ELECTROPHORETIC DEPOSITION OF CARBON NANOTUBES: TOWARDS ROLL-TO-ROLL MANUFACTURING AND NOVEL MULTIFUNCTIONAL COMPOSITE SENSORS

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ABSTRACT

This research focuses on the utilization of electrophoretic deposition (EPD) as an innovative technique for integrating nanostructured films into fiber-based composites, resulting in the creation of multiscale smart textiles. The use of an aqueous dispersion system in EPD offers the potential for large-scale manufacturing, thanks to its advantageous features such as room temperature processing, absence of harsh chemicals, and flexibility in selecting substrate fabrics. In this study, carbon nanotubes (CNTs) that were functionalized with a cationic polymer were deposited onto various fabrics to assess their multifunctionality as piezo-resistive sensors for detecting human motion. By controlling EPD processing parameters like electric field and deposition time, the morphology of the CNT coatings on non-conductive fabrics could be customized due to the unique film formation mechanism. When incorporated into stretchable wearable woven fabrics, the CNTs formed a nanostructured conductive network, resulting in exceptional sensitivity for detecting arm bending and inhale/exhale motion. The resistance change observed reached up to 3000%. Furthermore, a laboratory-scale roll-to-roll pilot line was developed, enabling continuous fabrication of multifunctional textiles and industrialization of smart composites. The outcomes of this research demonstrate the significant potential of EPD-processed CNT-based resistive sensors in motion detection, robotics, and clinical device applications, particularly when combined with large-scale manufacturing capabilities.

1 INTRODUCTION

Nanostructured materials often have remarkable mechanical and physical properties. For example, carbon nanotubes (CNT) have both high modulus and strength and their nanocomposites exhibit low electrical percolation thresholds. Incorporating the versatile nanomaterials into a conventional textile composite system enables the development of novel multifunctional materials. [1] For more than a decade, our group has been researching carbon nanotube-based hierarchical composites for multifunctional applications such as strain sensors or flexible wearable sensors using the tailorable nanocomposites architecture. Electrophoretic deposition (EPD) is a scalable and efficient processing technique enabling specific manipulation of the microstructure of the nanocomposite coating on high-performance textiles. [2,3] We use an aqueous EPD process, which can be conducted at room temperature for modifying the properties of the hybrid multi-scale composites. Unlike other hybridization techniques, such as chemical vapor deposition, our processing technique does not require hazardous chemicals or intensive high temperature/pressure processing conditions, and can be readily scaled-up for production.

Leveraging EPD, carbon nanotubes are deposited on various textile structures, such as non-woven, woven, braided and knitted. Deposition occurs under ambient temperatures from water as a solvent and is capable of depositing onto a wide range of natural and synthetic fibers including cotton, wool, polyester, nylon, and aramid. [4,5] These coated fibers and fabrics can be used as novel garment-based sensors. By depositing carbon nanotubes on stretchable knitted fabrics, wearable sensors to detect human motion with ultra-high sensitivity are created. The carbon nanotube coating is thin, flexible and soft to the touch; there is no significant change in the fabric's texture. The robust bonding of the carbon nanotubes to the surface of the fibers makes the coating more durable.

In this paper, CNTs are functionalized with a cationic polymer, polyethyleneimine (PEI) in water solvent, and deposited on the non-conductive fabrics to develop multifunctional composites. The uniformly coated CNT films processed by EPD, in particular, exhibit great piezo-resistive sensitivity, enabling to detect the minute structural deformation or external pressure exerted on the hybrid composite structure. The novel EPD process capable of tailoring the micro/nanoscale structures of composites has shown its potential to be applied to large-scale structures such as bridges and pipelines, which leads to the development of roll-to-roll manufacturing system to continuously fabricate the hybrid composites and smart textiles.

2 PROCESSING OF HIERARCHICAL COMPOSITES

2.1 Carbon Nanotube Functionalization and Electrophoretic Deposition

Multi-walled carbon nanotubes (MWCNT) oxidized and functionalized with cationic polymers form a stable aqueous dispersion due to the repulsive interaction between positively charged particles. CNTs were oxidized with ozonolysis and functionalized with polyethyleneimine (PEI) in water solvent. [3] Amine functional groups on the branched polymer, PEI, protonate under mild acidic condition, creating the positive surface charge of CNTs. Under the application of an electrical potential gradient, charged nanotubes readily migrate towards and are deposited on the substrate fabric in contact with the oppositely charged electrode, as shown in Figure 1. Coating of various conductive and non-conductive materials such as carbon, glass or aramid fibers has been demonstrated in our prior work [6]. CNT-PEIs form a conductive network and exhibit resistance change in response to mechanical deformation. Controlling the microstructure of nanomaterials within the multifunctional composites is a critical factor that significantly influences the efficacy of the multifunctional application.

