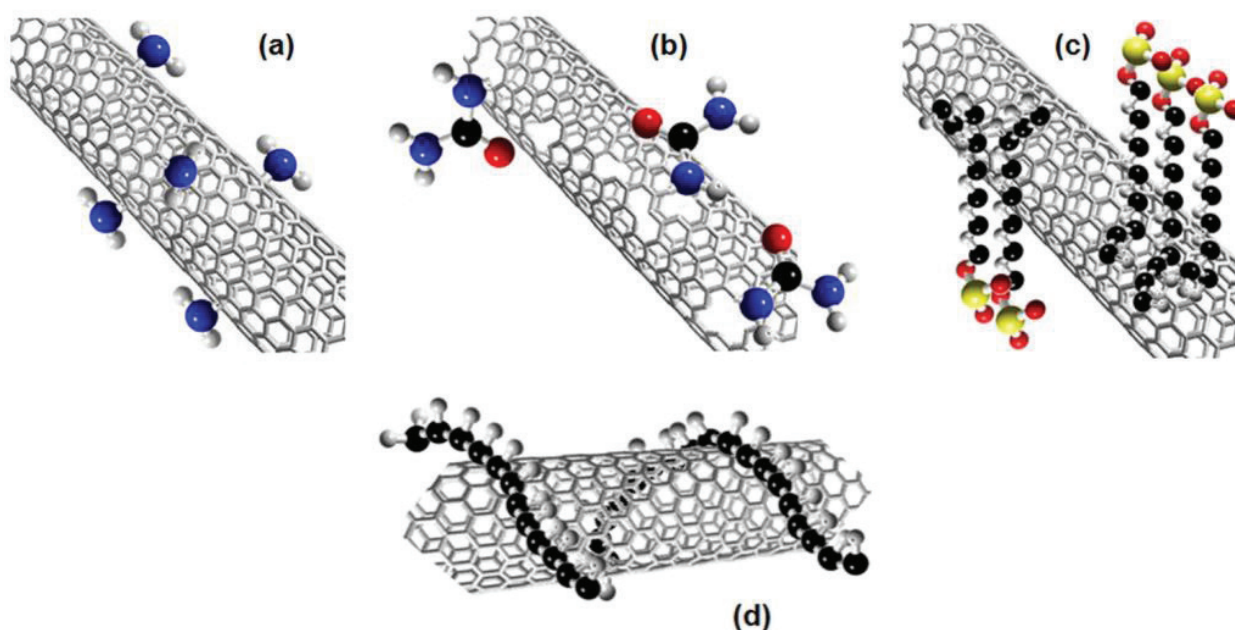
## 2. Water dispersibility of CNTs

Because of strong van der Waals attraction, the CNTs pack into bundles that aggregate into tangled networks, and thus do not disperse well in the water in their pristine state [9]. For optimal performance in most applications, the CNT should be separated into individual tubes

or bundles of only a few tubes. Dissolution of CNT in water has been facilitated by suitable enhancement of the surface of the nanotubes.

Generally, there are two mechanisms to disperse nanotube. In the mechanical mechanism, nanotube disentanglement is done by sonication and high-shear mixing. Sonication cut the longer nanotube into pieces to disperse CNT easily into water. As a result, the aspect ratio of nanotube also decreases in this way. Besides this, the stability of the dispersion is poor. Nevertheless, the chemical mechanism incorporates both covalent and non-covalent methods. In covalent functionalization, chemical modifications can be performed at the sidewall site, which causes the transformation of  $sp^2$  into  $sp^3$  hybridized carbon atoms [14] or at the defect sites via amidation or esterification reactions of carboxylic residues obtained on CNTs [15]. Usually, this sidewall modification or defect functionalization are the continuation of CNT treatment with strong acid such as  $HNO_3$ ,  $H_2SO_4$  or a mixture of them, or with strong oxidants such as  $KMnO_4$ , ozone, and reactive plasma, which open the tubes and consequently produce oxygenated functional groups such as carboxylic acid, ketone, alcohol, and ester groups. Therefore, they produce different types of chemical moieties onto the ends and defect sites of these tubes, which in turn significantly change the mechanical properties of CNTs by destroying the perfect structure of CNTs as well as disruption of  $\pi$  electron system in nanotubes, which is detrimental to transport properties of CNTs. Furthermore, strong oxidants or concentrated acids are environmentally unfriendly, which are often used for CNT functionalization. **Figure 1** shows the different kinds of CNT functionalizations.

A non-covalent mechanism associated with the adsorption of the chemical moieties onto the nanotube surface, either via  $\pi$ - $\pi$  stacking interaction such as in DNA, uncharged surfactants, etc., or through coulomb attraction in the case of charged chemical moieties [16]. Compared to covalent functionalizations, non-covalent functionalizations are more capable of preserving



**Figure 1.** Different type of functionalization possibilities of CNTs: (a) covalent sidewall functionalization, (b) covalent defect sidewall functionalization, (c) non-covalent adsorption of surfactants, and (d) wrapping of polymers. Adapted from Ávila-Orta et al. [16].

intrinsic properties of CNTs when improving exfoliation and interfacial bonding. Though, the concern of this approach is the presence of physically bound modifier molecules on the surface, such anomalies can be removed easily by washing. Besides, this method increases the solubility of CNTs, making them less toxic and preserving the electrical properties of CNTs. Polymer wrapping method are widely used non-covalent approach that attributed to the physical association of polymers with CNTs. Polymers can wrap around CNTs, forming supramolecular complexes and most of the nanotubes are found as single tubes associated with at most a single layer of polymer. A smaller number of aggregates consisting of more than one nanotube are also remained at the dispersion. The advantage is that a stable suspension is observed for months. Stabilizing dispersions of carbon nanotubes (CNTs) is a major challenge, since it is a prerequisite to high performance of CNT in a large field of applications.

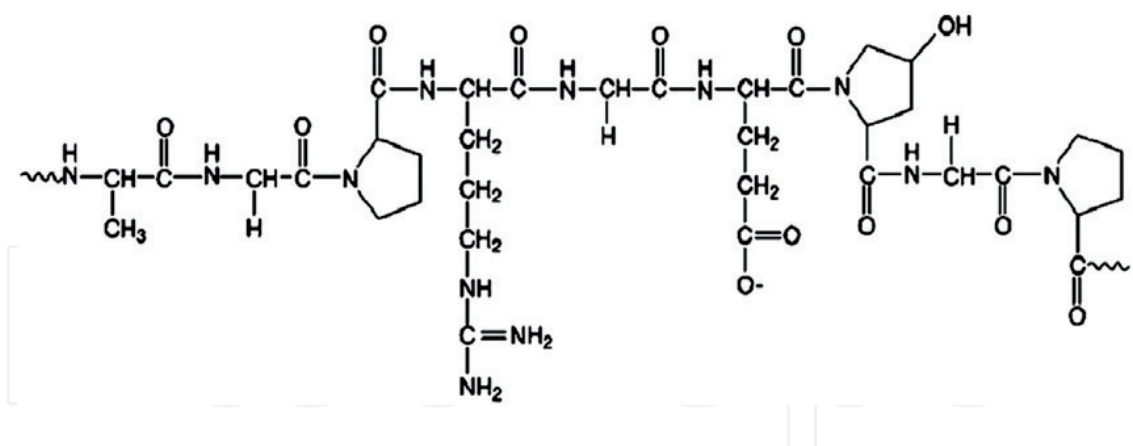
### 3. Methodology of gelatin-wrapped CNTs

Water dispersible CNTs without changing their physical properties are a significant challenge and a prerequisite for their applications [4–8]. For this reasons, polymer wrapping method can be the best option for CNT dispersion, because, in this method, polymer and surfactants are used to exfoliate the nanotube from the nanotube bundles by wrapping the individual nanotube surface while enabling their dispersion in aqueous solutions [12, 13]. As a result of polymer wrapping, polymers and surfactants stay in the sample synchronously to intact the physical properties of CNTs. The remaining polymers and surfactants create impurity in the samples, which in turn influence the CNT application. Therefore, easily decomposable polymer can be used to get rid of this issue as well as to produce safe nanotube materials for the nano-bioscience and technology. Here, we used the biocompatible, non-immunogenic gelatin to wrap the surface of CNTs enabling their dispersion in water [17]. Moreover, gelatin is an environment-friendly material and easy to remove from the CNTs by heating in water and filtering. This method is safe compared to the other methods available in the literature, as no hazardous reagents are used here.

#### 3.1. Molecular structure of gelatin

Gelatin has a noticeable property of forming elastic gels at room temperature for relatively low concentrations (a few per cent of gelatin in water). It is a denatured collagen and contains different amino acid content. Collagen, which is the major protein present in animal bones, skin, and connective tissue, consists of rigid bar-like molecules that arranged in fibers are interconnected by covalent bonds. These molecules have three polypeptide chains such as glycine, proline, and 4-hydroxyproline, and they are arranged in a triple helix that is stabilized by hydrogen and hydrophobic bonds. Gelatin is a mixture of  $\alpha$ -chains (one polymer/single chain),  $\beta$ -chains (two  $\alpha$ -chains covalently cross-linked), and  $\gamma$ -chains (three covalently cross-linked  $\alpha$ -chains) [18]. Gelatin also has a mixture of single and double unfolded chains of hydrophilic character. The physical properties of gelatin depend on amino acid compositions, relative content of  $\alpha$ -chains,  $\beta$ - or  $\gamma$ -components, and higher molecular weight aggregates. A typical structure of gelatin is -Ala-Gly-Pro-Arg-Gly-Glu-4Hyp-Gly-Pro- which is shown in **Figure 2**.





**Figure 2.** A typical Structural unit of gelatin. Adapted from Ref [18].

There are two types of gelatin depending on acid or alkaline treatment. Type A gelatin (isoionic point of 6–9) is collected from acid-treated collagen, whereas alkali-treated precursor is responsible for manufacture type B (isoionic point of 5) gelatin. Usually type A gelatin and type B gelatin are successively extracted from pigskin and beef skin [19].

### 3.2. Properties of gelatin

The properties of gelatin are influenced by the intrinsic factors such as the source, age of the animal, and type of collagen. Gelatins produced from cattle and pigs' bones and skins are mostly used in commercial. Recently, gelatin from fish and poultry has received considerable attention and may serve as important commercial gelatin sources into the future [20]. This is because proteins derived from these sources may possess similar functional properties like mammalian. Moreover, fish gelatin is free from bovine spongiform encephalopathy (BSE) which is commonly called mad cow disease and more religiously acceptable.

Gelatin macromolecules can display a wide variety of conformations under specific conditions such as temperature, solvent, and pH. It can form a physical thermos-reversible gel at room temperature or below 40°C for relatively low concentrations. If the temperature is raised, the gel “melts,” becoming liquid again [19]. This reversible conformational nature of gelatin makes it a suitable dispersing agent of carbon nanotube dispersion, which can be removed thermally.

