

DEVELOPMENT OF CARBON NANO-TUBES ON CARBONIZED-COTTON FOR MULTI-FUNCTIONAL APPLICATIONS

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ABSTRACT

Cotton is one of the most abundant biomaterials on earth and also most commonly used in our daily life. The aim of this work is a value-addition to the cotton cloth in single step carbonizing and simultaneously growing carbon nanotube (CNT) on the surface of carbonized cotton (CC) by chemical vapor deposition (CVD) method. The amount of CNT evolution on CC surface can be controlled by changing the pre-catalyst concentration in cotton cloth. The as prepared material shows an excellent electrical conductivity, superhydrophobicity, oleophilicity, high capacitance and electromagnetic interference (EMI) blocking properties. We anticipate that such novel multifunctional CNT-CC could be used for oil spills cleaning reinforced material for conductive flexible composites, EMI shielding composites, and energy storage applications.

1 INTRODUCTION

The burgeoning demand for multifunctional materials with low weight/volume ratio has been pushed continuously forward by various industries, including automotive, satellites, electronics, smarttextiles and aerospace. The multifunctionality typically comprises structural functions (such as strength, flexibility, stiffness, porosity, wear-ability etc.) and non-structural functions (such as thermal and/or electrical conductivity, sensitivity to various agencies or medium, radiation or electrometric wave shielding, energy storages etc.). When both functions are integrated into a system together, it may possible to design a smart functional material within a limited space for many weight/volume sensitive applications.

In this perspective, CNT is a unique material for multifunctional applications due to its excellent structural and non-structural properties [1-3]. In order to get optimum benefits from CNTs, it should be deposited or dispersed uniformly on or into others substrates/medium, which is one of the tedious tasks at the present time. For example, in the case of polymeric composites used CNT filler should be dispersed uniformly to avoid percolation and form continuous network all over the matrix [4, 5]. Although fabrication of free standing 3D-CNT structure is one of the ways to solve such challenges, preparation of large size 3D-CNT materials are still remained in limited scale [5]. Another alternative way to address such problem is to grow or deposit CNTs on carbon, quartz, and basalt fiber cloth [6-8]. But those materials themselves have high density, for example, carbon (1.6 to 2 g/cm³) and quartz or basalt fiber (2.5 to 3 g/cm³). Since cotton fabrics possess a hierarchical porous structure with complicated fibrous surface morphology and abundant functional groups (i.e. hydroxyl -OH groups) [9-11], such characteristics allow to deposit a certain amount of pre-catalyst for nucleation of CNTs on the carbonized fiber surface during processing in CVD, as discussed in our previous work [12].

Motivated by above discussion, we developed CNT on carbonized cotton (CC) cloth by a single step CVD method. The CNTs in the CNT-CC cloth offers multifunctional properties for many applications, such as oil-spills cleaning, reinforced material for conductive flexible composites or EMI shielding composites, and energy storages.

2 EXPERIMENTAL PROCEDURE

In this work, 100% commercial mercerized cotton with a weight of 120 g/m² was used as substrates and iron sulfate, cobalt nitride, and nickel nitride were used as a catalyst to facilitate CNT growth on the cotton cloth by a CVD method. In a typical experiment, 1.0 g of cotton was dipped into the solution of above catalyst (0.1 M, 20 mL) for 15 min. Then the cloth was squeezed by hand to remove excess water and dried by a hair drier. In order to grow CNTs on CC, a piece of pristine cotton was placed in a ceramic boat and put in the inner tube of CVD and heated to 800 °C under the flow of argon gas. When the temperature was reached at 800 °C, the condition was held for 60 min under flowing argon and H₂ gas, while first 30 min was considered for carbonization and last 30 min allowed to grow CNTs on the carbonized cotton by flowing C₂H₂ gas. For comparison, the pristine cotton sample was carbonized in the same conditions flowing argon and the resulted sample was named as CC.

