Freestanding Carbon Nanotube Films Fabricated By Post-Electrophoretic Deposition Electrochemical Separation

Jyotishka Biswas†, Jaron S. Rottman-Yang†, Isabel Gonzalo-Juan, and James H. Dickerson

†Co-First Authorship

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BRIEF. The development of a novel method for producing buckypapers following electrophoretic deposition of carbon nanotubes is presented.

ABSTRACT. A novel technique of producing freestanding carbon nanotube films (buckypapers) using electrophoretic deposition (EPD) and post-EPD electrochemical separation (PEPDECS) is introduced. Carbon nanotubes (CNTs) were deposited from an aqueous suspension onto stainless steel substrates using a direct current deposition procedure. Following drying and reinsertion of the electrodes into deionized water, a reversal in the direction of the current between the electrodes and an increase in the voltage applied facilitated an intact separation of the film from the substrate. The surface structure was studied using scanning electron microscopy; chemical surface groups on the CNTs on both sides of the buckypaper were identified using Fourier transform infrared spectroscopy. PEPDECS yielded sheets with no apparent change of the surface structure or strength and with mechanical properties similar to those of buckypapers produced using other techniques. Analysis revealed that the likely mechanism that allows PEPDECS for the carbon nanotubes involves the metal-catalyzed electrochemical reduction of double bonds present in molecules that coat the CNTs. This suggests the potential for wider applications involving CNT films as well as applications involving similar nanostructures.

INTRODUCTION.

Carbon nanotubes (CNTs) are smaller-than-microscopic structures of purely carbon atoms, arranged into tubes 3000 times thinner than human hairs [1]. Since their popularization in 1991 [2], CNTs have received attention for their unique electrical and physical properties [3]. Recent interest in fabricating sheets of CNTs, or "buckypapers," (BPs) has been driven by potential industrial and commercial applications, such as water purification and filtration [4, 5], energy storage devices [6-9], and electronics [3, 6-9]. Industrial-scale manufacturing of supercapacitors and photovoltaic devices could be made possible if there was an inexpensive method for producing buckypapers. Currently, they can be produced through a variety of methods. For instance, buckypapers in which CNTs are all aligned in the same direction have been produced using the *domino pushing* technique [10], magnetic field-assisted deposition [11, 12], and other techniques [13], but the buckypapers are attached to the underlying steel plates that are required for all these techniques. Buckypapers that are unidirectionally aligned tend to be strong in the direction of alignment but weak in the normal direction. However, these films are highly conductive and are desirable for electronic uses.

Contrastingly, randomly-oriented CNT films are desirable for their overall strength, high surface area, and flexibility [3]. Electrophoretic deposition (EPD), in which an electric field is used to deposit charged CNTs or other nanoparticles from a suspension onto a substrate, is a commonly used technique in creating buckypapers [1, 3, 13-16]. Separation of deposited films from their substrates has posed a challenge, and there are a limited number of reported techniques. A sacrificial polymer layer technique, in which a soluble polymer lies between the deposited material and the substrate, has produced freestanding nanoparticle films [17]. Additionally, a razor-assisted mechanical liberation technique has also been employed for buckypaper production [3]. However, both these methods are time and resource intensive, and are not efficient for large-scale production of buckypaper. These disadvantages motivated the search for a simpler method to liberate CNT films that requires no additional materials or precise mechanical techniques.

In this study, we investigate the efficacy of a new approach for the liberation of CNT films from their deposition electrodes. Post-EPD electrochemical separation (PEPDECS) involves casting a film onto a substrate by EPD, reintroducing it into a water bath and liberating the film from the underlying substrate by applying a reversed-polarity higher voltage to the electrodes. Films produced by PEPDECS were then studied to determine the mechanism that allows deposition and complete liberation from the substrate.

MATERIALS AND METHODS.

Treatment Preparation.

CNT suspensions used in the development of this method were Aquacyl AQ0101, aqueous, multiwalled carbon nanotube (MWCNT) suspensions (1 wt%, specified average length 1.5 μm, carbon purity > 95%, Nanocyl Inc., Belgium,). The as-received CNT suspensions were centrifuged for 90 minutes at 2172 xg to remove large aggregates and impurities as previously discussed [3]. The substrates used for deposition were 0.004 in thick, 316L stainless steel (McMaster Carr, USA) that were cut into 2.5 cm x 5.0 cm electrodes.

Film Fabrication.