Gelatin has different amino acid composition and the molecular weight distribution based on their type. The gel strength, viscosity, pH, and melting point of gelatin depend on their structure and the amino acid chain [18–20]. Generally, gelatin with the higher number of amino acids chains have higher gel strength, which in turn increases the melting point. Over a wide range of pH values, gelatin behaves like polyampholyte, where the gelatin macromolecule has mixed anion and cation character, which also has uncharged hydrophilic and hydrophobic groups [20]. This in turn makes gelatin molecules soluble in water but may also cause them to be adsorbed at charged or hydrophobic surfaces.

### 3.3. Preparation of gelatin dispersed CNTs

Pristine SWNT powder (Nanostructure & Amorphous Materials Inc., diameter = 1–2 nm, length = 5–30 μm, purity = 90%), MWNTs (Sigma-Aldrich, outer diameter = 10–30 nm, inner

diameter = 3–10 nm, length = 1–10  $\mu\text{m}$ , purity >90%), and gelatin (Wako 1st Grade, appearance: yellowish-brown and crystalline powder) are used as received to prepare the mixture and the mixture is observed to check the dispersion ability. 5 mg raw carbon soot and 20 mg gelatin were mixed with 20 ml of pure water (Wako Pure Chemical Industries Ltd.). Both MWNT and SWNT soot was used with gelatin to prepare the mixture. An ultrasonic homogenizer equipped with a microtip sonotrode (VC 130, Vibra Cell, Sonics & Materials Inc.,  $f = 20\text{ kHz}$ , 6 mm $\phi$  probe) was intermittently operated to stir the mixture. The input power of homogenizer was always kept at 20 W and the mixing was for 60 min, where the duty ratio was 60%. The collected gelatin-SWNT and gelatin-MWNT dispersion last above a month at room temperature.

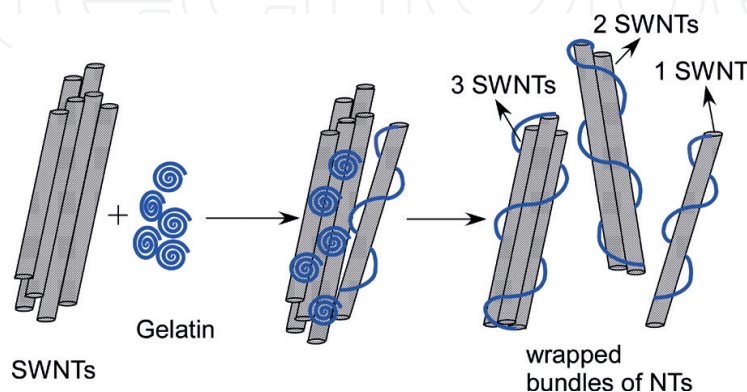
## 4. Evaluation of dispersibility of the CNTs with gelatin

The CNTs have a tendency to aggregate owing to the attractive interaction between their sidewalls. CNTs can be hydrated by gelatin, which can wrap around their sidewalls [17], as schematically shown in **Figure 3**.

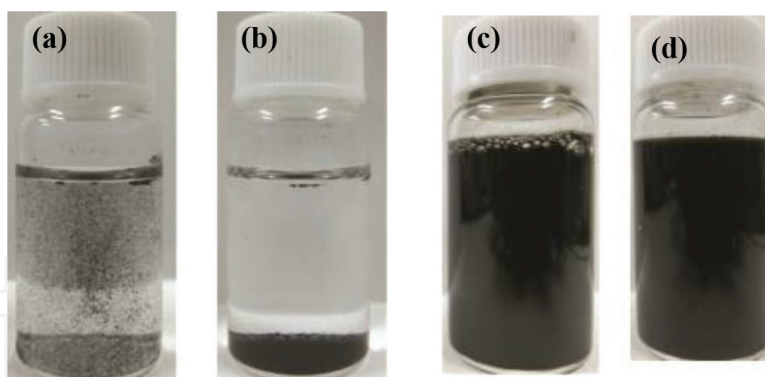
### 4.1. Visual inspection of gelatin-CNT dispersibility

The resulting hydrophobic nature is responsible for their poor solubility in water, and CNTs are precipitated in water as shown in **Figure 4(a)** and **(b)**. Most polymer wrapping methods depend on the physical adsorption of the polymer on the surface of the CNTs to increase the solubility of the nanotubes.

Gelatin is a natural water-soluble biopolymer that is composed of 18 types of amino acid chains [21, 22]. The amino acid chains of the gelatin wrap around the sidewalls of the CNTs through a hydrophobic-hydrophobic interaction [17, 21, 23]. Gelatin has zwitterionic structure and the amino acid chain of the gelatin has hydrophobic nature. CNTs' surfaces are also hydrophobic. This hydrophobic-hydrophobic interaction may include a hydrophilic group to the CNTs' surface, which in turn disperses CNT into water, as shown in **Figure 4(c)** and **(d)**. The CNT dispersion is found to last over a month.



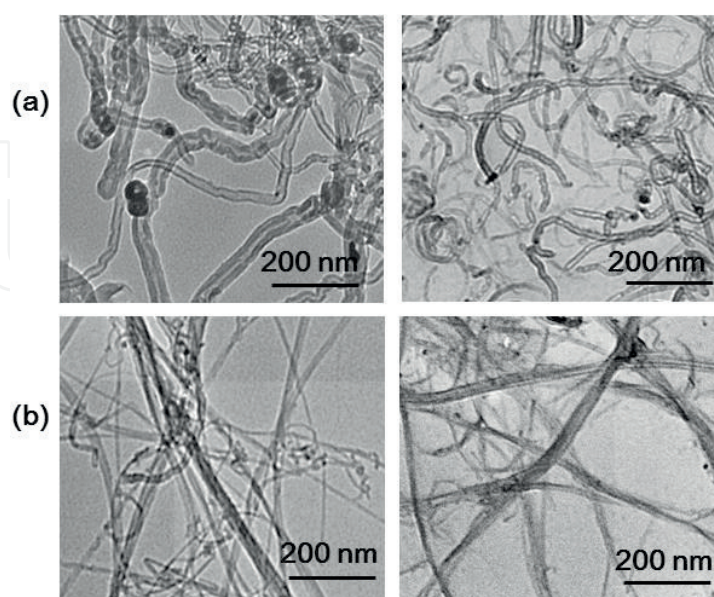
**Figure 3.** Schematic showing wrapping of SWNTs with gelatin. Adapted from Maria and Mieno [17].



**Figure 4.** Photographs of (a) SWNT dispersion in water immediately after sonication, (b) SWNT precipitate in water after a few hours, (c) SWNT dispersion in gelatin-water solution immediately after sonication, and (d) stable SWNT-gelatin dispersion after 1 month.

#### 4.2. TEM observation of gelatin-CNT dispersion

To observe the dispersion state of the wrapped CNTs in water, one drop of the solution is placed on a copper grid coated with a collodion film for the image observation from the transmission electron microscope (TEM, JEOL JEM1400, accelerating voltage 100 kV). **Figure 5** is a typical TEM image where it is shown that the CNTs are well wrapped with gelatin. It is seen that the gelatin uniformly wrapped around the entire surface of tubes making the SWNTs opaque and surfaces rough as compared with unwrapped SWNTs. The wrapping mechanism of polymer is believed to be driven largely by thermodynamics to eliminate hydrophobic interface between the tubes and the aqueous medium. In case of growth technique of NT, metal particle is used in the electrode as a catalyst to grow SWNTs and then remain attached to the SWNTs as impurity. Usually, amorphous carbon and metal nanoparticles are produced



**Figure 5.** Typical TEM images of (a) pure MWNTs and (b) pure SWNTs. Left side shows the pristine nanotubes and right side shows the dispersed nanotube bundles in aqueous gelatin solution.

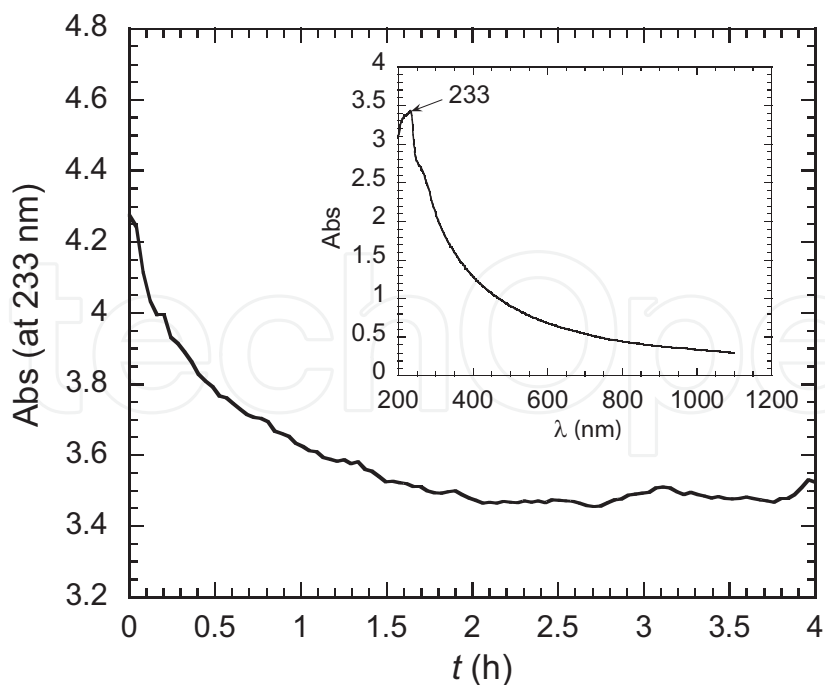


with the SWNTs as byproducts. These byproducts can be dispersed by gelatin also and can be removed from SWNTs dispersion by filtration. Another worth mentioning advantage of using gelatin as a dispersing agent is that dried gelatin-wrapped CNTs are easily re-dissolved in water with sonication.

#### 4.3. Investigation by UV-visible spectrometer

A UV-visible spectrometer (JASCO Co., V-630) was used to examine the dispersion stability of the dispersed solution. For this experiment, 1 mg of raw soot and 5 mg of gelatin were mixed with 10 ml of pure water to make the sample. The sample was placed in a quartz cuvette ( $1.0 \times 1.0 \times 4.5 \text{ cm}^3$ ) and time variation of absorbance (Abs) at a wavelength of 233 nm was measured for 4 h. Here, the wavelength was chosen corresponding to the maximum absorbance region of the UV-visible spectra. **Figure 6** shows the time variation of absorption spectrum for gelatin-SWNT dispersing liquid at a wavelength of 233 nm. It is noticed that the absorbance started to decrease for more than 1 h and then shows a stable nature with the increase of time, which indicates the stability of gelatin-SWNT dispersion.

From the above analysis, it is found that the gelatin-CNT dispersion is very stable and CNTs do not precipitate in water. Therefore, it can claim that the gelatin molecules wrap around CNTs and CNTs are separated and dispersed in water. This easy way to make dispersed solution of CNT has great impact on the application field. CNT composite material can be made by using this gelatin-CNT dispersion as gelatin can be easily removed by heating and filtration.



**Figure 6.** Absorbance vs. time at  $\lambda = 233 \text{ nm}$  to measure the stability of the gelatin-SWNT dispersion. Inset shows the UV absorption spectrum of the solution.