3 RESULTS AND DISCUSSION

Due to ionization of hydroxyl groups (-OH groups) of cotton cellulose in water, slightly negative charges generated on the surface [13] that allows to deposited any catalyst of Co²⁺/ Fe²⁺/Ni²⁺ on its surface by electrostatic forces, as illustrated in Figure 1(a). This deposition technique offers the different shades of colored cotton according to the color of catalysts (Figure 1(b)). The digital photos (Figure 1(b-c)) show the changes in color after CNT growth and carbonization of catalyst treated and pristine cotton. The obtained samples were named as CNT-CC-Co, CNT-CC-Fe, and CNT-CC-Ni for Co²⁺, Fe²⁺, and Ni²⁺ pre-catalyst treated cotton, respectively.

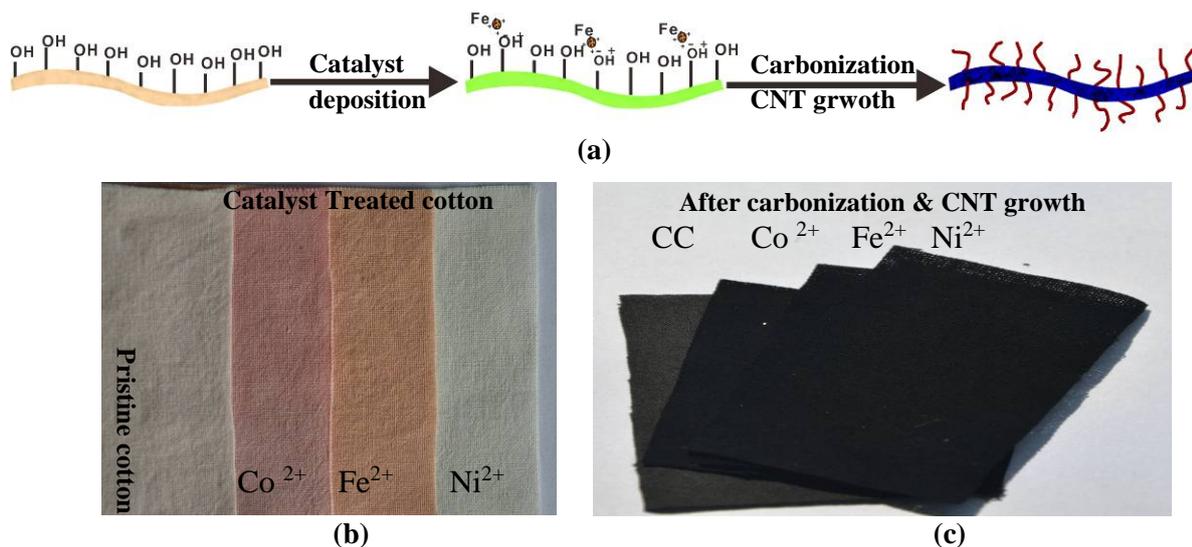


Figure 1: Materials and methods: schematic showing preparation of CNT-CC material (a), digital photos of pristine and different catalyst treated cotton (b), CC and CNT-CC cloth prepared from different catalyst treated cotton (c).

3.1 Morphology and Structural Properties

The morphological change of fibers due to the carbonization and CNT growth was examined on a scanning electronic microscope [14]. The CC sample exhibited a twisted ribbon-like shape of cotton fibers, as shown in Figure 2(a), known as convoluted and convex/concave structures. In high-resolution SEM images for CC samples reveal a smooth fiber morphology with a twisted structure,

and the measured diameters are varied from 6 to 8 μm (Figure 2(a-b)). After carbonization of catalyst treated cotton, a uniform distribution of iron particles was found over the surface of carbonized fibers (Figure 2(c)).