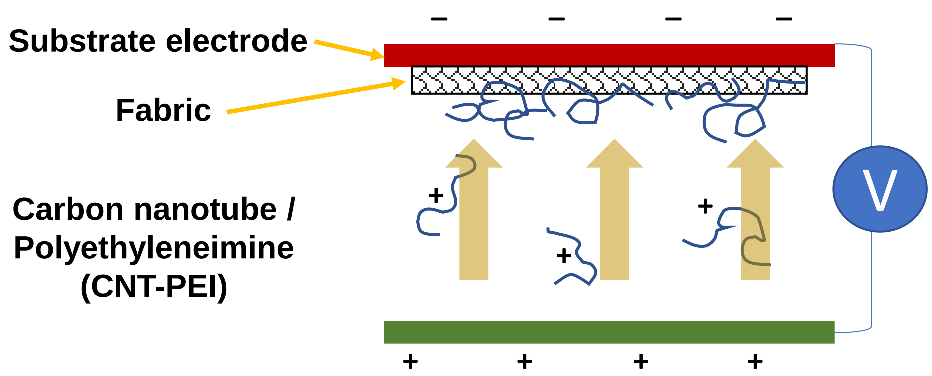


Figure 1. Schematics of electrophoretic deposition of functionalized carbon nanotube on the non-conductive fabric substrate.

2.2 Nanocomposite Sensor Manufacturing

The nanocomposite sensors are manufactured using the EPD process discussed above. For applications in stretchable sensors, the carbon nanocomposite coating is deposited on a knit fabric made of stretchable materials, and has loops in its microstructure, which enable the stretchability. The fabric is backed against a stainless-steel electrode during the EPD process. It is necessary to ensure that the fabric remains in contact with the electrode for uniform coating. Elastic bands are used to create slight tension in the fabrics. A counter electrode, also of stainless steel is kept parallel to the electrode with fabric in contact using spacers made of non-conductive material. The specimens are coated for about 15 minutes, using a field strength of ~ 28 V/cm. Figure 2. Shows the plain (uncoated) and coated knit fabric at different length scales. For applications to measure pressure using thin and flexible fabrics, a similar EPD procedure is used, with slightly different processing parameters and a non-woven fabric made using randomly oriented aramid fibers. The areal weight of the non-woven aramid used in this study is ~ 50 grams/square meter, but other areal weights and materials can also be used.

Figure 2. Photographs and SEM micrographs of the uncoated (top row) and coated (bottom row) knit fabric at different length scales.

3.2 Tailorable Morphology of CNT-PEI Coatings

Hybridization of nanomaterials via EPD and the coating morphology is dependent on processing parameters such as temperature, nanoparticle concentration in dispersion, and applied electric field. We extensively investigated the nanotube deposition behavior and the resulting morphologies under different processing conditions. Figure 3 shows electrophoretically coated carbon nanotube films on glass fibers using direct current (DC) and alternating current (AC) electric fields. High contrast images were obtained using scanning gallium ion microscopy (SGIM), which differentiates the regions depending on the electrical conductivity. The conductive areas (carbon nanotube coating) appear bright, and the non-conductive matrix and glass fiber appear dark. Charged particles driven by the AC field can penetrate the tow and are deposited within the inter filament regions to form a denser network compared to that of the DC field. For DC-EPD, a relatively thicker layer is formed on the fabric's surface, and a thin layer is formed around all the fibers.

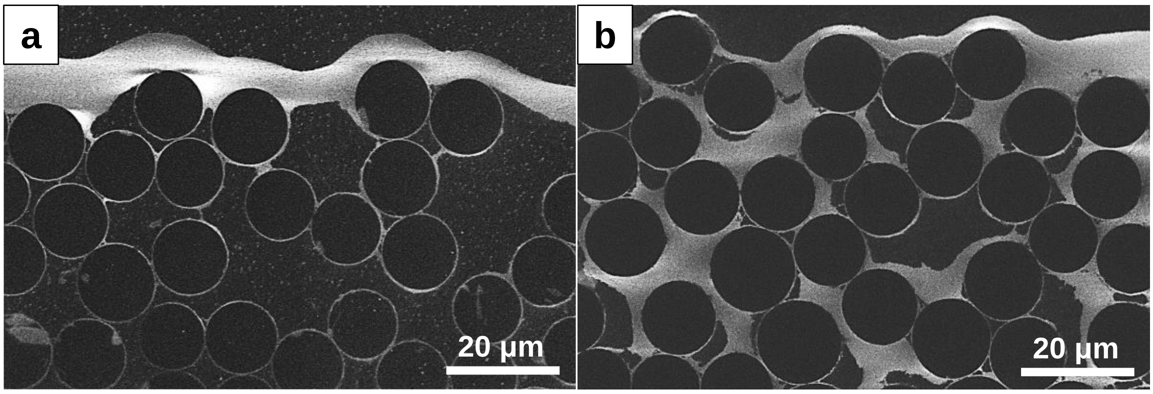
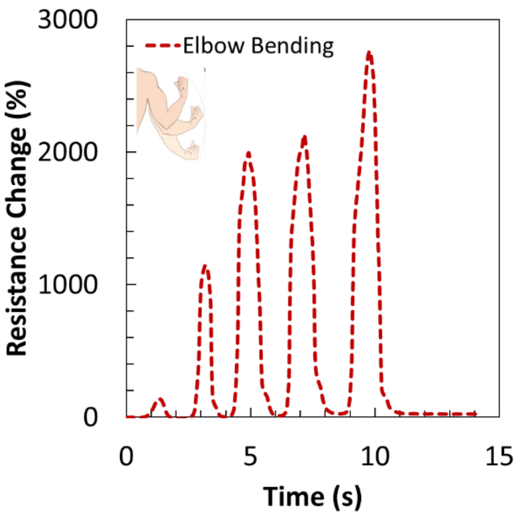