## 5. CNT/polymer composites

Generally, composites are composed of two or more materials, which exhibit the unique properties of combined materials. These composites, such as polymer composites, have enhanced mechanical properties because they combine the properties of high modulus carbon fibers and polymer [24]. The additive has great effect in polymer composites because the modulus, strength, and high-fracture toughness of composites are built upon on the nature of additive. By employing the nanoscale CNT into a polymer system results in very short distance between the fillers; thus, the properties of composites can be largely modified even at an extremely low content of filler. Thus, CNT/polymer composites, consisting of CNT as additives and polymer matrices, are considered to be an important group of relatively inexpensive materials for many engineering applications. In order to successfully introduce CNTs in large-scale industrial applications, they need to be homogeneously embedded into light-weight polymer to make nanocomposites. The combination of mechanical and electrical properties of individual nanotubes makes them the ideal reinforcing agents in a number of applications. CNT-polymer composites are promising as new generation materials, and the importance for nanocomposites will increase as miniaturization becomes more important in areas, such as computing, sensors, biomedical, and many other applications [25]. Therefore, CNT/polymer nanocomposites are one of the utmost investigated composite because of the easy fabrication of polymer matrix without damaging CNTs. Another advantage is the low cost of polymer for which mass production of nanocomposites would be possible in the future.

### 5.1. Objective of CNT/cellulose composite

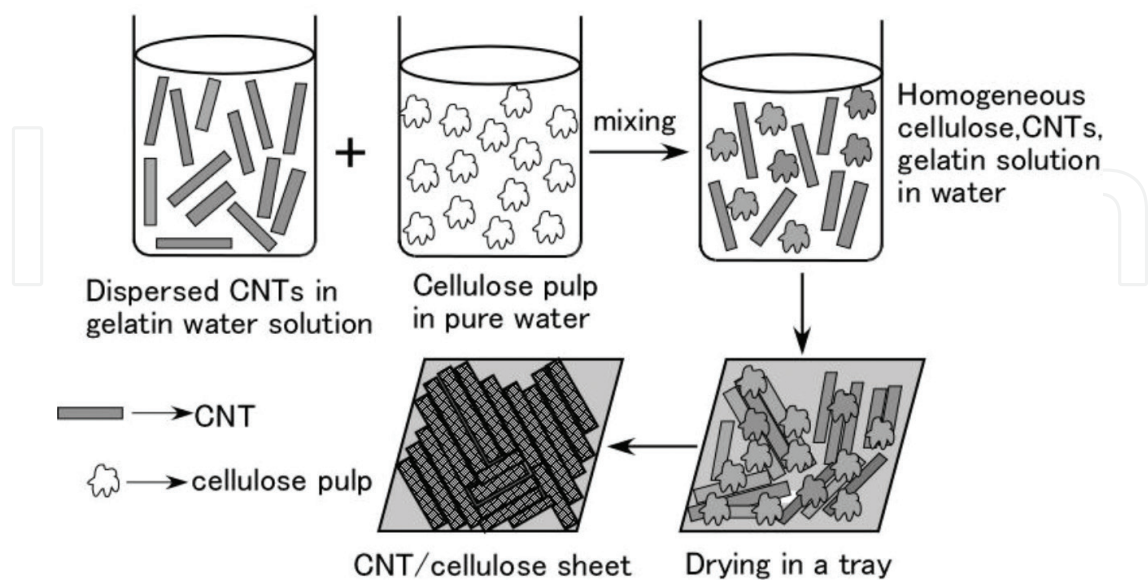
Recently, the rapid development of portable device hardware has aroused huge demand for lighter and more efficient heat-transfer materials [25]. As the overweighted heat-transfer materials have delayed the development of portable device hardware, it is required to develop light, flexible, inexpensive, and even roll up or wearable devices for multifunctional portable electronics [6, 26, 27]. In this case, composite materials consisting of carbon nanotubes and cellulose can be the ideal solution [28, 29], because nanocomposites have the potential to significantly surpass the properties of conventional bulk materials. The difficulties in developing such nanocomposites are dispersion of nanotubes, CNT-polymer interactions, manufacturing cost, and performance of the composite. Cellulose have attracted great attention with expertise in diverse areas [30, 31] as a renewable source-based biodegradable polymer and becomes a major medium for displaying and transmitting information owing to its potential compostibility, mechanical stability under atmospheric conditions, and ability to absorb ink [32]. Carbon nanotubes (CNTs) are regarded as one of the most versatile additives of composites because it can improve mechanical and electrical characteristics of cellulose [33]. Especially, homogeneous distribution of CNTs in the cellulose matrix has predominantly contributed to improve its characteristics. CNT forms a conducting network using its electron donating and accepting ability in the composite [6, 34–36]. These CNT/cellulose composite materials have some outstanding properties such as being highly strong, electrically

and thermally conductive, and the usage of these materials have been widely investigated [35–38]. CNT/pulp has been prepared by a paper making process, which is a fast, simple, robust, low-cost, and readily scalable process. The properties of the resulting CNT/cellulose paper sheet are also identified and reported here.

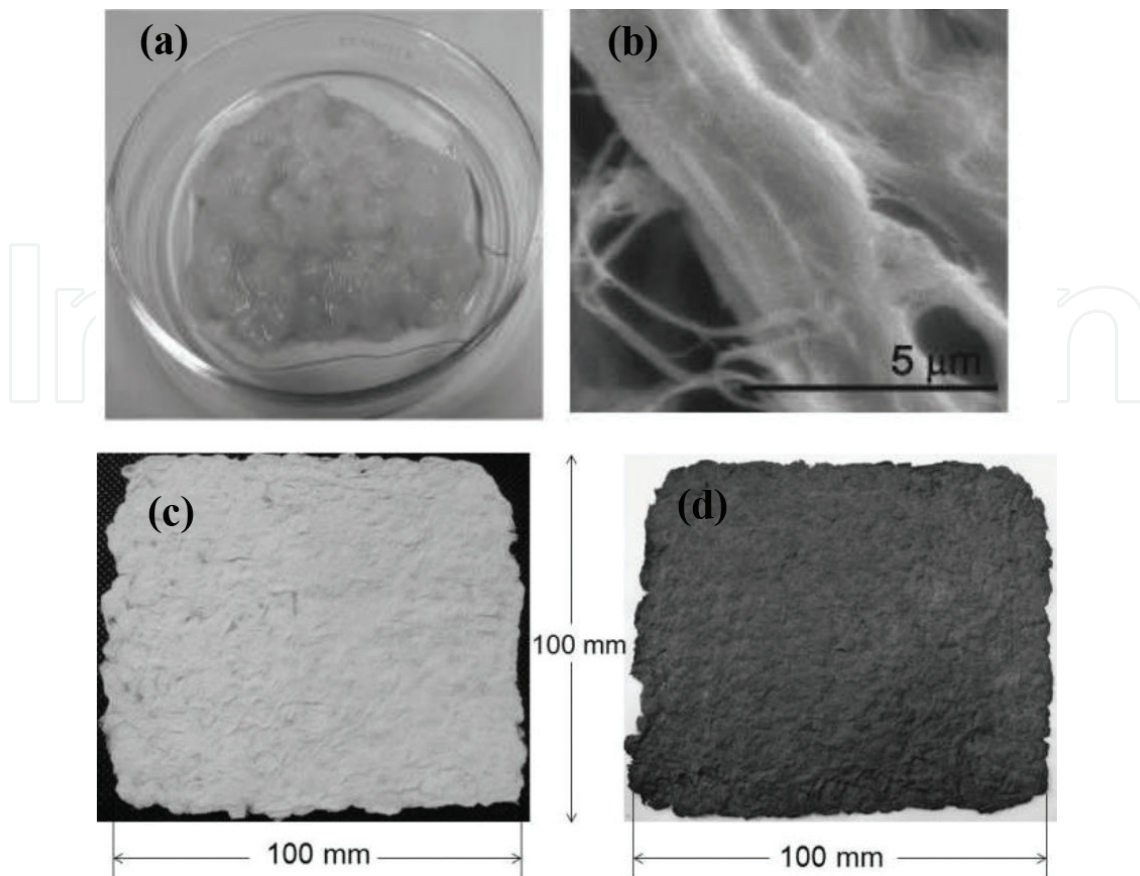
5.2. Fabrication of CNT/cellulose composites

The most important part of preparation of CNT/cellulose composites is to improve the interaction between the pulp fibers, gelatin and multiwalled carbon nanotubes (MWNTs) to optimize the paper making process for CNT/cellulose composites. MWNTs and geletin are purchased from Sigma-Aldrich and Wako Pure Chemical, respectively, which are used as received. Cellulose fibers used here are obtained directly from manufacturing facility, where cellulose is processed with a beater to get uniform pulp in the sheet.

At first, the cellulose suspension is made by soaking the fibers into pure water and blended for 20 min. 10 mg of MWNTs (outer diameter = 10–30 nm, inner diameter = 3–10 nm, length = 1–10  $\mu\text{m}$ , purity >90%) and 30 mg of gelatin are sonicated with 10 ml of pure water by using a supersonic homogenizer (Sonic vibra cell, VC 130, Sonic & Materials Inc.,  $f = 20\text{ kHz}$ , 6 mm $\phi$  probe) at an input power of 20 W for 60 min. Then, 300 mg of cellulose suspension is added to the CNT dispersion and blended for 20 min. The final solution is poured into a tray dish and dried at room temperature to get a paper sheet. A possible paper making process is schematically shown in **Figure 7**. The obtained paper sheets have a thickness of about 0.2–0.4 mm. **Figure 8** shows the image of the cellulose pulp, SEM image of the pulp, and CNT/cellulose coposit sheet.



**Figure 7.** A schematic of the paper making process for the fabrication of CNT/cellulose composite sheets. Adopted from Maria and Mieno [37].



**Figure 8.** (a) Image of the cellulose pulp that used for making the sheet, (b) SEM image of the pure cellulose pulp at low magnification ( $\times 5000$ ), (c) photographs of a pure cellulose sheet (left), and (d) a CNT/cellulose sheet (right).

### 5.3. Presence of CNTs on the composite sheet

The image of the uniform distribution of MWNTs in the CNT/cellulose composite is taken by a SEM (JEOL JSM 6510LV, operating voltage of 10 kV) to observe the morphology of the sheet as well as the presence of CNT into the composites. It is observed from **Figure 9** that CNTs cover surface of almost all fibers of the sheet. Some CNTs seem to form bridge-like structure with paper fibers. The SEM images clearly reveal that the interconnected networks established by the individual CNTs so that numerous electrical paths can be formed. In contrast with the SEM observation, Raman measurement (JASCO NR-1800, using a laser for excitation,  $\lambda = 532$  nm) also confirmed the presence of CNTs in the paper sheets. It is observed that Raman peaks of both G-band and D-band and radial breathing modes generated from CNTs, as shown in **Figure 10**.

