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Green, Scalable, Binderless Fabrication of a Single-Walled Carbon Nanotube Nonwoven Fabric Based on an Ancient Japanese Paper Process

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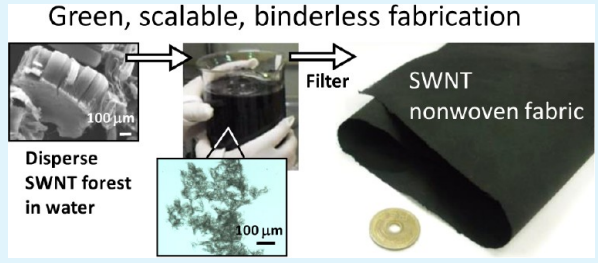
Supporting Information

ABSTRACT: We propose a fabrication method for carbon nanotube (CNT) nonwoven fabrics based on an ancient Japanese papermaking process where paper is made from natural plant fibers. In our method, CNT nonwoven fabrics are made by a scalable process of filtering binder-free, aqueous suspensions of CNTs. The aqueous suspension of these entangled single-walled carbon nanotube (SWNT) aggregates enabled smooth filtration through a cellulose filter with large pores (8 μm). The "wet SWNT cakes," which were composed solely of SWNT and water and obtained after filtration, were press-dried to fabricate an SWNT nonwoven fabric. This environmentally friendly process employs water and the raw CNT material alone. Moreover, the scalability of this process was demonstrated by manufacturing a large area (A3, 30 × 42 cm; thickness: 40−150 μm), self-supporting SWNT nonwoven fabric with a density of 0.4 g/cm^3, a basis weight of 0.2 g/m^2 , a porosity of 63%, and a specific surface area of 740 m^2/g. This SWNT nonwoven fabric is anticipated to find application as functional particle-supported sheets, electrode materials, and filters.



KEYWORDS: *carbon nanotubes, nonwoven fabric, dispersion, water, filtration, green process*

INTRODUCTION

Nonwoven fabrics are porous materials that can be manufactured via a number of processes. These include chemically bonding fibers layered in either a single or random directions by adhesive resins, entangling fibers by mechanical treatment or pressurized water flow, and thermally fusing fibers.[1] Nonwoven fabrics are important industrial films that have varied usages from air filters, liquid filters, separators for batteries and capacitors, electrical insulation materials, apparel materials, and medical materials. However, the most common nonwoven fabric is paper. An ancient Japanese paper manufacturing method, known as "*Kamisuki*" (*kami*: paper; *suki*: gathering/scooping), uses aqueous suspensions of natural plant fibers to produce paper.[2] There are two variations of *Kamisuki*: namely, "*Nagashisuki*" that employs a binder (plant-based viscous liquid) and "*Tamesuki*" where no binder is used. Here, we employ the latter.

In the "*Tamesuki*" process, fibers shortened for easier water dispersion are dried over a filter in a filtration process. The process entails suspending the raw material in water, followed by filtration, press-drying, and separating the paper from the filter. In the filtration process, the pores of the filter are more easily blocked when the suspension consists of fine fibers. Therefore, in papermaking, the fibers are intentionally not dispersed into such fine particles and are dried by using a filter with large pore sizes for smooth filtration.

Among nonwoven fabrics, those made from carbon fibers have been employed in a variety of applications ranging from high-temperature furnace lining materials, mechanical reinforcement materials, filtering materials, electrode materials, and water purification by microbial film formation on the fabric. Within this paradigm, the technological development of carbon-fiber-based nonwoven fabrics has seen a shift from macrofiber nonwoven fabrics to nanofiber nonwoven fabrics because of the demand for higher specific surface area, i.e., surface area per weight.[3] Higher specific surface area leads to improved adsorption capacity, higher capability to support functional particles, and improved filtering properties for finer particles.