Figure 3. Scanning gallium ion micrographs of a cross-sectional view of CNT-PEI/glass fiber/epoxy composite. Different types of electric fields, (a) DC and (b) AC, lead to unique morphologies that can be tailored based on the specific applications.

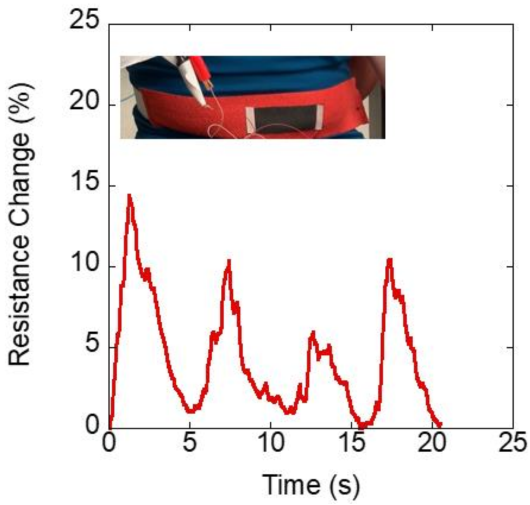
3 CARBON NANOTUBE-BASED PIEZORESISTIVE SENSORS

The change in resistance in carbon nanotube-based piezoresistive sensors is due to change in tunneling gaps between the nanotubes and the increasing or decreasing number of contact points between the nanotube coated fibers. Multiple mechanisms such as stretching of fibers, compression of fibers in a yarn due to stretching of the fabric, increasing, or decreasing contact points between yarns of adjacent loops, and contact pressure between the intertwined loops.

Using electrophoretic deposition, carbon nanotubes are deposited on stretchable knit fabrics to create functional garments to measure human movements. Figure 4(a) shows the percentage change in resistance when the subject bends their arm. Initially, the arm is straight and extended and no change in resistance is observed. As the subject bends the arm with gradually increasing angles in each cycle, the change in resistance increases. Here, the fabric undergoes biaxial stretching due to the flexing of the elbow which leads to an extremely high sensitivity and change in resistance. Figure 4(b) shows a carbon nanotube sensor worn over the waist/stomach region by a person. The resistance increases because of the expansion and contraction due to breathing. As the person inhales, the stomach expands, leading to stretching of the base fabric (red in color) and the sensor (black). As the sensor is stretched, the electrical resistance of the sensor increases. In figure 4(b), the subject inhales different amounts of air; with the highest in the first breath and decreasing for the next two cycles. The amount of expansion is proportional to the change in resistance.



(a)



(b)

Figure 4. (a) Resistance change (%) when the sensor is worn on an elbow while bending the arm to different levels and (b) resistance change (%) when the sensor is worn over the stomach and the subject breaths in and out. The sensors are extremely sensitive, showing an ~2700% change in resistance when worn over elbow and detecting minute movements due to breathing and different levels of inhalation.

4 ROLL-TO-ROLL EPD PILOT LINE

Due to room temperature processing, rapid deposition, and not using hazardous chemicals, electrophoretic deposition is amenable to scale-up to a continuous roll-to-roll manufacturing system. Preliminary experiments have been conducted on fiber tow and woven fabric level prior to constructing the pilot-scale system. [7] According to our previous research about CNT deposition mechanism, the direct contact between the substrate fabric and backing electrode is crucial, and aqueous EPD system generates the bubble on the electrode due to the water electrolysis [3]. As the bubble might be trapped between the fabric and electrode, it was shown that the stainless-steel mesh could effectively reduce the captured bubbles and expedite the deposition. The electrode mesh size with 32 x 32 was used considering the CNT-PEI deposition yield and rolled up into an endless belt shape that continuously maintains the proper contact with moving fabric.