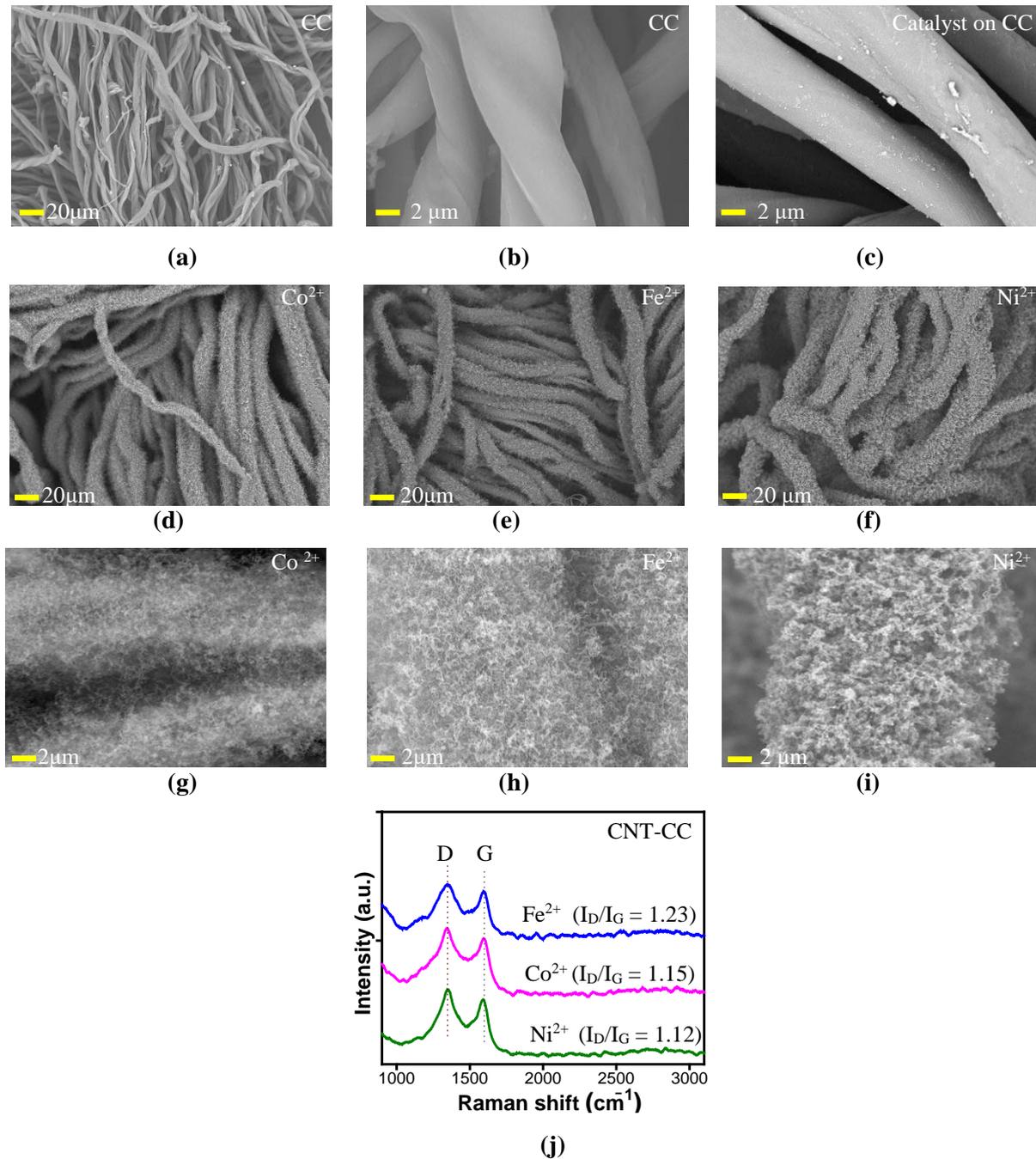


Figure 2: Morphology and structure analysis: SEM image of CC sample (a-b), Iron catalyst treated CC (c), CNT-CC prepared from Co catalyst (d and g), CNT-CC from Fe catalyst (e and h), CNT-CC from Ni catalyst (f and i), Raman spectra of different CNT-CC samples (j).

In contrast, all the CNT-CC samples resulted from different catalysts show a worm-like skeleton with an increased on apparent diameter of fibers, which seems to be 12-18 μm (Figure 2(d-i)). A close examination of the high-resolution SEM images reveals that numerous protruding nanowires are randomly surrounded on the entire fiber surface (Figure 2(g-i)), suggesting the existence of nanotubes on the fiber surface. It was found that Co yielded a finer and longer CNT compared to the CNTs

grown with other catalysts. For Ni catalyst, compact and highly curled CNTs were deposited homogeneously on fibers compared with Fe or Co catalyst treated sample.