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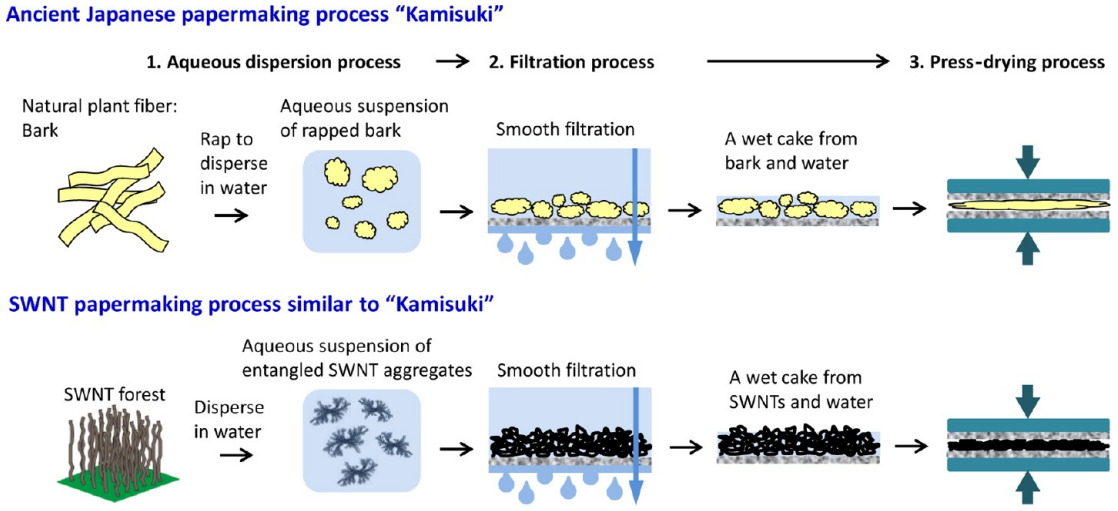

Figure 1. Ancient Japanese papermaking process "*Kamisuki*" (*kami*, paper; *suki*, gathering/scooping) comprising aqueous dispersion, filtration, and press-drying, and SWNT papermaking process similar to "*Kamisuki*".

Carbon nanotubes (CNTs) possess the smallest diameters of any carbon-based fiber and thus boast the highest specific surface area. Thereby, nonwoven fabrics made of CNTs can be expected to exhibit markedly improved performance. A nonwoven fabric made of CNTs was reported as buckypaper[4−6] by Smalley et al. Subsequently, Baughman et al. reported that an actuator fabricated from electrolyte-filled buckypaper underwent large deformation using only a low drive voltage of several volts, which was difficult to achieve with conventional ferroelectric actuators.[7] Furthermore, Kane et al. showed that buckypapers are ideal for use as fine particulate filters by demonstrating the filtration efficiency with monodisperse aerosols of 50−500 nm.[8] Buckypapers were also utilized as a scaffold for single-walled carbon nanohorns showing the high power capability as capacitor electrode material.[9] Gun'ko et al. carried out in situ deposition of gold nanoparticles on CNTs during filtration, and clarified a significant increase in the electrical conductivity of buckypaper.[10] Furthermore, Liang et al. reported that a CNT-sheet-reinforced bismaleimide composite with mechanically stretched buckypaper showed the tensile strength and Young's modulus comparable to those of a carbon-fiber-reinforced composite for high-performance structural applications.[11]

Buckypaper is typically fabricated from filtration of CNT dispersions.[4−6] This process inherently possesses several problems. First, commonly, a binder (e.g., surfactant) is required to create a uniform CNT dispersion.[12−16] Therefore, these binders require removal, which is inherently difficult. Second, the dispersion process to create a homogenous dispersion of isolated CNTs results in significant CNT length reduction to several micrometers.[17] Third, filtration of such a dispersion of isolated CNTs requires a fine membrane filter (0.1−5 μm), which can be easily blocked, and hence, productivity is low (e.g., producing thick films is difficult).

In this paper, we apply the ancient Japanese paper manufacturing method, *kamisuki*, to propose a buckypaper manufacturing process based on binder-free, aqueous suspensions of entangled aggregates of long, as opposed to isolated and shortened, CNTs. Using the *kamisuki* method as a base, single-walled CNT (SWNT) vertically aligned structures (forests) several hundred micrometers in height were dispersed into entangled aggregates several hundred micrometers to 2 mm in size in water without a binder. These suspensions of entangled aggregates were then filtered using a cellulose filter with a large pore size (8 μm) to obtain buckypaper. This method could be easily transferred to continuous large-area production. Moreover, thick films (several tens of μm) could be manufactured easily. As a demonstration, a large-area buckypaper was fabricated (A3 size (30 × 42 cm); thickness: 55 μm), which was shown to possess a very high specific surface area (740 m^2/g), porous and light (bulk density: 0.4 g/cm^3; basis weight: 0.2 g/m^2; porosity: 63%), and a self-supporting film composed solely of high-purity SWNTs.