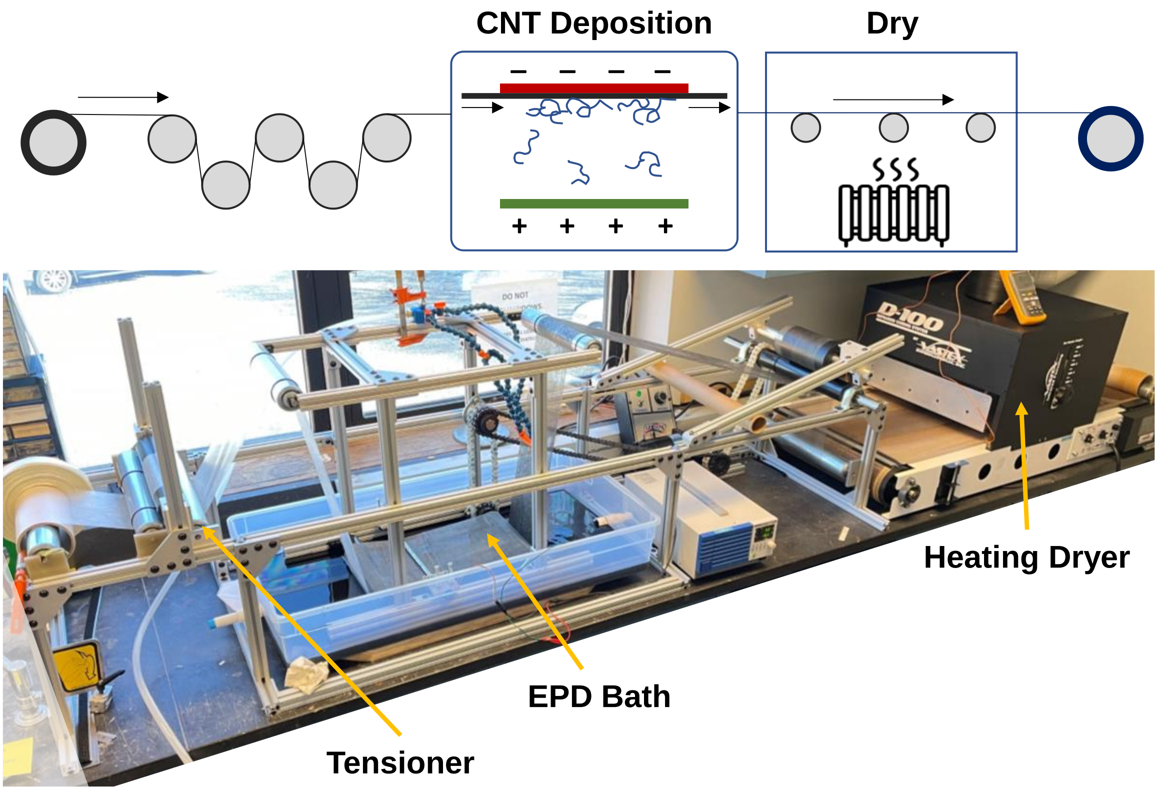


Figure 5. Schematic diagram of continuous deposition system for scale-up of nanomaterial embedded multifunctional composites and a pilot-scale manufacturing system consisting of EPD bath, tension control system and heating dryer.

5 CONCLUSIONS

Electrophoretic deposition is an innovative technique to integrate the nanostructured films into the fiber composites to create the multiscale smart textiles. Along with the use of aqueous dispersion system, EPD has a potential to be scaled up for large-scale manufacturing due to the amenable features such as room temperature processing, no use of harsh chemicals and flexibility in selecting the substrate fabrics. In this research, carbon nanotubes (CNTs) functionalized with a cationic polymer were deposited on various fabrics to introduce surface charge, which creates the stable dispersion and ionic mobility under the application of electric field. Based on the unique film formation mechanism, the morphology of CNT coatings on the non-conductive fibers can be tailored through the control of EPD processing parameters such as electric field and deposition time. In particular, the use of alternating current (AC) electric field changed the deposition mechanism suppressing the influence of water electrolysis, resulting in the denser CNT network within the fiber bundles. Microstructure change can lead to the mechanical and functional performance of hierarchical composites. The CNT coated fabrics were characterize their multifunctionality as a piezo-resistive sensor to detect human motion. Incorporated with stretchable wearable woven fabrics, the CNT with nanostructured conductive network exhibited extreme sensitivity to detect the arm bending and inhale/exhale motion with the resistance change up to 3000%. Roll-to-roll pilot line was designed in the laboratory scale, enabling the continuous fabrication of multifunctional textiles and industrialization of the smart composites. The outcome of this research demonstrated the great potential of CNT-based resistive sensors processed by EPD towards the motion detection, robotics and clinical device applications, together with the large-scale manufacturing capability.

ACKNOWLEDGEMENTS

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