MWCNTs-like protection layer formation on bacterial cellulose bundles as a potential material for suspended resonator

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***Abstract*— Suspended carbon naotubes (CNTs) resonator is a sensitive detector for chemical and biological applications. Small sizes of CNTs can enhance sensitivity, but increase complexity for fabrication. In order to overcome the challenges, a novel technique has been developed to produce a long, sensitive and high tensile strength carbon nanotubes (CNT) coated bacterial cellulose (BC) bundle. This study demonstrates the use of ultrasonication to perform carboxyl functionalized multi-walled carbon nanotubes (MWCNTs–COOH) self-assembling on the surface of BC bundles (BC/MWCNTs) *via* hydrogen bonds. Ultrasonication can disrupt dense cellulose network and produce the long BC/MWCNTs bundles ranging from 30 to 100 µm. Raman spectroscopy shows a drop at peak of hydroxyl (–OH, 3700 m^{-1}) and carbonyl (C=O, 1600 cm^{-1}). This indicates the formation of the continuous MWCNTs-like protection layer on BC surface. Electrical properties of the BC/MWCNTs bundles showed linearity from -6 V to +6 V. Composites with BC treated by higher ultrasonic powers, 100 W, show higher conductivity comparing to 80 W. Sensitivity from 10^{-7} to 10^{-9} A of long BC/MWCNTs composite bundles is reported in this paper. This technique may be competitive to the current state of carbon nanotubes resonator.**

I. Introduction

Suspended CNT resonator is widely investigated in past few years. Small sizes of CNTs provide high sensitivity in detection. Atomic mass sensitive [1] and high-quality factors (Q) resonators [2] have been demonstrated the potential in sensing application. Chemical and biological [3 - 6] detection *via* nanowires or CNTs have also been studied. In order to fabricate suspended CNTs resonator, nanofabrication techniques such as e-beam evaporation, e-beam lithography and hydrofluoric acid (HF) wet etch process need to be used [7]. Therefore, fabrication of suspended CNTs remains challenging and costly due to the short length of CNTs (Fig. 1) around 20 – 100 nm. This leads to great difficulties in positioning CNTs during fabrication [7]. Heavy use of e-beam lithography makes the fabrication process costly and time-consuming [8]. Moreover, wet etch process is hard to be controlled and undercut may occur. BC fiber with long length ranging from 10 to 150 µm [9] and high tensile strength up to 94 GPa [10] may be an alternative to overcome the above limitations. As reported by Guhados *et al.* [10], the Young's modulus of a single strand of BC fiber can be up to 78 ± 17 GPa. With introducing MWCNTs into BC, conductivity and elastic properties of BC would be significantly improved [11]. Long, stiff and elastic BC/MWCNTs composite can potentially scale up the size of suspended micro-/nanotubes resonator and enhance resonant frequency and sensitivity (Fig. 1b).

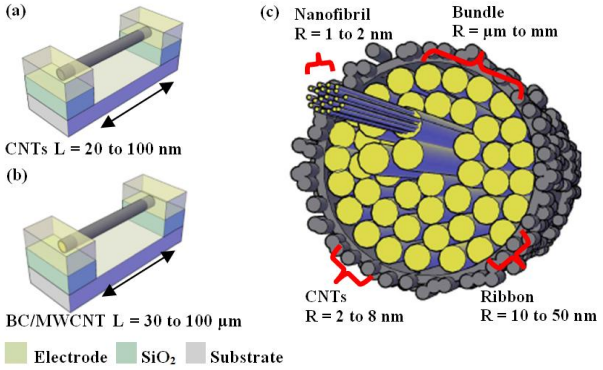

Figure 1. (a) Schematic of typical suspended CNTs resonator (b) schematic of composite based resonator where L indicates length (c) schematic of MWCNTs layer protected BC bundles where R indicates radius.

In order to put a single strand of BC/MWCNTs composite into suspended tube resonator, regeneration of BC fiber would be an alternative. Regenerate bacterial cellulose (RBC) is a commonly used technique for producing BC fiber with the use of organic or inorganic solvents such as N-methylmorpholine-N-oxide (NMMO), dimethylacetamide /lithium chloride (DMAc/LiCl) or zinc chloride (ZnCl) [13 - 15]. Homogeneous and standardized RBC fiber will be produced after wet-spinning process. However, poor tensile strength of RBC fiber has been reported [14] due to the use of solvent system. Moreover, BC will potentially dissolve in solvents such as HF [16] during wet etching process in the fabrication of BC/MWCNTs resonator.