### 5.4. Properties of CNT/cellulose composites

#### 5.4.1. Electrical properties of the CNT/cellulose composite sheet

As CNT forms the conducting paths into the cellulose sheet, composites shows considerable resistance. Resistance is measured of 10 randomly chosen measuring points on both sides (A side and B side) of



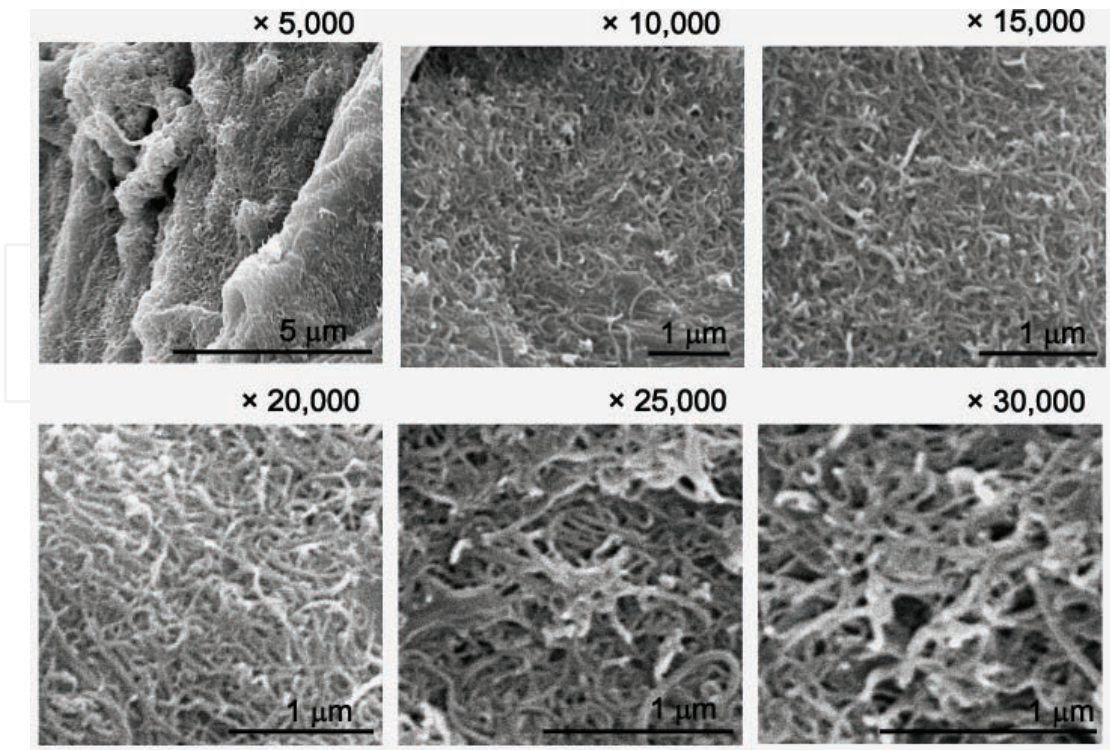


Figure 9. SEM images of the CNT-paper sheet at different magnifications taken at an operating voltage of 10 kV.

a CNT/cellulose paper sheet by the needle-electrodes, and the distance between needle-electrodes are kept constant at 20 mm. The distributions of the resistances are shown as histograms in Figure 11.

It is found that the electrical conductivity of the CNT/cellulose paper sheets is highly uniform. In case of 5 mg MWNTs added sheet, the A side has resistance,  $R = 2.61 \text{ M}\Omega$  (standard deviations,  $s = \pm 0.08$ , electrical conductivity,  $\sigma = 1.91 \text{ mS/m}$ ) and the B side has resistance,  $R = 2.60 \text{ M}\Omega$  (standard deviations,  $s = \pm 0.05$ , electrical conductivity,  $\sigma = 1.92 \text{ mS/m}$ ). When 10 mg of MWNTs are added, the A side has resistance,  $R = 1.14 \text{ M}\Omega$  (standard deviations,  $s = \pm 0.04$ , electrical

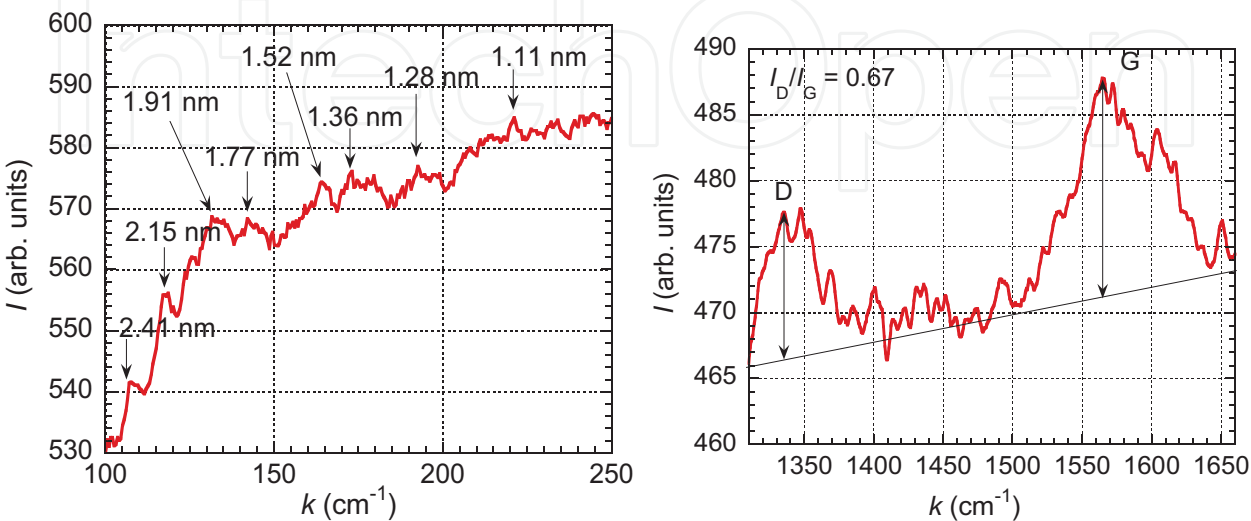
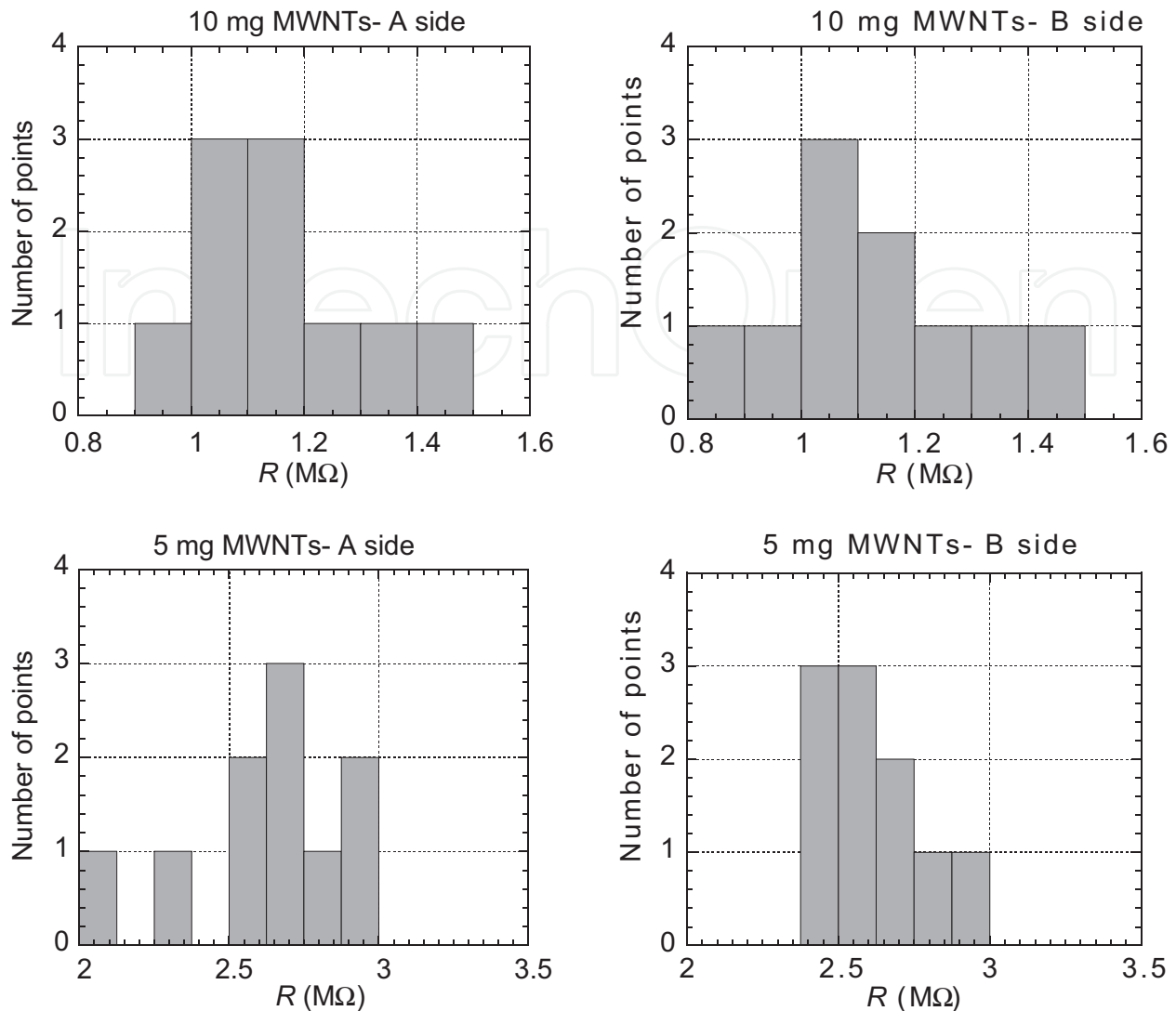


Figure 10. Raman spectra of the CNT/cellulose paper sheet. RBM modes are shown on the left side and the G and D bands are shown on the right side.

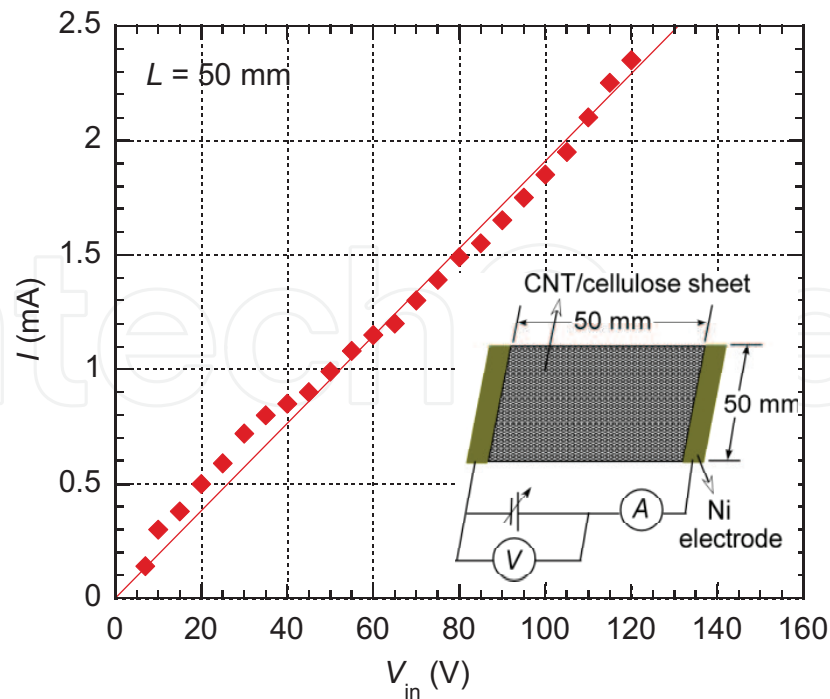


**Figure 11.** Histograms of measured resistance on the both sides of the CNT/cellulose paper sheet. Resistances are decreased with the increase of MWNTs content.

conductivity,  $\sigma = 4.38$  mS/m) and the B side has resistance,  $R = 1.103$   $M\Omega$  (standard deviations,  $s = \pm 0.05$ , electrical conductivity,  $\sigma = 4.53$  mS/m). Therefore, it is noticed that the conductivity can be improved by increasing the amount of CNTs added to the cellulose [37].  $I$ - $V_{in}$  characteristic curve shows the ohmic conduction on the paper sheet as shown in **Figure 12**.