The quality of CNT structures was verified by Raman spectra of different samples (Figure 2(j)), and a highly intense D-band attributing to the defects and lattice distortions at 1340 cm^{-1} was observed in all samples, whereas a relatively faint peak of G-band was revealed at 1590 cm^{-1} . The intensity ratio of D- to G-band (I_D/I_G ratio) were 1.23, 1.15 and 1.12 for CNTs created from Fe^{2+} , Co^{2+} and Ni^{2+} catalyst respectively, indicating sp^3 hybridization dominance and defects in the CNT-CC sample. This structural disorder in CNTs originated from the nano-size terminated graphitic planes and other imperfect sites like kinks, vacancies, heteroatoms, open rings, heptagon and pentagon pairs in the material [15].

3.2 Electro-chemical properties

The electrochemical behavior of CNTs was studied by measuring cyclic voltammetry (CV) at the potential window of 0 to 1V and electrochemical impedance in the symmetric two electrodes system (Figure 3). The redox peaks were observed in the CV curve of CNT-CC-Fe (Figure 3(a)), due to the presence of iron oxides on carbonized fibers, which may work as pseudocapacitance material. The CNT-CC-Ni sample displayed the most rectangular CV among the three samples, indicating ideal electrical double layer capacitance (EDLC) material for high performance energy storages. Although CNT-CC-Co sample exhibited the largest shape of CV among the three samples, its shape was not perfectly rectangular as others, indicating that such electrode materials are not ideal for EDCL capacitor.

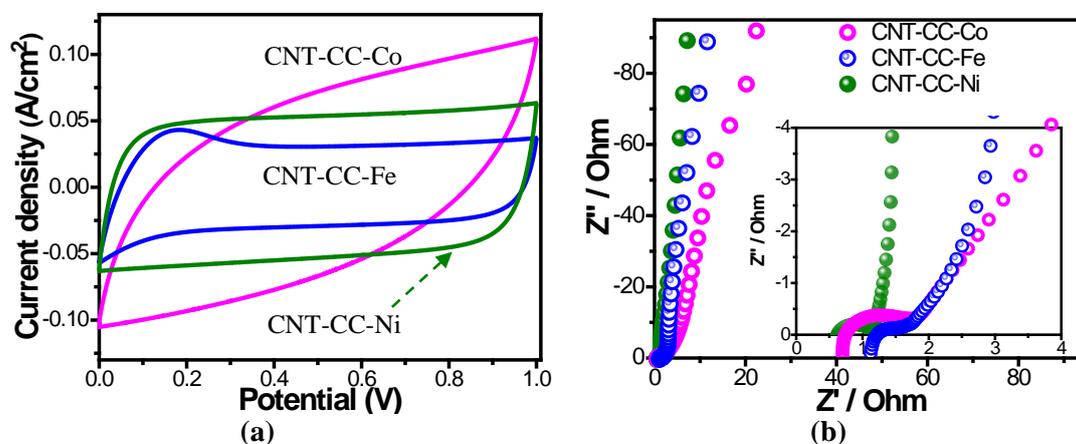


Figure 3: Electrical chemical performance: CV of different samples at 100 mV/s (a), Nyquist plot of different samples (b).

The electrochemical impedance data are analyzed using Nyquist plots (Figure 3(b)), displaying a smaller semicircle at highest frequency following by a transition to nearly vertical line (Figure 3(b) and inset), indicating faster ion diffusion and transfer into the porous structure of CC cloth. The equivalent series resistance (i.e. intersection point with X axis) values are approximately $0.6\ \Omega$, $0.7\ \Omega$ and $1.1\ \Omega$ c for CNT-CC prepared from Ni, Co, and Fe catalyst respectively, suggesting a lower charge transfer internal resistance onto electrode materials.