The EPD apparatus and deposition schemes reported by Rigueur et al. were utilized for the initial CNT deposition onto the steel electrodes [3]. Vertically aligned electrodes, placed in a parallel plate configuration with a separation of ~1 cm, were inserted into the CNT suspension for periods ranging from 0.5 minutes to 10.0 minutes (Figure 1). A BK Precision 1787B power supply applied a constant DC voltage, ranging from 2.1 V to 2.8 V; a Keithley 2010 autoranging digital multimeter monitored the electrophoretic current.

At the conclusion of the EPD experiment, the electrodes were extracted from the suspension to compact with the EPD voltage maintained for an additional 5.0 minutes. This step enabled further densification of the CNT film [17-20], which enhanced the film's homogeneity compared to purely evaporative processes. Immediately thereafter, the films were gently rinsed in deionized water to remove extant dip-cast material (material that remains on the film due to surface tension). The resulting films were then kept at room temperature until the deposited films were visibly dry. The aforementioned step constituted a single (1x) deposition process; the 1x process could be repeated on the same substrate (multiple depositions) to yield thicker buckypapers.

Film Liberation and Analysis.

CNT films were liberated following EPD using two different techniques. The first technique involved "mechanical cleavage" where the deposited films were manually lifted from the substrate with a razor [3]. The second involved post-EPD electrochemical separation (PEPDECS), following exfoliation of the edges of the electrodes to sever CNT connections between the two faces of the electrodes, in which the coated EPD electrodes were placed in a second parallel plate setup. The separation between the electrodes was decreased to approximately 0.5 cm. Deionized water was used as the PEPDECS suspension and a reversed bias of 20.0 V was applied across the electrodes, opposite the direction of the original EPD current (Figure 1).

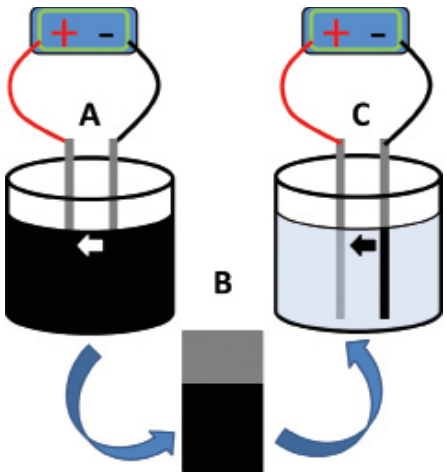

Figure 1. EPD and PEPDECS schematic. (A) The initial deposition of the film occurs on the anode due to the negative charge of the specified MWCNTs. (B) The film is then kept at room temperature until it is visibly dry. Before the separation procedure, the edges of the substrate, where parts of the BP reside, are exfoliated to eliminate effects due to "wrapping" of the film around the electrode. (C) The film, still attached to the substrate, is then inserted into deionized water; the direction of the applied electric potential is reversed. The voltage is removed from the system upon film separation.

After clear separation of the CNT film from the substrate, the voltage was removed and the film extracted from the water with forceps. Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups present on the surfaces of the attached and liberated films, using a Bruker Tensor 27 FTIR instrument. A Hitachi S-4200 scanning electron microscope (SEM) was used to image the surfaces of the films.

RESULTS AND DISCUSSION.

In a typical PEPDECS experiment of three depositions of 10.0 minutes each, films separated from the substrate within five minutes of applied voltage. Resulting films did not reattach to the electrode and, at a certain undetermined thickness, were able to be removed from the deionized water with no damage. Some bubble formation on the electrodes was observed during the initial EPD, causing minor surface irregularities on all of the films in this study. Much bubble formation was observed during the PEPDECS phase. The surfaces of the liberated films exhibited no appreciable degradation after the process, as evidenced by SEM images in Figure S1. The structure revealed is a generally horizontal planar orientation of CNTs with some random vertical variation. The surface is tightly packed and entangled yet porous. The EPD-PEPDECS scheme produced buckypapers exhibiting similar physical properties to those produced using EPD followed by mechanical cleavage. After drying the films post-PEPDECS, the buckypapers exhibited good stability and were not prone to tearing during normal handling, as illustrated in Figures 2A-2B.