EXPERIMENTAL SECTION

SWNT Synthesis. SWNTs were synthesized in a fully automated 100-tube furnace by water-assisted chemical vapor deposition. C_2H_4 was employed as the carbon source on an Fe−Ni−Cr alloy foil, and Fe/Al_2O_3 was used as the catalytic metal film. A combination of helium (He) and hydrogen (H_2) at 1 atm pressure was used as the carrier gas (total flow rate: 1000 sccm), and the quantity of steam was regulated (concentration: 100−150 ppm). By using C_2H_4 (100 sccm), the SWNTs were grown at 750°C over a period of 10 min. The heights of the SWNT forests synthesized were 100 μm up to 1 mm.

Materials. Ultrapure water, purified using a Milli-Q ultrapure water manufacturing unit, was used to disperse SWNTs. The surfactant sodium deoxycholate was obtained from Wako Pure Chemical Industries.

Fabrication of SWNT Nonwoven Fabric. *Dispersion.* SWNTs were suspended in water by using a high-pressure jet mill homogenizer (130 to 150 MPa; total of two passes; Star Burst Labo HJP-17007R, Sugino Machine) to fabricate entangled SWNT aggregates (CNT concentration: 0.025 wt %). The jet mill, which discharges the suspension from a nozzle at high pressure to exfoliate the materials, is capable of suspending long SWNTs while minimizing shortening of the CNT length. The jet mill thus has great advantages over other dispersion methods, such as ultrasonication. Isolated dispersions of SWNTs were formed by adding SWNTs (CNT concentration: 1 wt %) to water in which the surfactant sodium deoxycholate (1 wt %) was dissolved, and carrying out ultrasonication for 300 min at 100 W and 35 kHz.

Filtration. Aqueous suspensions of entangled SWNT aggregates (1.0, 1.25, or 2.5 g of SWNT suspended in 4, 5, or 10 L of water, respectively) were filtered through a cellulose filter (pore size: 8 μm; qualitative filter paper No. 2, Whatman) by vacuum drawing in an A3 size (30 × 42 cm) pool. For isolated SWNT dispersions, filtration was