In this study, BC network was disrupted by ultrasonication in order to produce high aspect ratio BC fiber. The process was solvent-free. MWCNTs-like protection layer as shown in Fig. 1c was then formed on a strand of BC bundles *via* ultrasonic mixing. Quality of the layer with different ultrasonic powers and concentrations of MWCNTs was evaluated. Raman spectroscopy was used to detect hydrogen bonding interaction between functional groups. Scanning electron microscopy and electrochemical workstation were used to identify the morphology of MWCNTs layer and conductivity of the composites respectively. Morphology showed that MWCNTs layer was deposited continuously on the surface of BC fiber. This attributed to hydrogen bonding interaction between MWCNTs and BC. Raman spectrum also showed a proof of principle. MWCNTs-like protection layer

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would resist to strong etchant such as HF during fabrication and provide conductivity as measured. As a result, MWCNTs-like protected BC bundles will be a potential material for larger size and higher sensitivity resonator comparing to suspended CNTs resonator in future.

II. Theory

BC bundles have high tensile strength due to interchain hydrogen bonding in cellulose [17]. In order to produce a strand of BC, Guhados' group use sonication to breakdown the dense BC network [10]. Mechanically disruption of the hydrogen bonding by ultrasonic techniques is achievable. However, power and operation times need to be controlled. We used ultrasonication to break down BC into micron-sized fragments. With increasing operating power of ultrasonic from 80 W to 100 W, the populations of BC debris were found increasing and much debris with diameter less than 25 μm was observed. Ultrasonic treatment released functional groups such as -OH and C-O-C group from dense BC network (Fig 2). This resulted in increasing hydrogen bonding interaction between MWCNTs and BC. With assistance of turbulent flow generated by ultrasonication, continuous MWCNTs-like protection layer will be formed on the surface of BC bundles (Fig. 1c).

III. Experiment Procedure

A. Gluconacetobacter xylinus cellulose preparation

Gluconacetobacter xylinus (ATCC 700178) was cultured in Hestrin and Schramm (HS) medium as received. The medium consisted of 2% (w/v), glucose, 0.5 % (w/v) yeast extract, 0.5 % (w/v) peptone, 0.27 % (w/v) disodium phosphate and 0.115 % (w/v) citric acid with pH adjusted to 5.0 [18, 19]. Cell was inoculated into 500 mL Erlenmeyer flask with 100 mL HS medium. The culture was incubated at 30 °C for 5 to 7 days until formation of pellicle at the air-liquid interface. The cellulose was fragmented by blender (Power hand mixer SK-250, SKO Products (USA) Inc, Flushing, New York, USA) until BC became a mush. The resulting slurry was then rinsed with 1% (w/v) sodium hydroxide at 60 °C for 90 minutes and washed by distilled water continuously until the color of cellulose turned white. The resulting BC was stored in glass vials at 4 °C to prevent drying.

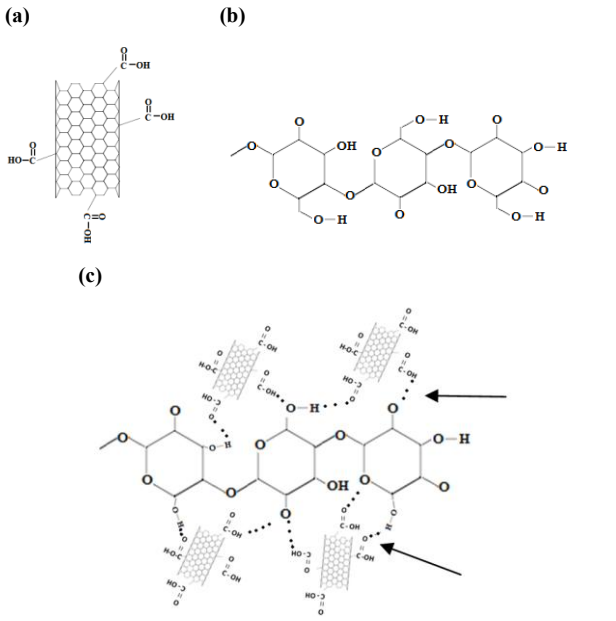

Figure 2. Chemical structure of the followings: (a) Carboxyl functionalized MWCNTs (b) Polysaccharide (c) Increase of hydrogen bonding interaction between BC and MWCNTs due to ultrasonic treatment (Indicated by arrows).