3.3 Effect of pre-catalyst concentration on electrical and surface wetting properties

The effect of catalyst loading on CNT fractions, weight density, electrical conductivity and surface wetting properties was observed by processing 0.05M, 0.1M and 0.25M FeSO_4 treated cotton in CVD. For discussion, the samples prepared from 0.05M, 0.1M and 0.25M catalyst loaded cotton were named as CNT-CC-I, CNT-CC-II, and CNT-CC-III, respectively. The CNT fractions were estimated according to the weight change of catalyst treated fabric in carbonization process with and without flowing process gas of CNT and results are summarized in Table 1. It is clear that with increasing pre-catalyst concentration the CNT fraction in CNT-CC also increased linearly. The highest CNT fraction

was found to be about $60 \pm 6\%$ for 0.25M FeSO₄ catalyst deposition and those values were $35 \pm 7\%$ and $47 \pm 5\%$, respectively, for CNT-CC-1 and CNT-CC-2. Due to removal of hydrogen and oxygen molecules from cotton cellulose skeleton in carbonization process, the pristine cotton density decreased more from 0.32 g/cm³ to 0.17 g/cm³, whereas densities of CNT-CC samples showed an increasing tempo following to the catalyst loading concentration, and the values were 0.29, 0.35 and 0.41 g/cm³ for CNT-CC-1, CNT-CC-2, and CNT-CC-3, respectively. Such values are about 6 to 12 times lower than carbon fiber of 1.7 to 2 g/cm³.

Sample	Pre-catalyst conc. (mol/L)	CNT fraction (%)	Density (g/cm ³)	Conductivity (S/cm)
Pristine cotton	-	-	0.32	--
CC	-	-	0.17	1.37
CNT-CC-1	0.05 M	35 ± 7	0.29	1.88
CNT-CC-2	0.10 M	47 ± 5	0.35	2.09
CNT-CC-3	0.25 M	60 ± 6	0.41	2.31

Table 1: Physical and electrical properties change due to carbonization and CNT growth

The electrical conductivity of the samples was measured according to a two probe method by Agilent Digital multimeter, as shown in Table 1 and Figure 4(a). The CC and CNT-CC exhibited a good electrical conductivity of 1.37, 1.88, 2.09 and 2.31 S/cm, respectively. It is important that those values were improved significantly after annealing the samples at 1000 °C for 1hr (Figure 4(a)), possibly due to the transformation of some amorphous carbon to graphite carbon.

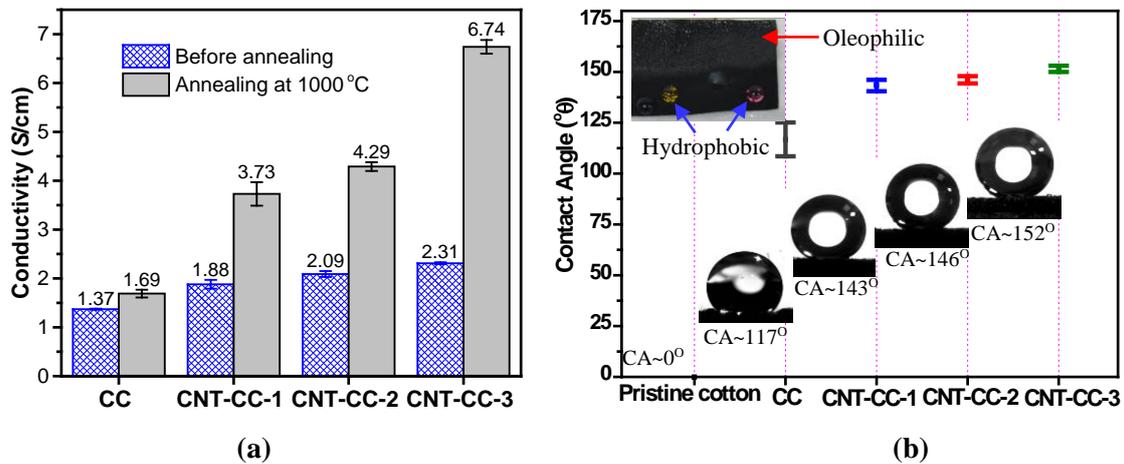


Figure 4: Electrical conductivity and surface wettability: Conductivity before and after annealing (a), Contact angle of different samples (b) and inset showing dyed water and crude oil droplets on CNT-CC-II.