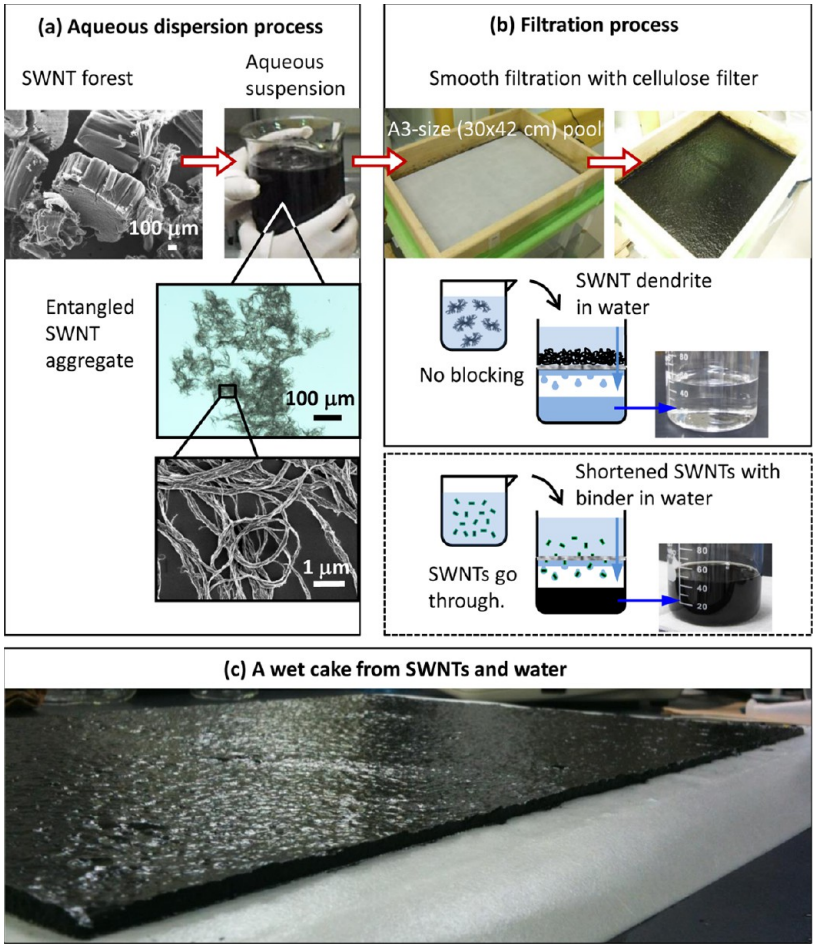

Figure 2. Fabrication process of nonwoven fabric from aqueous suspension of entangled SWNT aggregates: (a) aqueous dispersion process of SWNT forest without a binder, showing the aqueous suspension of entangled SWNT aggregates, (b) filtration process with an A3 size (30 × 42 cm) pool equipped with a cellulose filter, leading to a smooth filtration with a transparent filtrate, whereas an aqueous solution of shortened SWNTs with a binder resulted in an unsuccessful filtration with a black filtrate. (c) A wet cake from SWNTs and water collected on the cellulose filter after filtration.

carried out by vacuum drawing through a cellulose filter 7 cm in diameter.

Press-Drying. Wet cakes obtained by filtering aqueous suspensions of entangled SWNT aggregates were sandwiched between two sheets of cellulose filter, pressed using two wooden sheets and two 6.5 kg steel sheets, and dried. After the wet cakes were naturally dried in their pressed forms for 3 days, they were dried overnight in a vacuum oven at 180 °C.

Characterization of Entangled SWNT Aggregates and SWNT Nonwoven Fabric. *Structure Observation.* The dispersed aggregate structure of the SWNTs and the surface and cross section of the SWNT nonwoven fabric were observed using a laser microscope (VK-9700, Keyence) and a scanning electron microscope (SEM; FE-SEM S-4800, Hitachi High-Technologies). The SEM sample for analyzing the dispersed aggregate structure of the SWNT was fabricated by spin-coating an aqueous suspension of SWNTs onto a silicon substrate.

Tensile Test. The tensile test samples were cut into a dogbone shape from the sheet with the dimensions of 40 mm (length) × 2 mm (width) × 0.05 mm (thickness). The extension rate and the gauge length were 1.0 mm/min and 20 mm. The tests were performed using a Micro Autograph MST-I (Shimadzu Co.) with a 100 N load cell. Five specimens were used.

Electrical Measurement. Electrical conductivity was measured using the four-point probe method (MCP-T610, Mitsubishi Chemical Analytech).

Surface Area Measurement. For the surface area measurement, nitrogen adsorption and desorption isotherms at 77 K were measured using a Belsorp Mini II Surface Area and Pore Size Analysis system (BEL Japan Inc.). A 30 mg portion of the sample was used for the measurement.

Structural Analysis. Structural analysis of SWNT nonwoven fabrics was carried out using XRD. $\theta-2\theta$ XRD was carried out using an RINT2100 (Rigaku) X-ray diffractometer with a Cu−Kα X-ray source at a total power of 1.2 kW.

■ RESULTS AND DISCUSSION

The traditional papermaking process entails disassembling a raw material (natural plant fibers), suspending in water, followed by filtration and press-drying (Figure 1). We carried out SWNT papermaking by following this basic manufacturing process. First, forests composed of long SWNTs with high purity were dispersed in water to form an aqueous suspension of entangled SWNT aggregates. Filtration was then carried out using a cellulose filter to create a "wet cake" composed solely of SWNTs and water. Finally, an SWNT nonwoven fabric was made via press-drying of the wet cake.