B. Ultrasonic fragmentation of bacterial cellulose

Bacterial cellulose was broken into micron-sized fragments by ultrasonic device (Branson 450 Sonifier, Branson Ultrasonics Co. Danbury, Connecticut, USA). The probe was placed at the air/liquid interface and operated at 80 W (BC-P80) and 100 W (BC-P100) level respectively. Samples were sonicated for 30 minutes.

C. MWCNTs dispersion and BC/MWCNTs composite preparation

Short length carboxyl functionalized MWCNTs were used upon received. Various concentrations of MWCNTs were introduced into DI water and dispersed by ultrasonication at an operation power of 80 W for 30 minutes. BC-P80 were mixed into 4 wt% (BC/4%M-P80), 8 wt% (BC/8%M-P80) and 16 wt% (BC/16%M-P80) MWCNTs. BC-P100 were also mixed into 4 wt% (BC/4%M-P100), 8 wt% (BC/8%M-P100) and 16 wt% (BC/16%M-P100) MWCNTs respectively. Composites were then mixed at a power of 30 W for 30 minutes. The composite was freeze-dried overnight.

D. Observation and characterization

The composites, fragmented BC and MWCNTs-COOH were analyzed by Raman spectrometer (RM-1000 micro Raman spectrometer, Renishaw Co. Ltd, Gloucestershire, UK) and scanning electron microscopy (Stereoscan S-360 SEM, Cambridge Instruments, Cambridge, UK) to analyze hydrogen bonding interaction. Electrical property of the composites was measured by electrochemical workstation (CHI 600, C-H Instruments Inc., Austin, Texas, USA).

IV. Result and Discussion

A. Raman Spectroscopy

Fig. 3 shows the Raman spectra of carboxyl functionalized MWCNTs, BC, and BC/MWCNTs composites. According to trace 1 and 2, the bands at 800, 2900 - 3300 and 3600 cm^{-1} represent C-O-C, CH_2 and -OH group from BCP-80 and BCP-100, respectively. In trace 8, the peaks at 1400 cm^{-1} and 1600 cm^{-1} indicate C-C rings and C=O group from MWCNTs-COOH. After ultrasonic mixing, traces 3 - 8 show all five characteristic lines mentioned above. The results point out MWCNTs is physically encapsulated by BC fiber. For BC treated by a lower power of 80 W, BC/16%M-P80, BC/8%M-P80 and BC/4%M-P80, a slight drop at the peaks of 1400, 1600 and 3600 cm^{-1} is observed. In traces 3 and 4, BC/16%M-P100 and BC/8%M-P100 show a more significant drop at the peaks of 1400, 1600 and 3600 cm^{-1} than former samples. This may attribute to various interactions between functional groups of BC and MWCNTs, such as hydrogen bonding. Interaction between carboxyl functional groups and