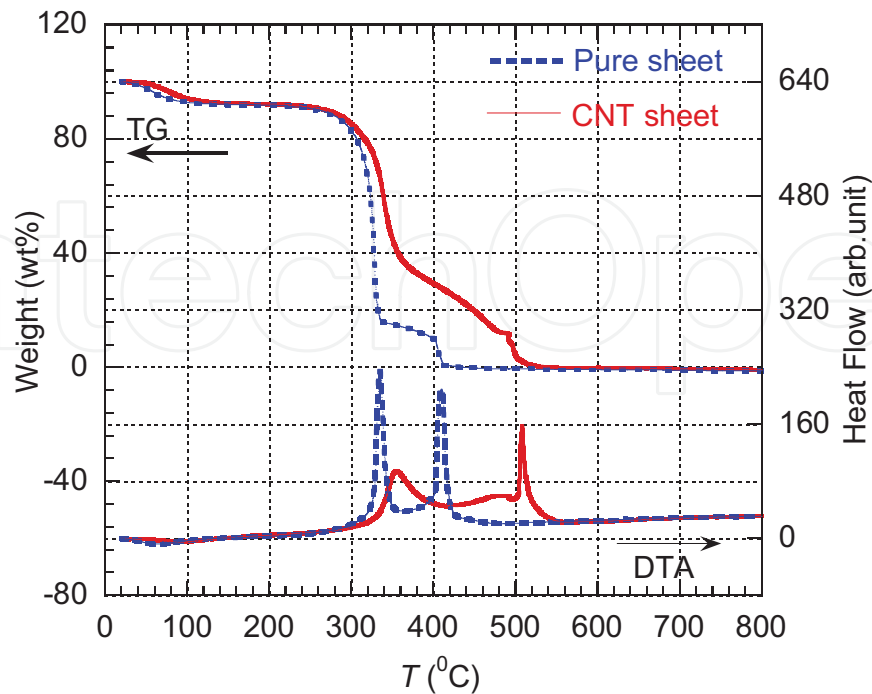
#### 5.4.2. Thermal properties of the CNT/cellulose composite sheet

TG/DTA (Rigaku Thermoplus Analyzer, TG8120) experiments for the cellulose sheet and the CNT/cellulose sheet are carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $800^\circ\text{C}$  and the curves are shown in **Figure 13**. DTA curves show that the thermal degradation of the both sheets occurs in two different steps in air atmosphere. In the first step of degradation, the cellulose sheet and the CNT/cellulose sheet begin to lose weight at  $332$  and  $355^\circ\text{C}$ , respectively, and the final combustion in second step occurs at  $409$  and  $507^\circ\text{C}$ , respectively. The final combustion of the CNT/cellulose sheet delayed by ca.  $100^\circ\text{C}$  is clearly observed from



**Figure 12.**  $I$ - $V_{in}$  curve for  $L = 50$  mm showing the linear conduction (inset: Schematic of the  $I$ - $V_{in}$  characteristic measurement setup).

the DTA curves, which indicate that cellulose sheets losses weight faster than CNT/cellulose sheet. From the TG curves, it is observed that the combustion rate of CNT/cellulose sheet is 22% less than that of the pure cellulose sheet. This result signifies that the thermal stability

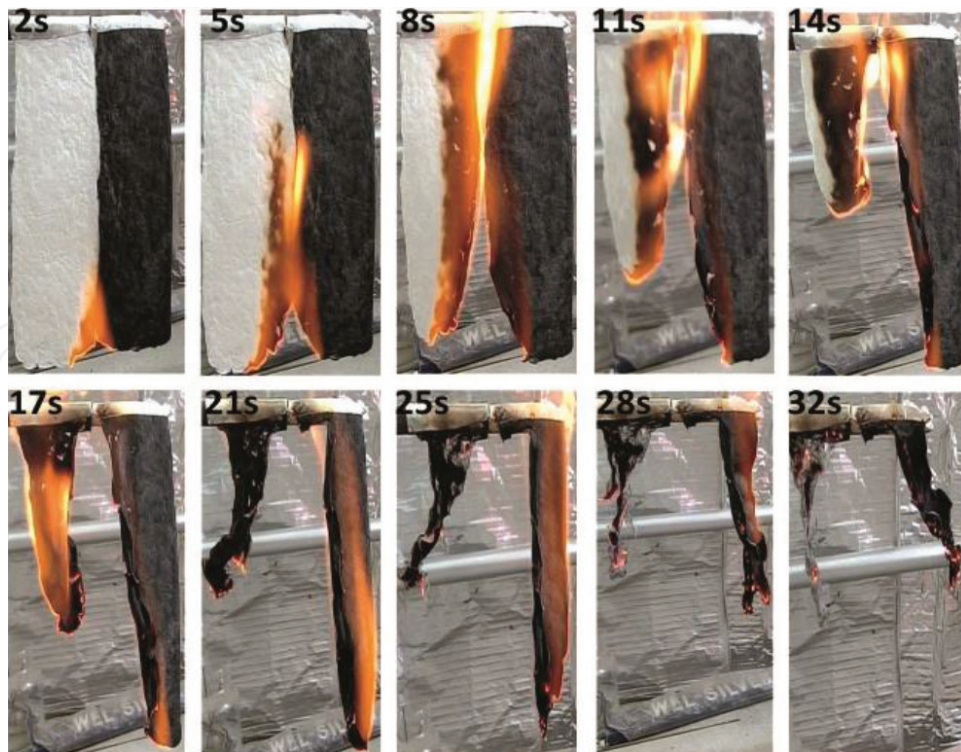


**Figure 13.** TG/DTA curves for the pure cellulose sheet (dotted line) and the CNT/cellulose sheet solid line).

of the sheet is improved by adding MWNTs [35, 37, 39]. There is also an additional peak at 477°C on the CNT/cellulose curve before the final combination peak, which corresponds to the combustion of the gelatin.

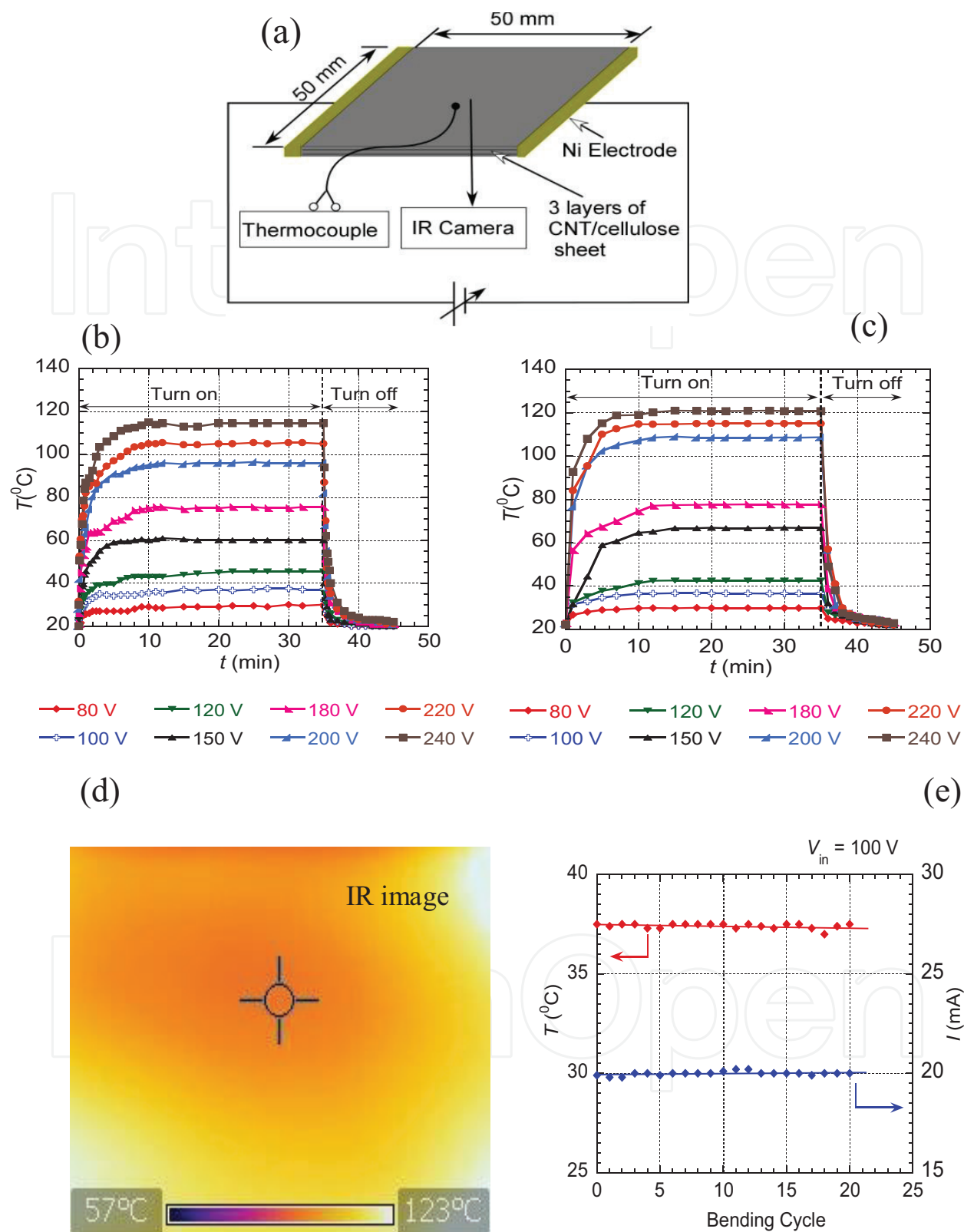
The flame retardancy test is carried out for both the cellulose and CNT/cellulose sheets. The combustion process is shown in **Figure 14**. Both the sheets are hanged on a metal supporter and ignited simultaneously by a gas flame. It is observed that the cellulose sheet burns quickly to ashes completely within 20 s, but the CNT/cellulose takes more than half minutes to burn and turns to charcoal, which indicates that added MWNTs improved the flame retardancy of the sheet [37].