SWNTs were grown from a sequentially sputtered Fe/Al_2O_3 as catalyst/support layer using a C_2H_4 carbon feedstock on an Fe−Ni−Cr alloy substrate by the water-assisted chemical vapor deposition (CVD) method.[18−20] In this method, a minute level (~150 ppm) of water is inserted into the growth ambient to increase catalyst activity. The SWNT forests were composed of

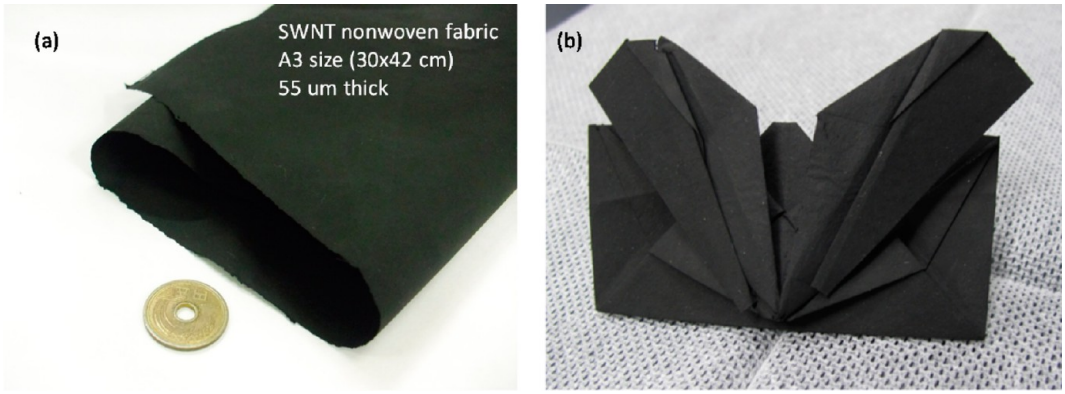

Figure 3. (a) SWNT nonwoven fabric with A3 size (30 × 42 cm) and 55 μm thickness (a coin placed nearby for the size reference). (b) "Origami" (Japanese helmet) made by folding the SWNT nonwoven fabric.

3 nm average diameter, long SWNTs (height: several hundred μm) of high purity (carbon purity: 99.98%) and high specific surface area (>1000 m^2/g), which were oriented perpendicularly on the substrate. These forests are ideal for a raw material for SWNT nonwoven fabrics. The quantity of SWNTs in these forests comprised only ∼3% by volume, the bulk density was low (0.03 g/cm^3), and the SWNTs were loosely entangled in a state whereby they could be easily dispersed.[21,22]

SWNT forests were removed from the growth substrate and added in water (1.25 g of SWNT in 5 L of water; CNT concentration: 0.025%) and dispersed using a wet-type jet mill that generates shear (130 MPa → 150 MPa; total of two passes) through turbulence to obtain entangled SWNT aggregates (Figure 2a). A sampling of this suspension of entangled SWNT aggregates was deposited onto a flat substrate for scanning electron microscope (SEM) observation, which revealed a fibrous entangled network structure ranging in size from several hundred micrometers to 2 mm and composed of bundles of loosely entangled SWNTs ranging in diameter from several hundred nanometers to ∼1.5 μm. Thus, by using a jet mill, dispersion was possible without compromising the quality of the SWNTs while preserving their length.[21,22] The loosely entangled forest structure directly led to the entangled aggregates form, which afforded a pore volume between bundles to be occupied by water. In general, the hydrophobicity of carbon materials makes dispersion in water difficult[23] and typically requires surface modification or binders such as surfactants to disperse them.[24,25] However, these SWNTs, despite being hydrophobic, did not precipitate in water because the pseudo one-dimensional, flexible SWNTs were loosely entangled, forming entangled aggregates; hence, these aggregates formed a macroscopic entangled network and exhibited long-term stability (>1 year).

Filtration was carried out using aqueous suspensions of these entangled SWNT aggregates (Figure 2b). We used a large pore size (8 μm) hydrophilic cellulose filter that enabled effective separation of water. The large entangled SWNT aggregates, several hundred micrometers to 2 mm in size, did not block the pores of the cellulose filter, and smooth filtration was possible. The suspensions (5 L) were filtered for 5 min to make an A3 size SWNT nonwoven fabric.