The CA measurement was performed to analyze the surface wetting behavior of as prepared materials against water. The pristine cotton material exhibits very rapid absorption for water due to the presence of hydrophilic hydroxyl groups (-OH) in cellulose, resulting in a complete wetting behavior against water. Contrary, carbonized CC fabric shows hydrophobic property with an average CA of $116.8 \pm 8.3^\circ$ (Figure 4(b)). On the other hand, a unique and remarkable surface feature (see Figure 2(e-h)) is created on carbonized fiber because of the randomly aligned CNTs on the fiber surface. These entangled and randomly aligned CNTs lead to the formation of a heterogeneous surface according to Cassie-Baxter's mechanism [16]; consequently, air pockets are formed onto nanostructured fiber surface, thus CNT containing CC cloth shows the superhydrophobic property. It has been observed that CA values were increased with increasing CNT weight fraction in CNT-CC fabric. The CA values for CNT-CC-1 and CNT-CC-2 were $135.7 \pm 2.9^\circ$ and $148.1 \pm 3.4^\circ$ respectively. Moreover, water droplets

were easily rolled away on the surface of the CNT-CC cloth as like as lotus leaf (inset in Figure 4(b)). This result implies very strong anti-wetting and self-cleaning property of CNT-CC cloth.

3.4 EMI shielding properties

The EMI shielding performance of CC and CNT-CC-III sample in the frequency range of 8.2-12.4 GHz (known as X-band) is plotted in Figure 5. For detailed understanding of EMI shielding properties, microwave reflection (SE_R), microwave absorption and total shielding effectiveness (SE_T) for different samples were calculated individually from the measured scattering parameters (S_{11} and S_{12}) [17] and those results are presented in Figure 5(a-b). It is clear that the microwave reflection by CNT increases steadily with the increasing frequency, whereby the CC shows a gradual decrease (Figure 5(a)). In contrast to the reflection behavior, EMI wave adsorption for CC and CNT-CC samples exhibits similar behavior as shown in Figure 5(b). Because of the conductive CNT introduction on CC, a large number of free electrons create in the system, which may improve the conduction current and much mobile charge carriers, consequently much attenuation of penetrating EMI waves [18].

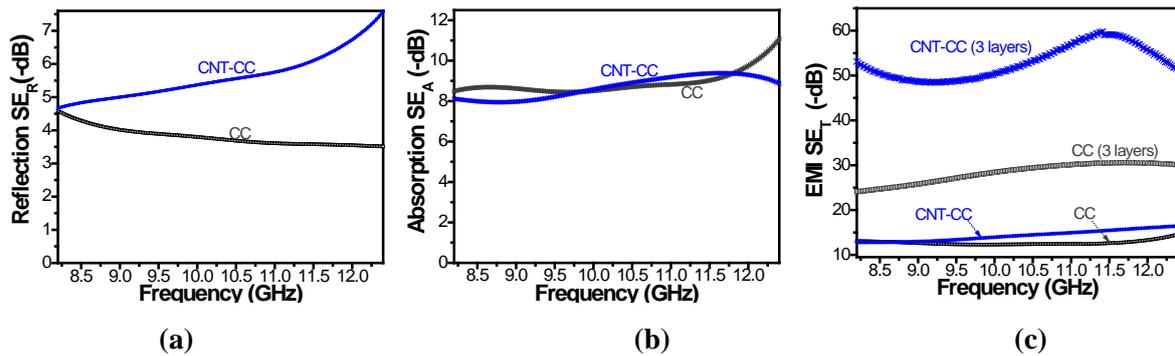


Figure 5: EMI shielding performance of different samples: microwave reflection (a), adsorption (b) and total EMI shielding (c).

In general, a material with SE_T values more than 20 dB, are considered as a good candidate for EMI shielding applications. Our obtained average SE_T values are 12.7 and 14.3 dB, respectively, for CC and CNT-CC-III samples, which is remarkably less than acceptable standard. We anticipate that the EMI shielding property can be improved by adding some dielectric polymer materials [167,168] and another alternate way is to use multilayer of those samples. For example, when 3 layers samples were employed for blocking EMI radiation, such values were reached to 28.3 and 52.9 dB, respectively, for CC and CNT-CC-III (Figure 5(c)). We hope that the presented CNT-CC cloth will be also a potential candidate for light-weight EMI shielding applications.

