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Layer-by-layer deposition of cationic and anionic carbon nanotubes into thin films with improved electrical properties

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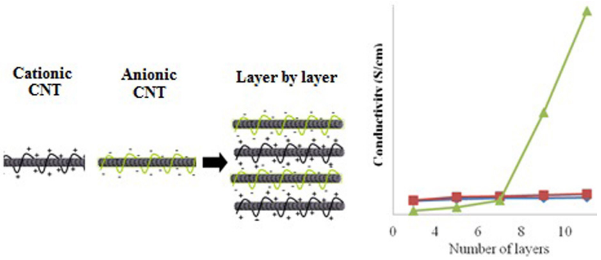
HIGHLIGHTS

- Carbon nanotubes were dispersed with cationic or anionic polyelectrolytes.
- Three different architectures were deposited into films using the layer by layer approach.
- The all CNT^+/CNT^- films displayed the best conductivity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the electrical properties of carbon nanotubes (CNTs) assembled into different architectures using the layer-by-layer technique have been investigated. The CNTs were modified with either anionic water-soluble polyaniline blend poly(sodium 4-styrenesulfonate) (PANI-PSS) or cationic poly(diallydimethyl ammonium chloride) (PDADMAC) to form negatively charged CNT^- and positively charged CNT^+. PANI-PSS was synthesized by interfacial polymerization of aniline using PSS as template. The first of the three architectures studied was assembled by the LbL deposition of anionic CNT^- and cationic CNT^+ while the two others were prepared by the deposition of only 1 type of CNTs (CNT^+ or CNT^-) with an oppositely charged polyelectrolyte to form PDADMAC/CNT^- and PANI-PSS/CNT^+. The thickness and surface roughness of the three different films were characterized by atomic force microscopy (AFM) while the electrical and optical properties were measured using a four points probe setup and a UV–vis spectrophotometer, respectively. The dispersion of the CNTs using PANI-PSS as capping agent was the least efficient when compared to the PDADMAC leading to a lower adsorption on a charged substrate. Interestingly, the layer-by-layer deposition of the CNT^-/CNT^+ films had a slower growth but displayed a superior electrical conductivity when compared to the other two architectures.

1. Introduction

Since their discovery by Iijima [1], carbon nanotubes have received much attention and have been used in numbers of applications such as electronic devices [2], energy storage [3] and chemical sensors [4–7]. It is well known that pristine CNTs cannot be dispersed in water and most organic solvents due to the attractive interactions between the individual nanotubes leading to the formation of aggregates. For this reason, CNTs must be modified before blending in a matrix and used as mechanical reinforcement or coated onto a substrate. The surface modification of the CNTs can mainly be achieved through covalent or non-covalent methods. Much work has been done, including by our group, to improve their dispersion through non-covalent bonding because it usually does not requires complex chemical reactions and tedious purification steps [8–10]. We have recently reported the "Just enough" modification of CNTs with chitosan which minimize the excess of polymer and therefore does not require time consuming centrifugation steps

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[11]. Because many applications are based on the CNTs electrical conductivity, for example in anti-static coating or electro-chemical sensors, CNTs have been associated with conducting polymer into composites materials. The benefit of dispersing CNTs using conducting polymer, instead of surfactant, is that the electrical properties of the CNTs can be improved. Several studies have reported the preparation of such materials using in situ polymerization of aniline with CNTs which could then be then further processed by spin coating [12,13]. Recently Suckeveriene et al. have reported the synthesis of hybrid polyaniline/CNT using an emulsion based interfacial polymerization in which the composite materials were casted into thin films having relatively low resistivity [14]. Nevertheless the coatings could not be deposited into nano-scale coatings and presented a thickness of several microns leading to the formation of cracks.

To achieve better control over the CNTs assembly into thin film, the layer-by-layer (LbL) technique also termed polyelectrolyte multilayers developed by Decher in the early 90s has been used in numbers of studies [15]. This technique is now widely used to prepare thin films of oppositely charged species. Virtually any kind of nanoparticles can be layered into the thin films as long as they carry a positive or negative charge at their surface to bind with the opposite layer [16]. Typically nanoparticles are layered in sequence with charged polyelectrolytes that produce an interconnected thin film composed of particles separated by the oppositely charged polyelectrolytes. Yet, in the case of CNTs, considered as tubular nanoparticles, their assembly with non-conducting polymer leads to films having poor electrical properties due to the insulating effect of the coating around the CNTs. Polyaniline is usually treated with sulfuric acid to produce a water soluble polymer as sulfonated polyaniline. Using the recently developed interfacial polymerization, the aniline monomer dissolved in chloroform polymerizes at the interface between the organic and aqueous phase in which the oxidant ammonium persulfate and Poly(styrene sulfonate) are dissolved. Within few minutes, a green polymer appears at the interface and dissolves in the aqueous phase due to a template effect from the PSS. In the absence of PSS as a template, Polyaniline remains insoluble in water and precipitate at the chloroform/water interface. When PSS is added the resulting water soluble polymer can be used to produce conducting thin film and can also be deposited using the LbL method. Our group has recently reported the LbL deposition of polyaniline prepared from the interfacial polymerization of aniline templated on PSS [17].