The wet SWNT cakes obtained on the filter were composed solely of SWNTs and water and could easily be pressed into arbitrary shapes (Figure 2c). These wet cakes were processed into the nonwoven fabric by press-drying them by sandwiching them between two cellulose filters, two wooden sheets, and two 6.5 kg steel plates. This manufacturing method employs no organic solvents or binders and is an environmentally friendly, green process that uses only water and the raw SWNT material.

As mentioned previously, the fabrication of nonwoven fabric, using long SWNTs as a raw material, is difficult with traditional buckypaper fabrication technology. Conventionally, buckypapers are fabricated through the filtration of dispersions of isolated CNTs in an organic solvent through membrane filters.[26,27] This process has several disadvantages. First, in achieving an isolated dispersion state, significant CNT shortening occurs.[17] Second, the filtration requires the use of membrane filters with small pore sizes (0.1−5 μm) as the CNTs pass through filters with larger pore sizes (>5 μm). However, small pores are easily blocked by CNTs at high densities.[27] Third, organic solvents, such as *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP), are required in large quantities, or alternatively, water is used in conjunction with a binder. Achieving high CNT concentration dispersions with those solvents has been challenging,[14,16,27] and consumption of large amounts of solvents and binders are unavoidable. The former creates a high environmental burden, and the latter requires subsequent removal of the binder.

The entangled SWNT aggregates in this research preserved the quality and length of the individual SWNTs. Because of their large size (several hundred μm to 2 mm), the suspensions could be filtered with a cellulose filter of large pore size (8 μm). The filtrate obtained was transparent (Figure 2b), and smooth filtration of the suspension was possible. In contrast, an isolated SWNT aqueous (plus binder) dispersion was also made by ultrasonication for comparison, but the filtration with a cellulose filter yielded a black filtrate because the shortened SWNTs passed through the filter (Figure 2b). The nonwoven fabric obtained based on this papermaking method using an aqueous suspension of entangled SWNT aggregates was self-supporting of size A3 (30 × 42 cm) and 55 μm thick (Figure 3a). This SWNT nonwoven fabric was flexible and bendable and possessed mechanical strength (tensile strength (σ): 3.6 MPa; Young's modulus (Y): 0.3 GPa) lower than that of paper (σ: 20−200 MPa; Y: 1.8−4.3 GPa) (Figure S1 in the Supporting Information).[28] However, these values for the mechanical strength of the SWNT nonwoven fabric rivals with those for conventional buckypapers (σ: 0.4−2.6 MPa; Y: 0.06−0.45 GPa).[29] The SWNT nonwoven fabric could also be used for "Origami", and the authors were able to make a Japanese helmet by folding the nonwoven fabric (Figure 3b). Furthermore, SWNT nonwoven fabrics of varied thickness