**Figure 15(b)** and **(c)** shows the temperature vs. time curves of the CNT/cellulose sheet by a thermocouple and by an IR camera during heating and cooling process. The schematic of the measurement are shown in **Figure 15(a)**. The experiment is carried out by measuring the variation in the temperature under the applied voltage,  $V_{in} = 80\text{--}220\text{ V}$ . Three layers of CNT/cellulose sheet has been used for reducing resistance low enough by which the passage of an electric current through a CNT/cellulose sheet releases heat due to Joule heating process [40]. Heating and cooling temperatures of the sheet are measured at the center of the sheet. It is observed that the heat starts to increase with time by applying a DC voltage and radiate from the sheet. The surface of the CNT/cellulose sheet reached above a maximum temperature of 120°C within 5 min depending on the applied voltage and become saturate at that maximum



**Figure 14.** Photographs of flame retardancy test for the pure cellulose sheet (left-white sample) and CNT/cellulose sheet (right-black sample). At  $t = 0\text{ s}$ , a flow is added on the bottom of the samples.





**Figure 15.** (a) Schematic of the heating test measurement of the CNT/cellulose sheet by a thermocouple and an IR camera. Temperature vs time curves during heating and cooling of the CNT/cellulose sheet measured (b) by a thermocouple and (c) by an IR camera. (d) Thermal image at  $V_{\text{in}} = 220 \text{ V}$  showing the uniform heating of the sheet where the temperature scales shown at the bottom part. (e) Variation of temperature and current after repeated bending, where the input voltage  $V_{\text{in}} = 100 \text{ V}$ .

temperature. Much higher temperature can be obtained by increasing the layers of the CNT/cellulose sheet and the sheet could be used as a flat-type electric heater.

During the test, all the samples are heated to maximum equilibrium temperature and then cooled naturally, and this heat releasing ability of the sheets is also measured. It is observed that temperature decreases exponentially to the room temperature within few minutes. Thermocouple-based measurements show a little lower value of temperature than the infrared-based measurements. This difference arises from the slow response of the thermocouple due to the slow heat propagation [41]. The IR image of the CNT/cellulose sheet as shown in **Figure 15(d)** indicates the uniformity of the heat dissipation. It clearly shows that high temperature area (glow area) is located at the center of the sheet. To study the flexibility of the CNT/cellulose sheet, the temperature and current are also measured by bending the sheet more than 90° for 20 times and the total time elapsed for the whole process is 80 min. **Figure 15(e)** shows the flexible nature of the paper sheet, because repeated bending of paper sheet does not make any significant change of the current conduction through the paper sheet, and temperature also remains almost constant. These results mentioned above indicate that CNT/cellulose sheet can be used as an electrothermal heating element [37].

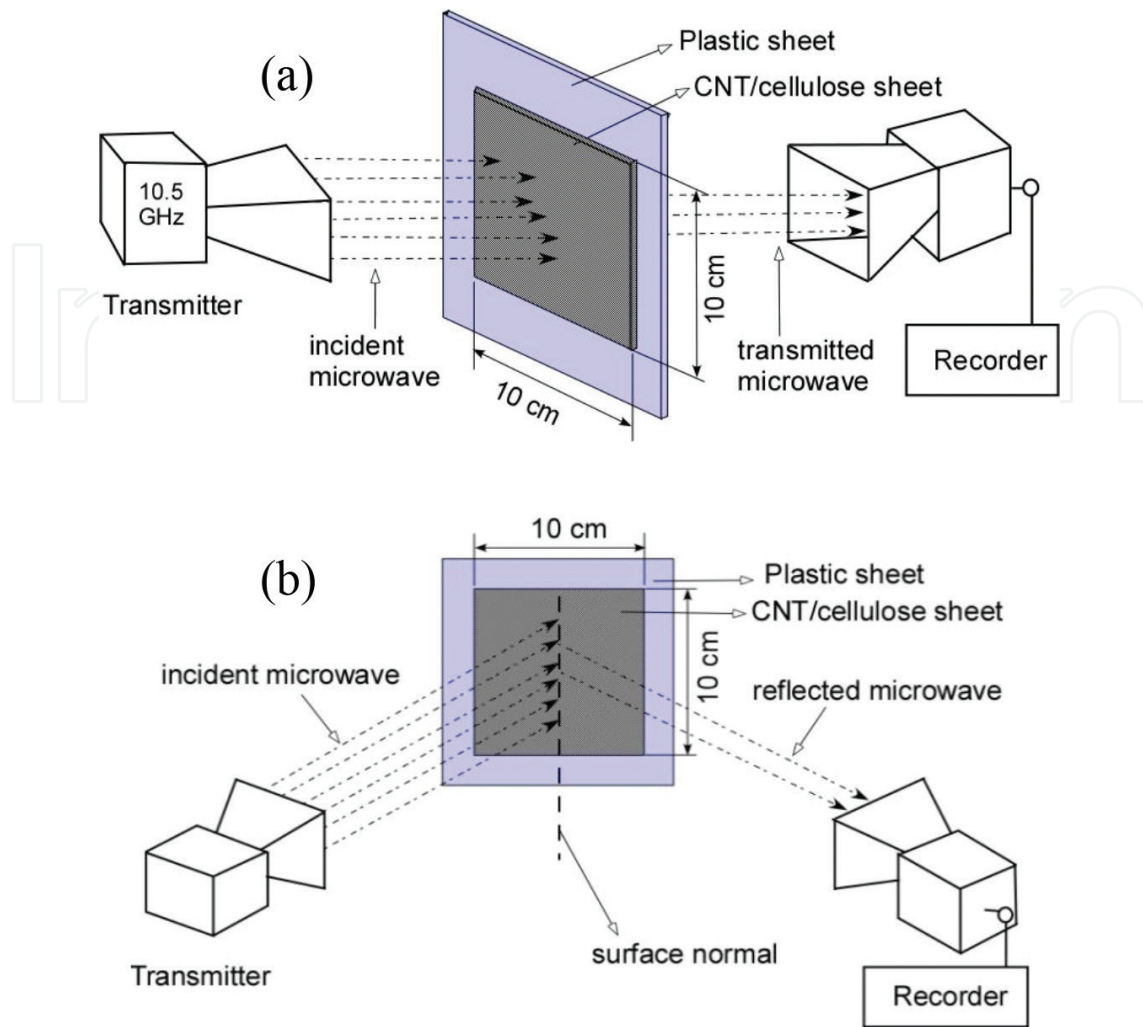
#### 5.4.3. Absorbing properties of the composite sheet

A gun-diode microwave transmitter and a recorder (Pasco Scientific WA-9314B,  $P_{\mu} = 10$  mW) of 10.5 GHz with horn antenna are used to measure the microwave absorption properties of the sheet. For this experiment, a size of  $100 \times 100 \times 0.3$  mm<sup>3</sup> of the both CNT/cellulose sheet and pure cellulose sheet are made for comparison. The pure cellulose sheet and the CNT/cellulose sheet are placed on a plastic substrate during the experiment. A schematic representation of the measurement of microwave absorption ability is shown in **Figure 16(a)**.

In this absorption ability experiment, the incident microwave is divided into two parts: the transmitted microwave and the absorbed one. To determine the reflection ability of the sheet, transmitter and receiver is set in such a way that the incident and reflected wave makes equal angles to the surface normal, as shown in **Figure 16(b)**. The experimental result of the absorption and transmission ability vs. the content of MWNTs of the CNT/cellulose sheet is shown in **Figure 17(a)**. The sheet with low content of MWNTs shows weak absorbing ability and the absorption increases with the increase of MWNTs content [37].

The absorption test is also carried out with the increase of thickness of the sheet as shown in **Figure 17(b)**. Few sheets of same thickness and same content of MWNTs (30 mg) are used for this experiment. During the experiment, thickness is increased by putting the sheet one after one on the plastic sheet. Absorption ability is found to increase with the increase of thickness as well as MWNTs content. This increase of absorption may occur due to the increase of conductivity with the increase of MWNTs content [37].

The CNT/cellulose sheets exhibit very small reflection and the reflections slightly improve with the increase of MWNTs content as shown in **Figure 18**. It is conjectured that interfacial electric polarization improves with the increase of MWNTs content due to the interaction of

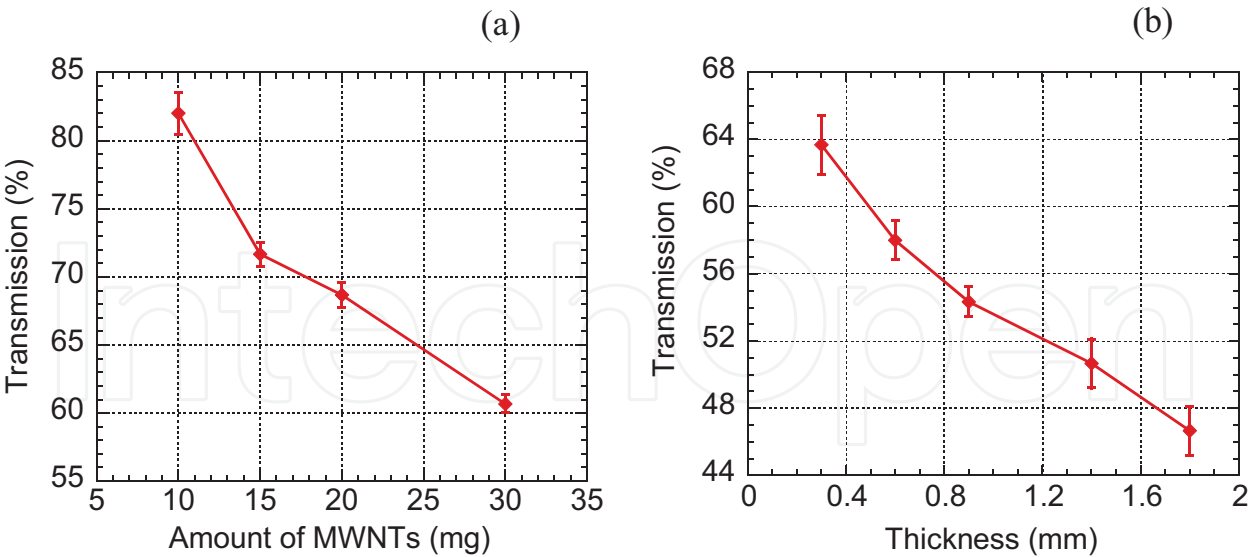


**Figure 16.** Schematic representation of the (a) microwave absorption measurement and (b) reflection measurement of CNT/cellulose sheet.

microwave radiation with the large number of charge multipoles between the MWNTs and cellulose, which causes reflection rather absorption as shown in **Figure 18(b)**. The results can be comparable with the previous examinations with the other composites of MWNT [42]. This means, there are several considerable factors, like the MWNTs content, thickness of sheet, the interfacial electric polarization, etc. to design a microwave absorbing material [37, 43]. It is also found that a zigzag setup of four sheets of same dimensions, each contains 30 mg MWNTs can absorb about 50% of the incident microwave. Therefore, this composite sheet may have great potential for microwave absorbing applications taking into account all the above results.