In this work, we used anionic and cationic CNTs modified with water-soluble polyaniline blend poly(sodium 4-styrenesulfonate) (PANI-PSS) and poly(diallydimethyl ammonium chloride) (PDADMAC), respectively. In an effort to find the most efficient structure having the fastest growth and the best electrical conductivity the two types of CNTs were deposited into 3 distinct architectures that were P^+/CNT^-, $CNT^{+/}P^-$ and CNT^+/CNT^-. The CNT composite films were characterized by AFM, UV–vis spectroscopy and four points probe in order to elucidate the effect of the thickness on the conductivity of the films.

2. Experimental

2.1. Chemicals

Poly(sodium 4-styrene sulfonate) (PSS, Mw = 70,000), poly(diallydimethyl ammonium chloride) (PDADMAC, Mw = 200,000–350,000), chloroform ($CHCl_3$), aniline monomer, ammonium persulfate (APS), and hydrochloric acid (HCl) were purchased from Aldrich Chemicals. Multiwall carbon nanotubes: CNTs (baytubes C 150 P, outer diameter distribution 5–20 nm and length 1–10 μm), were purchased from Bayer Thailand. All chemicals were of analytical grade and used as received without further purification. All aqueous solutions were prepared with double distilled water.

2.2. Surface modification of the CNTs

The synthesis of PANI-PSS to be used as the anionic polyelectrolyte was carried out according to the previously reported method [17]. For the dispersion of the CNTs using PANI-PSS, 5 mg of CNTs were dispersed in 100 ml solutions of various PANI-PSS content (0.01, 0.02, 0.05, 0.10, 0.125 and 0.15% weight). The mixture was sonicated using a 130 W Ultrasonic Processor (VCX 130 PB) in an ice bath for 1 hr. The preparation of cationic CNTs modified with PDADMAC was done by mixing 5 mg of CNTs in 100 mL of various PDADMAC content with concentration of 0.01, 0.05, 0.1, 0.2, 0.3 and 1.0 mM or expressed in weight% 0.0016, 0.008, 0.016, 0.032, 0.048, 0.16% (w/w). The solutions were stirred and sonicated using the same probe sonicator for 1 h. The turbidity of the solution of the dispersed CNTs was measured at 550 nm using UV–vis spectroscopy.

2.3. LbL self assembly of CNTs

The polyelectrolyte multilayers technique was used to assemble the CNTs into thin films. To improve the adhesion of the CNTs on the glass slides, a primer coating composed of 6 PDADMAC-PSS layers was first deposited to generate a positively charged hydrophilic substrate. Then, the pre-coated glass slides were sequentially dipped in either cationic or anionic species to form the desired architectures. The alternate LbL films of each positive and negative charge polyelectrolytes were achieved by repeating this process until the desired number of layers was reached after which the films were dried in a stream of nitrogen and stored.

2.4. Characterization

The optical properties of the CNT thin films were measured using Ultraviolet-visible (UV–vis) spectra (Specord S100, Analytikjena spectroscopy) and the morphology of the CNTs was characterized by transmission electron microscope, (TEM) JEOL-JEM-2100. The surface roughness of the thin films was measured by Atomic force microscopy, (AFM) (caliper, Veeco) used in taping mode. The thickness of the films was measured with the AFM by scratching the surface of the film with a sharp tool and scanning the step edge of the scratch. The electrical properties of the composite films were measured with a homemade four points probe setup.

3. Results and discussion

When considering the layer-by-layer deposition of nanoparticles into thin films, sufficient electrostatic charges must be present at their surface for stable adsorption. Nanoparticles such as CNTs need to be modified with either anionic or cationic polyelectrolytes before deposition. Cationic PDADMAC or anionic PANI-PSS were mixed in various amounts with the CNTs and sonicated to produce a black dispersion. Upon mixing, a polymer layer of either PDADMAC or PANI-PSS is formed around the surface of the CNTs as can be seen on the TEM image in Fig. 1. The pristine nanotubes seen in Fig. 1A had an initial diameter of 7–10 nm and the thickness of the PDADMAC (Fig. 1B and C) and PANI-PSS (Fig. 1D and E) polymer coating could be measured to be 3.5 nm and 10 nm respectively using TEM. The PANI-PSS, appears to provide a thicker coating probably because it is the result of the interfacial polymerization of PANI bundled with PSS which act as a template as described earlier. The PANI-PSS polymerized from the interfacial process does not produce single strand copolymers but instead thicker polymer bundles. While the exact structure of the PANI-PSS bundle is still