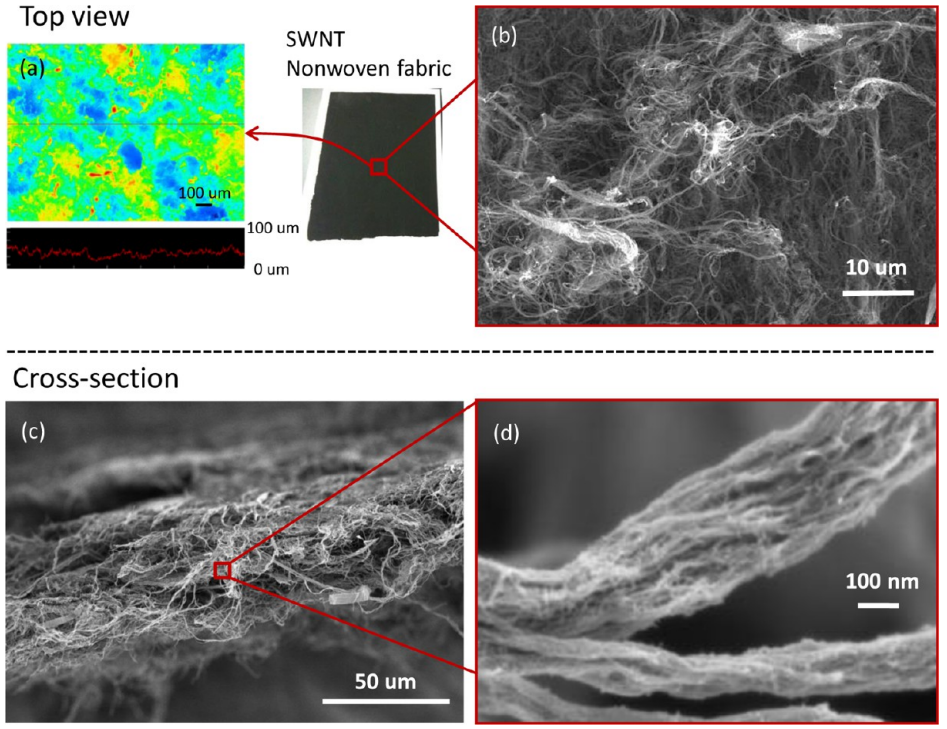

Figure 4. Structure observation of SWNT nonwoven fabric: top view by (a) laser scanning microscope image with the surface roughness and (b) SEM image showing a highly fibrous surface and porous structure. (c, d) Cross-sectional SEM images of the cut nonwoven fabric showing a fibrous structure derived from entangled SWNT aggregates prior to papermaking.

(40, 55, and 150 μm) could be fabricated by varying the aqueous suspension quantity of the entangled SWNT aggregates.

Laser microscope and SEM observations were carried out to investigate the surface structure of SWNT nonwoven fabrics (Figure 4). Observation of the top surface of a nonwoven fabric 55 μm thick (observation range: 1.4 × 1.4 mm^2) with a laser microscope indicated a surface roughness of 25 μm, which corresponds to a highly fibrous surface typical of a nonwoven fabric (Figure 4a). Observation of the top surface of a nonwoven fabric by SEM revealed a porous structure in which pores existed between entangled SWNTs (Figure 4b). This was the structure derived from the entangled SWNT aggregates prior to papermaking, indicating that no significant bundling due to SWNT agglomeration was apparent, and the SWNT aggregate structure prior to papermaking was preserved.

This SWNT nonwoven fabric was cut by scissors, and their cross sections were observed using SEM to investigate their internal structures (Figure 4c,d). A fibril structure identical to that prior to papermaking was observed in the cross section, whereby fibrils several hundred nanometers to ~1.5 μm in diameter derived from entangled SWNT aggregates were loosely entangled.

Next, the pore structure of the SWNT nonwoven fabric was assessed using nitrogen adsorption−desorption isotherms and Brunauer−Emmett−Teller (BET) specific surface area (SSA) analysis.[30] A high specific surface area of 740 m^2/g was obtained. While, in principle, all SWNT buckypapers should exhibit a high SSA, large values are not always measured due to low purity and dense packing. For example, pores may exist, but too small for nitrogen to enter. This condition could occur when the CNTs pack very densely and with long contacts along the side walls. Another example where the specific surface area will be lower than expected is if the pores are small and require more time for the intercalation of the nitrogen molecules. Therefore, this relatively high value indicates that the selectivity of the SWNT and the purity are high, and the pores throughout the bulk are sufficiently large for nitrogen molecules to enter to adsorb. We expect that the deviation from the ideal 1315 m^2/g stems from a combination of these factors and the presence of carbonaceous impurities. Moreover, the porosity of the SWNT nonwoven fabric was high (63%). A porous SWNT nonwoven fabric was thereby verified. A Barrett−Joyner−Halenda (BJH) plot of the mesopores derived from the adsorption isotherms revealed pore sizes in the range of 2−30 μm (Figure 5). While the total volume of mesopores in the SWNT nonwoven fabric was small compared with that in the SWNT forest prior to dispersion in water, this pore size was smaller than that of an aligned, high-density SWNT solid.[31] Specifically, the bulk

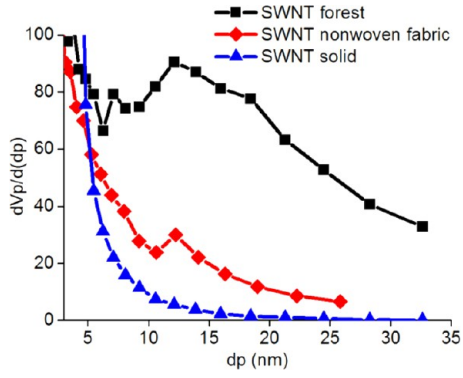

Figure 5. Porous structure of SWNT nonwoven fabric: A Barrett−Joyner−Halenda plot of the mesopores derived from the N_2 adsorption isotherms of SWNT forest, SWNT nonwoven fabric, and SWNT solid.