3.5 Fabrication of composites

The adsorption capacity of the different polymeric matrix by CNT-CC-III samples was measured quantitatively by immersing in epoxy resin or polydimethylsiloxane (PDMS). It was found that the sorption values were 800 ± 95 and 742 ± 42 % for epoxy and PDMS, respectively, as shown in Figure 6 (a). The composites fabrication performance of flexible CNT-CC-III cloth was studied by fabricating PDMS and epoxy resin based two polymeric composites (inset in Figure 6). The inset digital photo suggests that a highly flexible and twistable PDMS/CNT-CC films can be prepared using the silicon resin polymer. The fractures of both composites were examined on a SEM, revealing a smooth fiber cross-section that is typical fracture morphology of brittle fibers (Figure 6(b-c)). Those fibers are surrounded by the solid epoxy or PDMS block. It is clear that the interface between fiber and epoxy or PDMS was damaged slightly by the induced load during fracturing, indicating the strong interfacial bond between CNT-CC and matrix for both composites. This suggests that the CNT networks of CNT-CC cloth toughen the matrix system and may provide a positive effect on crack propagation. This strong interfacial bonding indicates that the as prepared CNT-CC materials could be a potential candidate for fiber reinforced composites.

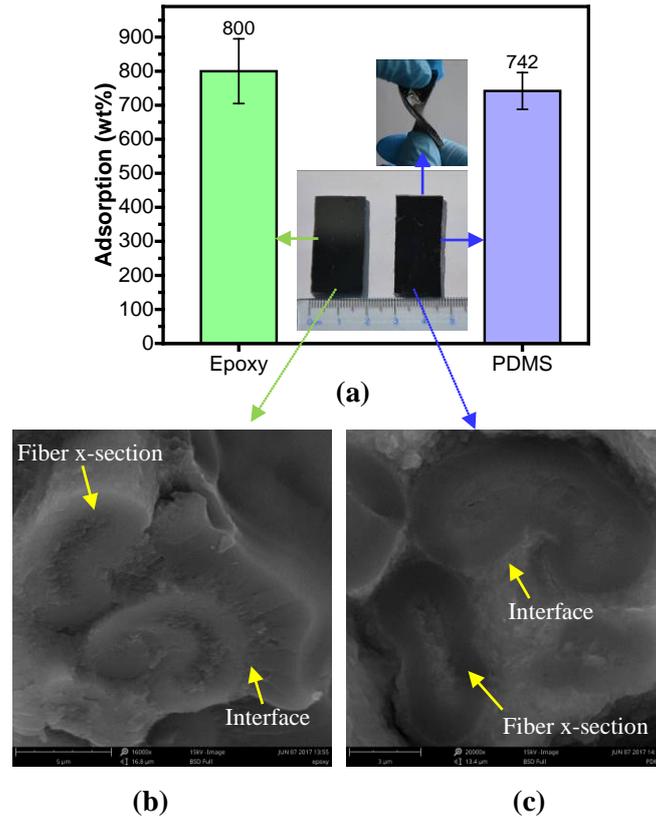


Figure 6: adsorption of epoxy and PDMS by CNT-CC-II cloth and inset showing composites prepared from epoxy and PDMS (a), Typical fractured SEM images of epoxy/CNT-CC (b) and PDMS/CNT-CC composites (c).

4 CONCLUSION

This work demonstrates a facile technique to develop multifunctional material by growing CNTs on carbonized cotton using a single step CVD method. This single step CVD method is highly energy efficient, environment-friendly due to dry processing and based on our abundant biomaterials. The as prepared material exhibits a low density, excellent electrical conductivity, high capacitance, superhydrophobic property and good EMI shielding performance. We anticipate that the flexible fibrous CNT-CC is a low-cost, sustainable and potential candidate for use in oil-spill cleaning, reinforced material composites, EMI shielding composites, and energy storage applications.

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