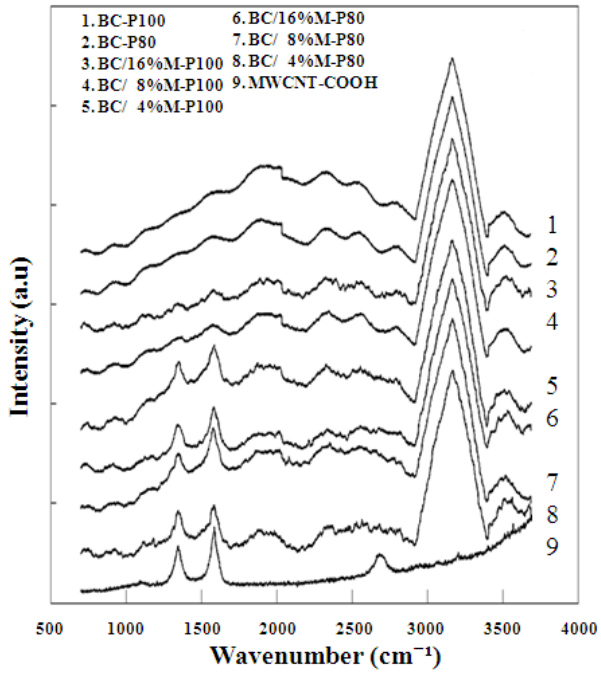

Figure 3. Raman Spectra for all samples. Ultrasonic power 80 W and 100 W are in terms of P100 and P80. Ratios of MWCNT, 4, 8 and 16 wt%, are in terms of 4%M, 8%M and 16%M. For example, BC/16%M-P100 is compostie of BC treated by 100 W and 16 wt% MWCNT. (1) BC-P100 (2) BC-P80 (3) BC/16%M-P100 (4) BC/8%M-P100 (5) BC/4%M-P100 (6) BC/16%M-P80 (7) BC/8%M-P80 (8) BC/4%M-P80 (9) MWCNTs-COOH.

released -OH and C-O-C group may lead to less vibration at 1400 cm^{-1}, 1600 cm^{-1} and 3600 cm^{-1}. The results suggest that higher power of ultrasonic treatment can disrupt the three-dimensional and dense network of BC. Functional groups are then released. Consequently, hydrogen bonding interaction is enhanced. Composition of MWCNTs also plays a role in the adhesion to bacterial cellulose. In traces 3- 4, higher ratio of MWCNTs, BC/8%M-P100 and BC/16%M-P100, shows a conspicuous drop in 1400 and 1600 cm^{-1} than BC/4%M-P100.

B. *Scanning Electron Microscopy*

Fig. 4 describes the morphology of the BC network before (Fig. 4a) and after (Fig. 4b and 4c) ultrasonic treatment. Without ultrasonic treatment, BC network remains crystalline and compact. The ultrasonic treatments make the native structure of the cellulose network become less dense to different extents. BC-P100, which is treated at higher power of 100 W than BC-P80, shows a less dense structure than the latter sample. Bundles and ribbon can be clearly observed. Table 1 shows the statistic of observable bundles after various treatments. Results suggest that the changed morphology is due to the ultrasonic operation power at different levels. The loose structure may invite more MWCNTs to get attach to the surface of BC bundles and enhance hydrogen bonding interaction.

Distribution of MWCNTs along the surface of BC bundles was observed under SEM. According to Fig. 5a and 5b, BC/16%M-P100 and BC/8%M-P100 shows around 60% surface of is covered by MWCNTs. A continuous MWCNTs layer deposits on the surface. However, BC/4%M-P100,

TABLE I. OBSERVABLE BUNDLES

Observable Bundles (Strands per image)		
BC	***BC-P80***	***BC-P100***
41	78	113

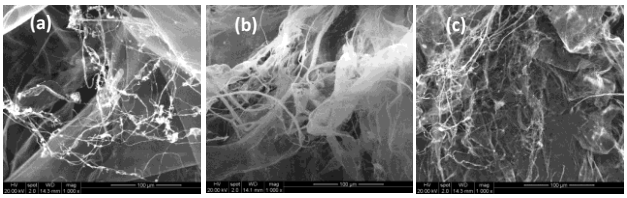

Figure 4. BC network before and after ultrasonic treatment (a) BC control (b) BC-P80 (80 W) and (c) BC-P100 (100 W).

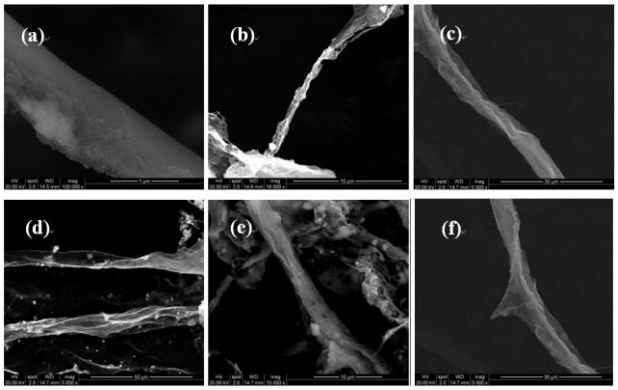

Figure 5. BC/MWCNT bundles (a) BC/16%M-P100 (b) BC/8%M-P100 (c) BC/4%M-P100 (d) BC/16%M-P80 (e) BC/8%M-P80 (f) BC/4%M-P80.