density of the SWNT nonwoven fabric was 0.4 g/cm^3, which is ~10 times larger than that of the SWNT forest (0.03 g/cm^3) and 0.7 times that of the SWNT solid (0.6 g/cm^3).[31,32] These facts indicate that the nonwoven fabric is a porous material that possesses mesopores in a region between an as-grown forest and an aligned, high-density solid. In addition, this SWNT nonwoven fabric (thickness: 55 μm) was lightweight with a basis weight (areal density) of only 0.2 g/m^2. Although this SWNT nonwoven fabric possessed a highly fibrous surface and porous structure, it could be endowed with a high conductivity (54 S/cm) by mechanical pressing to increase the bulk density.

Furthermore, X-ray diffraction (XRD) measurements were carried out to analyze the structure of the SWNT nonwoven fabric (Figure 6).[33,34] A (002) peak attributable to the "contact points" between individual SWNTs was clearly observed.[31] While XRD shows the contacts/bundling of the CNTs,[35] it does not indicate the nature of the contacts or bundling (i.e., the dense hexagonal packing or simple intermittent crossings). However, the (002) peak exhibited significant broadness, which indicated the loose entanglement of the SWNTs (Figure 4d).

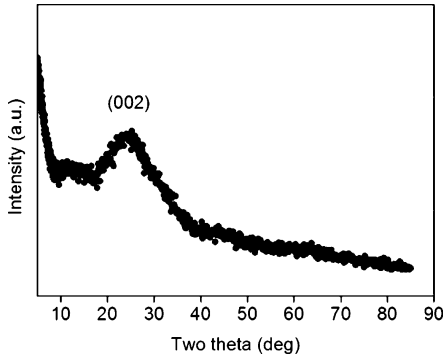

Figure 6. XRD line profile of SWNT nonwoven fabric showing a (002) peak attributable to the "contact points" between individual SWNTs.

It is worthwhile to indicate that, while we demonstrated the method to produce SWNT nonwoven fabric using SWNT forests, we expect that this method is completely general to any variety of CNTs, made from any process, provided that the CNTs possess sufficient length and purity to create the network structure required to assemble the nonwoven fabric. Second, while CNT forests are not yet industrially available, a kilogram-scale mass production pilot plant is now online utilizing the continuous synthesis of CNT forests fed by belt conveyors.[36,37] The comment of the scalability of this method was considered with both this pilot plant and other currently mass produced CNTs (of sufficient length and purity) in mind. Therefore, we believe that the production of SWNT nonwoven fabric is scalable and feasible. The following application developments are anticipated for this SWNT nonwoven fabric according to its various properties: (1) functional particle-supported sheet that exploits the high specific surface area; (2) electrode materials that utilize the high specific surface area, porous structure, and high conductivity; (3) liquid filters based on a material composition of high-purity CNTs alone (no impurities) and a porous structure; and (4) water-purifying materials that exploit the high specific surface area and porous structure (treatment of organic substances by microbial film formation).

CONCLUSIONS

We have developed a CNT nonwoven fabric manufacturing technology based on an ancient Japanese papermaking method, using entangled SWNT aggregates produced from long SWNT forests dispersed only in water without a binder. This process demonstrates a great advantage over conventional CNT nonwoven fabric (buckypaper) manufacturing technology that utilizes large quantities of organic solvent and binders, which must, subsequently, be disposed of and removed, respectively; thus, this method creates a large environmental burden. In contrast, this process, which uses only water and the raw material, is environmentally friendly. Our manufacturing technology, however, can be employed for continuous large area production. Furthermore, because entangled aggregates can be fabricated with the SWNT length and quality preserved, the inherent properties of CNTs can be exploited without the CNT surface damage and shortening that accompany the conventional isolated CNT dispersion process.

ASSOCIATED CONTENT

Supporting Information

A stress–strain curve from tensile test of SWNT nonwoven fabric. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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