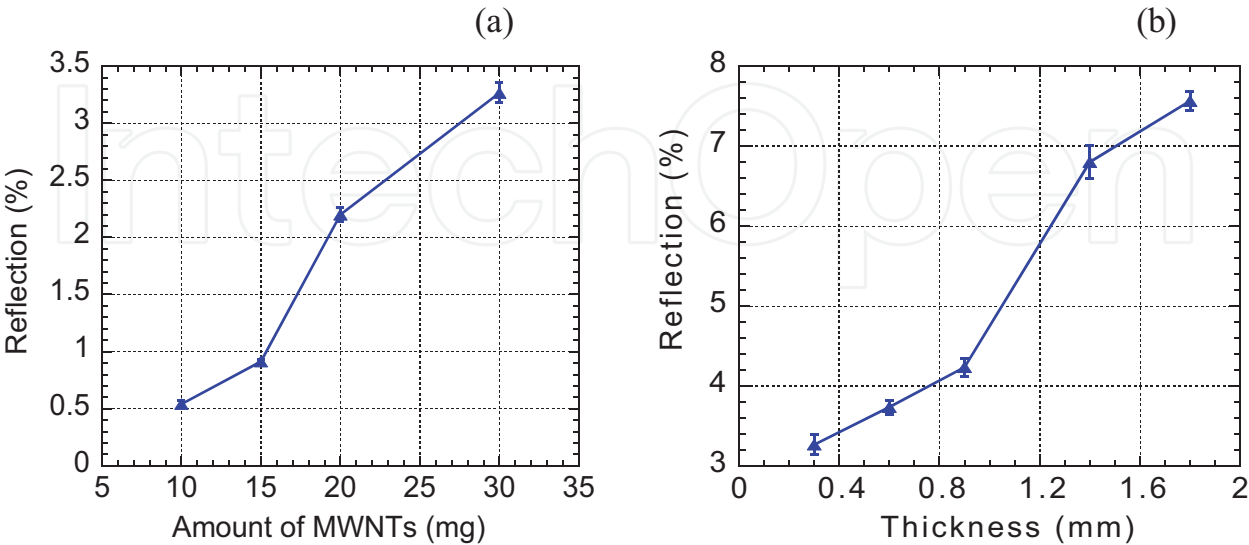
*5.4.4. Aqueous absorption speed of CNT/cellulose composites*

Generally, cellulose sheets have high absorption speed, which in turn degrades their functional, structural, and mechanical properties. CNT/cellulose composite shows the significant improvement on the aqueous absorption properties without degradation resulted from the



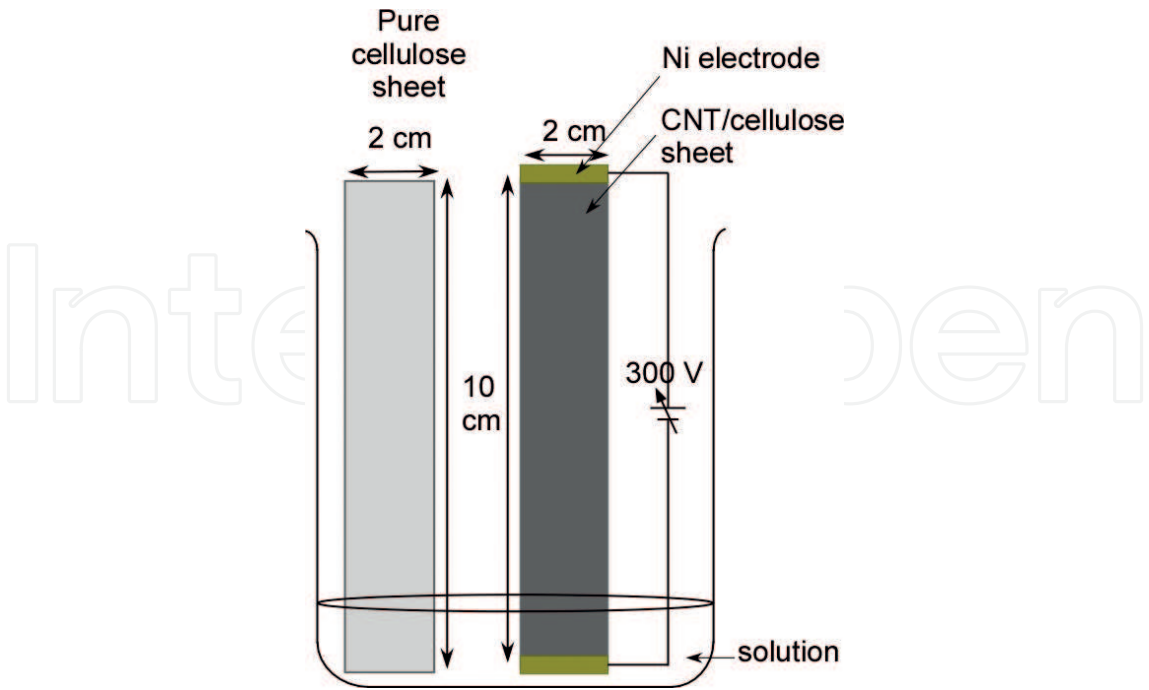
**Figure 17.** Variation of transmission property of the CNT/cellulose sheet (a) with the increase of MWNT content and (b) with the thickness, where MWNT content increases with the thickness.

addition of carbon nanotubes in the cellulose. The pure cellulose sheet and CNT/cellulose sheet are prepared with a size of  $100 \times 20 \times 0.3 \text{ mm}^3$  for this experiment. In this experiment, the samples are immersed in color and saline. Both the cellulose and CNT/cellulose sheets start to absorb aqueous solution immediately after the immersion and keep the sheets in the solution until they get wet completely. The schematic of the absorption speed measurement is shown in **Figure 19(a)**. The absorption speed, weight changes of the CNT/cellulose sheets are measured from this experiment and compared with the pure cellulose sheet. Absorbed amount of saline by the sheets are calculated by measuring the weight changes of the sheets after the experiment.



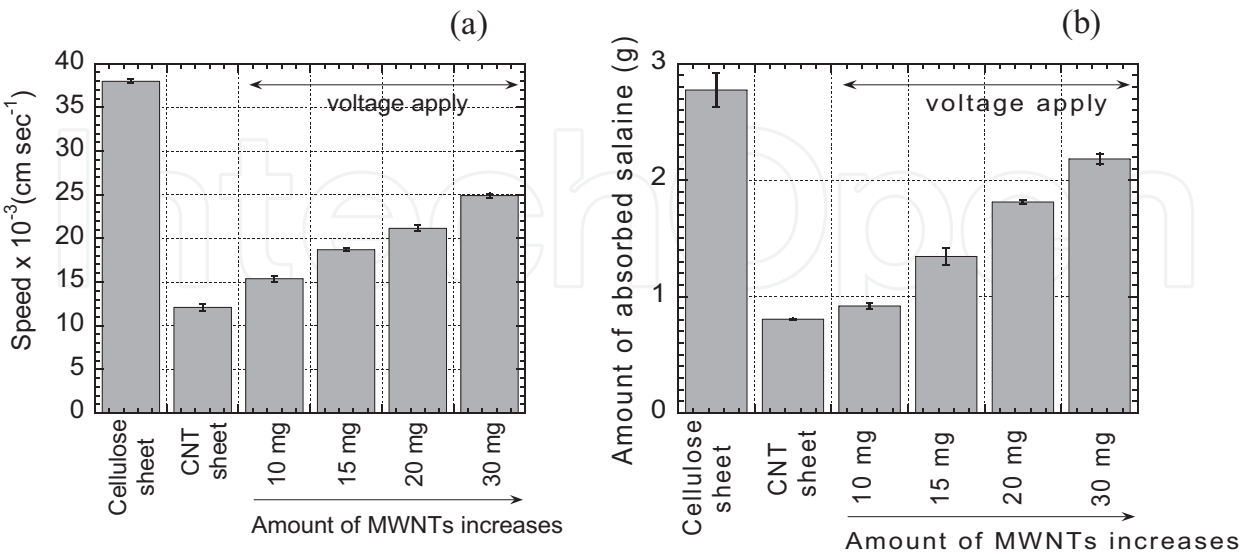
**Figure 18.** Variation of reflection property of the CNT/cellulose sheet (a) with the increase of MWNT content and (b) with the thickness, where MWNT content increases with the thickness.





**Figure 19.** (a) Schematic of the absorption speed measurement of the CNT/cellulose sheet. (b) Absorption speed of the cellulose sheet and CNT/cellulose sheet in different solutions and conditions.

**Figure 19(b)** shows that the absorption speed of the cellulose sheet is very high in both color and saline. On the other hand, the CNT/cellulose sheet has low absorption speed. A high voltage, ~300 V, is applied through Ni electrode to the CNT/cellulose sheet to investigate the changes in speed, and it is found that the absorption speed increases significantly in both color and saline.



**Figure 20.** (a) Absorption speed of the cellulose sheet and CNT/cellulose sheet with the increase of MWNT content, (b) amount of absorbed saline with the increase of MWNT content.

The high voltage is also applied by changing the polarity and it does not have any noticeable effect in absorption speed. It is also evident from **Figure 20** that absorption speed and absorbed amount increases with the increase of MWNT content and by applying voltage. This may indicate that the absorption speed and absorbed aqueous amount of the CNT/cellulose sheet is controlled by the MWNT loading [37]. Addition of MWNTs in the sheet or and high voltage may responsible to increase the diffusive energy of the aqueous molecule to penetrate through the sheet. Absorption speed is also governed by other factors, for example cellulose pulp content, dispersion of MWNT, and homogeneous mixing of MWNT with the cellulose in the sheet. This increasing behavior of absorption speed of the composite sheet indicates the mechanical reliability of the composite.

## 6. Summary

This work provides a simple and effective method for dispersing CNTs in water by using gelatin in order to broaden the application of CNTs. Gelatin wraps the surface of the nanotube to form a stable dispersion, which remains stable for more than a month. This wrapping method does not affect the physical properties of the nanotube. In addition, it can be easily removed from the nanotubes after the dispersion of nanotubes by heating in water and filtration.

The applications of CNTs as composites offer new opportunities to produce cost-effective electronics. CNT-based sheet has been prepared by using a paper making process. MWNTs improve the mechanical, thermal, and electrical properties of cellulose. SEM investigation confirms the homogeneous distribution of MWNTs in the cellulose, which can be attributed to the improvement of its characteristics. Both sides of the CNT/cellulose sheet show uniform electrical conductivity, which is enhanced by increasing the MWNTs content. IR image of the sheet clearly shows the temperature homogeneity of the surface. Thermal stability and the flame retardancy of the sheet are also found to be improved. The sheet has also strong absorbing of electromagnetic waves, which makes them important for microwave technology applications. These electrically conductive and electromagnetic-wave-absorption properties can be useful in radar wave absorbing, electro thermal heating elements, and 2D electric circuit applications, electromagnetic shields, etc.