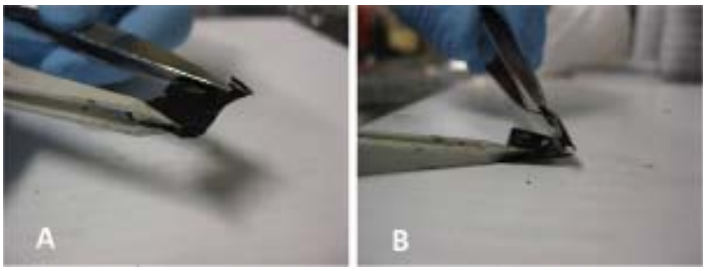

Figure 2. Photographs showing PEPDECS-liberated CNT films. (A) shows the relatively intact shape of the film and (B) demonstrates the flexibility and stability of the films. The tear seen on the edge of the film in (B) was inflicted during the removal of the film from the water in which PEPDECS was conducted.

Films deposited under the same parameters but liberated using separate methods were virtually indistinguishable without chemical analysis. The PEPDECS technique has been used in the separation of more than ten films deposited under standard EPD conditions reported by Rigueur et al [3].

FTIR spectra of four different CNT film surfaces –the inner surface of a mechanically separated film, a surface of a film not yet liberated from the substrate, and both surfaces of a PEPDECS film– were analyzed to determine possible electrochemical mechanisms for the developed process (Figure S2). Differences among the FTIR spectra of the films were observed primarily at three peak positions (1149 cm^{-1}, 1411 cm^{-1}, and 1449 cm^{-1}), corresponding to a C=C bond in the organic chain of the CNT surfactant. The peaks appeared in the films separated without PEPDECS (Figures S2A, S2B) and appeared to be absent in the film separated with PEPDECS (Figure S2C). These FTIR results indicate that hydrogenation of the organic chain of the CNT surfactant was the primary chemical change that occurred during PEPDECS.

The nature of the electrochemical system during PEPDECS suggested that the hydrogenation occurs through a heterogeneous metal catalyzed process [21]. This process involved the adsorption of the double bond on the electrode, which acted as a metal catalyst, and a two-step reduction of the bond by molecular H_2 [21]. The double bond, originally present in the organic chain of the CNT surfactant, was likely adsorbed on the steel substrate through carboxyl bonding, forming carbon-metal bonds (Figure 3A). The pH of the PEPDECS suspension was measured to be 5; the reduction half-reaction at the cathode was, therefore, favored by equilibrium, producing the molecular H_2 necessary to reduce the double bond (Figure 3B). The H_2 dissociated upon adsorption onto the catalyst and broke the carbon-metal bonds between the steel and the surfactant molecules, facilitating the removal of the film from the surface of the electrode (Figure 3C).

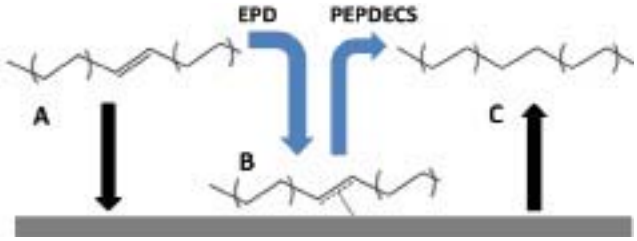

Figure 3. Electrochemical deposition scheme for EPD and PEPDECS. (A) During EPD, CNTs reach the positive electrode and are linked onto it by a double bond located in the organic chain of the surfactant. (B) During PEPDECS, hydrogen generated from electrolysis of water reacts with the complex [(surfactant double bond)-(steel)], reducing the double bond and (C) releasing the CNTs.

CONCLUSION.

PEPDECS was shown as a feasible and reliable method for removing electrophoretically deposited CNT films. The EPD-PEPDECS scheme produced buckypapers of appreciable flexibility and integrity with structural characteristics comparable to those of buckypapers fabricated using mechanical cleavage, the only other prevalently used technique. The developed process is industrially efficient and does not involve any additional materials, reducing human interference in film production. The mechanism allowing for convenient liberation of the film appears to be the breaking of carbon-metal bonds on the surface of the steel substrate, reaffirming the potential of this process to be employed in a broad range of applications, possibly including similar colloidal suspensions and systems.

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SUPPORTING INFORMATION.
Figure S1. SEM Micrographs
Figure S2. FTIR of CNT Films

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Jyotishka Biswas is a student at Hume-Fogg Academic Magnet High School and enrolled in the School for Science and Math at Vanderbilt.

Shalom Rottham-Yang is a student at Hume-Fogg Academic Magnet High School and enrolled in the School for Science and Math at Vanderbilt.