sample with lower ratio of MWCNTs, can show only 10% surface of BC is covered by MWCNTs in Fig. 5c. For lower operation powers of 80 W, BC/16%M-P100, BC/8%M-P100 and BC/4%M-P100 cannot find any continuous MWCNTs layer in Fig. 5d, 5e and 5f. 80 W may not be enough to disrupt the dense BC network, thereby hindering the formation of smooth MWCNTs layer on BC surface.

C. *Electrical Properties*

A bundle of composite was detached by using a pair of tweezers and then soldered to electrode in Fig. 6.

Fig. 7 shows an increasing trend of electrical conductance in composite with higher ratio of MWCNTs or operation power. In general, higher ratio of MWCNTs increases the conductivity of the composites. BC/16%M-P100, BC/8%M-P100 and BC/4%M-P100, samples were treated by higher ultrasonic power than remaining samples, show higher conductivity. It may relate to the disruption of cellulose structure after ultrasonic treatment. Honeycomb-like cellulose structure will invite more MWCNTs to attach on the surface of cellulose. Increase of MWCNTs may enhance the conductance and lead to higher sensitivity as a mass detector. Sensitivity ranging from 10^{-7} to 10^{-9} A shows the potential to make a GHz sensitive detector.

Sensitivity and long length of BC/MWCNTs bundles will be beneficial in enlarging the scale of resonator and achieving high sensitivity as a suspended tube resonator. Roughness of

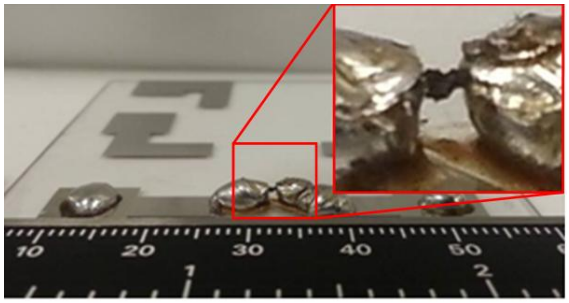

Figure 6. Set up for electrical properties measurement.

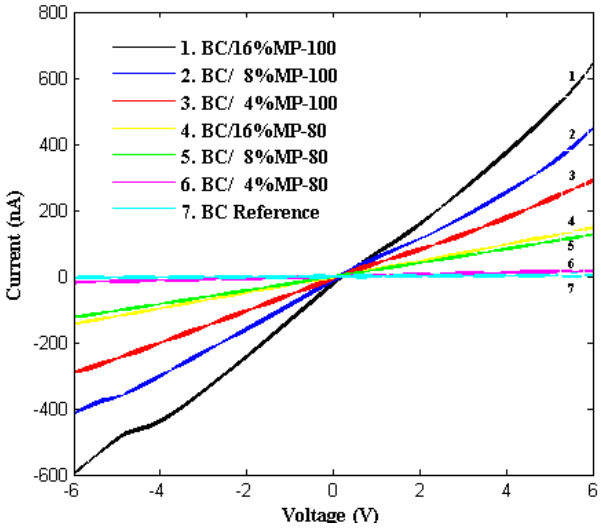

Figure. 7 Current-voltage (I-V) curve for suspended composites bundles.

MWCNTs coating, resonance frequency and Q-factors of the composite fabricated resonator will be evaluated.

V. Conclusion

A methodology of composite preparation is reported. Evaluation of hydrogen bonding interaction and morphology of single bundles BC/MWCNTs composite were conducted by Raman scan and SEM. High ultrasonic power can breakdown interchain hydrogen bonding and make BC network become less dense. BC bundles and ribbon can then be produced by ultrasonic treatment. Moreover, the loose BC structure will invite more MWCNTs to get attach on the surface of BC bundles, thereby forming a continuous MWCNTs layer. The MWCNTs-like protection layer coated BC bundles shows sensitivity up to 10^{-7} to 10^{-9} ampere and long length ranging from 30 to 100 μm. In future, this long, sensitive and stiff composite bundle will be fabricated as a resonator for further application.

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