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## Author details

Kazi Hanium Maria<sup>1,2\*</sup> and Tetsu Mieno<sup>2,3</sup>

\*Address all correspondence to: kazimaria@du.ac.bd

1 Department of Physics, University of Dhaka, Dhaka, Bangladesh

2 Graduate School of Science and Technology, Shizuoka University, Shizuoka, Japan

3 Department of Physics, Shizuoka University, Shizuoka, Japan

## References

- [1] Endo M, Strano MS, Ajayan PM. Potential applications of carbon nanotubes. In: Jorio A, Dresselhaus G, Dresselhaus MS, editors. Carbon Nanotubes-Topics in Applied Physics. Heidelberg: Springer; 2008. p. 13-26
- [2] Iijima S. Helical microtubules of graphitic carbon. *Nature*. 1991;**354**:56-58. DOI: 10.1038/354056a0
- [3] Baughman HR, Zakhidov AA, de Heer WA. Carbon nanotubes—The route toward applications. *Science*. 2002;**297**:787-792. DOI: 10.1126/science.1060928
- [4] Yan XB, Tai XZ, Chen JT, Xue JQ. Fabrication of carbon nanofiber–polyaniline composite flexible paper for supercapacitor. *Nanoscale*. 2010 Nov 8;**3**:212-216. DOI: 10.1039/c0nr00470g
- [5] Chen C, Yang QH, Yang Y, Lv W, Wen Y, Hou PX, Wang M, Cheng HM. Self-assembled free-standing graphite oxide membrane. *Advanced Materials*. 2009 Apr 20;**21**:3007-3011. DOI: 10.1002/adma.200803726
- [6] Nishide H, Oyaizu K. Toward flexible batteries. *Science*. 2008 Feb 8;**319**:737-738. DOI: 10.1126/science.1151831
- [7] Brosseau C, Boulic F, Queffelec P, Bourbigot C, YLe M, Loaec J, Beroual A. Dielectric and microstructure properties of polymer carbon black composites. *Journal of Applied Physics*. 1997;**81**:882-891
- [8] Mdarhri A, Carmona F, Brosseau C, Delhaes P. Direct current electrical and microwave properties of polymer-multiwalled carbon nanotubes composites. *Journal of Applied Physics*. 2008;**103**:054303-054309
- [9] Fei B, Lu H, Hu Z, Xin JH. Solubilization, purification and functionalization of carbon nanotubes using polyoxometalate. *Nanotechnology*. 2006 Feb 21;**17**:1589-1593. DOI: 10.1088/0957-4484/17/6/010

- [10] Krueger A. Carbon nanotubes. In: Carbon Materials and Nanotechnology. Weinheim: Wiley-VCH; 2010. p. 123-281. DOI: 10.1002/9783527629602.ch3
- [11] Zimmerman JL, Bradley RK, Huffman CB, Hauge RH, Margrave JL. Gas-phase purification of single-wall carbon nanotubes. *Chemistry of Materials*. 2000;**12**:1361-1366. DOI: 10.1021/cm990693m
- [12] O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, Haroz E, Kuper C, Tour J, Ausman KD, Smalley RE. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. *Chemical Physics Letters*. 2001;**342**:265-271. DOI: 10.1016/S0009-2614(01)00490-0
- [13] Hill DE, Lin Y, Rao AM, Allard LF, Sun YP. Functionalization of carbon nanotubes with polystyrene. *Macromolecules*. 2002;**35**:9466-9471. DOI: 10.1021/ma020855r
- [14] Dang ZM, Wang L, Zhang LP. Surface functionalization of multiwalled carbon nanotube with trifluorophenyl. *Journal of Nanomaterials*. 2006;**2006**:1-5. Article ID: 83583. DOI: 10.1155/JNM/2006/83583
- [15] Kim WJ, Nairs N, Lee CY, Strano MS. Covalent functionalization of single-walled carbon nanotubes alters their densities allowing electronic and other types of separation. *The Journal of Physical Chemistry C*. 2008;**112**:7326-7331. DOI: 10.1021/jp710919b
- [16] Ávila-Orta CA, o González- Morones P, Espinoza-González CJ, Martínez-Colunga JG, Neira-Velázquez MG, Sáenz-Galindo A, López-López LT. Toward greener chemistry methods for preparation of hybrid polymer materials based on carbon nanotubes. In: Suzuki S, editor. *Syntheses and Applications of Carbon Nanotubes and their Composites*. Intech; 2013. p. 167-192. DOI: 10.5772/51257
- [17] Maria KH, Mieno T. Effect of gelatin on the water dispersion and centrifugal purification of single-walled carbon nanotubes. *Japanese Journal of Applied Physics*. 2015;**55**:01AE04. DOI: 10.7567/JJAP.55.01AE04
- [18] Elzoghby AO: Gelatin-based nanoparticles as drug and gene delivery systems: Reviewing three decades of research. *Journal of Controlled Release*. 2013;**172**:1075-1091. DOI: <http://dx.doi.org/10.1016/j.jconrel.2013.09.019>
- [19] Aramwit P, Jaichawa N, Ratanavaraporn J, Srichana T. A comparative study of type a and type B gelatin nanoparticles as the controlled release carriers for different model compounds. *Materials Express*. 2015;**5**:241-248. DOI: 10.1166/mex.2015.1233
- [20] Kozlov PV, Burdygina GI. The structure and properties of solid gelatin and the principles of their modification. *Polymer Reviews*. 1983;**24**:651-666. DOI: 0032-2861/83/060651
- [21] Zheng W, Zheng YF. Gelatin-functionalized carbon nanotubes for the bioelectrochemistry of hemoglobin. *Electrochemistry Communications*. 2007;**9**:1619-1623. DOI: 10.1016/j.elecom.2007.03.007



- [22] Kim Y, Minami N, Kazaoui S. Highly polarized absorption and photoluminescence of stretch-aligned single-wall carbon nanotubes dispersed in gelatin films. *Applied Physics Letters*. 2005;**86**:073103. DOI: 10.1063/1.1863448
- [23] Djabourov M, Papon P. Influence of thermal treatments on the structure and stability of gelatin gels. *Polymer*. 1983;**24**:537. DOI: 0032-3861/83/050537
- [24] Rogers JA, Someya T, Huang YG. Materials and mechanics for stretchable electronics. *Science*. 2010;**327**:1603-1607. DOI: 10.1126/science.1182383
- [25] Hu LB, Pasta M, FLa M, Cui LF, Jeong S, Deshazer HD, Choi JW, Han SM, Cui Y. Stretchable, porous, and conductive energy textiles. *Nano Letters*. 2010;**10**:708-714. DOI: 10.1021/nl903949m
- [26] Yan XB, Tai XZ, Chen JT, Xue JQ. Fabrication of carbon nanofiber–polyaniline composite flexible paper for supercapacitor. *Nanoscale*. 2010;**3**:212-216. DOI: 10.1039/c0nr00470g
- [27] Li X, Rong J, Wei B. Electrochemical behavior of single-walled carbon nanotube supercapacitors under compressive stress. *ACS Nano*. 2010;**4**(10):6039-6049. DOI: 10.1021/nn101595y
- [28] Tanaka T, Sano E, Imai M, Akiyama K. Electrical conductivity of carbon-nanotube/cellulose composite paper. *Journal of Applied Physics*. 2010;**107**:054307. DOI: 10.1063/1.3319675
- [29] Yun S, Kim J. Multi-walled carbon nanotubes–cellulose paper for a chemical vapor sensor. *Sensors and Actuators, B: Chemical*. 2010;**150**:308-313. DOI: 10.1016/j.snb.2010.06.068
- [30] Klemm D, Heublein B, Fink HP, Bohn A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie, International Edition*. 2005;**44**:3358-3393. DOI: 10.1002/anie.200460587
- [31] Kim J, Yun S, Ounaies Z. Discovery of cellulose as a smart material. *Macromolecules*. 2006;**39**:4202-4206. DOI: 10.1021/ma060261e
- [32] Turner MB, Spear SK, Holbrey JD, Rogers RD. Production of bioactive cellulose films reconstituted from ionic liquids. *Biomacromolecules*. 2004;**5**:1379-1384. DOI: 10.1021/bm049748q
- [33] Ebbesen TW, Lezec JH, Hiura H, Bennett WJ, Ghaemi FH, Thio T. Electrical conductivity of individual carbon nanotubes. *Nature*. 1996;**382**:54-56. DOI: 10.1038/382054a0
- [34] Kashiwagi T, Du F, Douglas JF, Winey KI, Harris RH Jr, Shields JR. Nanoparticle networks reduce the flammability of polymer nanocomposites. *Nature Materials*. 2005;**4**:928-933. DOI: 10.1038/nmat1502
- [35] Rahman MJ, Mieno T. Conductive cotton textile from safely functionalized carbon nanotubes. *Journal of Nanomaterials*. 2015;**2015**:978484-1-978484-10. DOI: 10.1155/2015/978484
- [36] Fugetsu B, Sano E, Sunada M, Sambongi Y, Shibuy T, Wang X, Hiraki T. Electrical conductivity and electromagnetic interference shielding efficiency of carbon nanotube/cellulose composite paper. *Carbon*. 2008;**46**:1256-1258. DOI: 10.1016/j.carbon.2008.04.024

- [37] Maria KH, Mieno T. Production and properties of carbon nanotube/cellulose composite paper. *Journal of Nanomaterials*. 2017;**2017**:6745029-1-6745029-11. DOI: 10.1155/2017/6745029
- [38] Beneventi D, Alila S, Boufi S, Chaussy D, Nortier P. Polymerization of pyrrole on cellulose fibres using a FeCl<sub>3</sub> impregnation- pyrrole polymerization sequence. *Cellulose*. 2006;**13**:725-734. DOI: 10.1007/s10570-006-9077-9
- [39] Ceylan O, Landuyt LV, Rahier H, De Clerck K. The effect of water immersion on the thermal degradation of cotton fibers. *Cellulose*. 2013;**20**:1603-1612. DOI: 10.1007/s10570-013-9936-0
- [40] Ragab T, Olsson C. Joule heating in single-walled carbon nanotubes. *Journal of Applied Physics*. 2009;**106**:063705. DOI: 10.1063/1.3204971
- [41] Kang J, Kim H, Kim KS, Lee SK, Bae S, Ahn JH, Kim YJ, Choi JB, Hong BH. High-performance graphene-based transparent flexible heaters. *Nano Letters*. 2011;**11**:5154-5158. DOI: 10.1021/nl202311v
- [42] Nwigboji IH, Ejembi JI, Wang Z, Bagayoko D, Zhao GL. Microwave absorption properties of multi-walled carbon nanotube (outer diameter 20-30 nm) epoxy composites from 1 to 26.5 GHz. *Diamond and Related Materials*. 2014;**52**:66-71. DOI: 10.1016/j.diamond.2014.12.008
- [43] Fan Z, Luo G, Zhang Z, Zhou L, Wei F. Electromagnetic and microwave absorbing properties of multi-walled carbon nanotubes/polymer composites. *Materials Science and Engineering B*. 2006;**132**:85-89. DOI: 10.1016/j.mseb.2006.02.045

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