

## Controlled thin layer coating of carbon nanotube-polymer composites for UV-visible light protection

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**Abstract**—A highly dispersed solution of multi-wall carbon nanotubes (MWCNT) and counterpart polymers was prepared in aqueous solution. A thin layer coating was deposited on glass substrates by using the layer-by-layer (LBL) method. A negative charged dispersion solution of MWCNT was obtained by oxidizing the MWCNT by immersion in nitric acid. Counterpart polymers, poly(diallyldimethylammonium chloride) (PDAA) and poly(acrylic acid) (PAA), were used as base materials. The zeta potential measurements of the MWCNT solution showed the strongest potential at pH 4 and strong polyanionic surfaces at pH 5. A home-made automatic LBL machine was used to coat the polycationic/anionic materials on glass substrates. The substrate was coated homogeneously by the LBL method and the transmittance from the range of ultraviolet (UV) to visible light was manipulated in the coating process. This simple technique might be effectively utilized for fabrication of micro-sensing and energy harvesting devices, and UV light protection.

Key words: Layer-by-layer, Carbon Nanotubes, Coating, Thin Film, Transmittance, Dispersion

### INTRODUCTION

The recent development of coating techniques based on nanomaterials has attracted considerable attention in areas such as aerospace, biotechnology, environment and even domestic electric appliances [1-7]. In addition, transmittance area can be changed easily with different nanomaterials. For example, early studies by Lantiat and Babonneau et al. [8] showed variable transmittance using Ag nanoparticles capped with dielectric  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , BN layers. It was reported that silica-titania nanocomposite [9], polystyrene/Au nanoparticle [10], and  $\text{Al}/\text{Al}_2\text{O}_3$  [11] can be used successfully to control the transmittance. Nanomaterial coatings have many advantages over other coating techniques, such as convenience and cost effectiveness. Nanomaterials also have high surface areas, high catalytic activity and chemical stability [5-7,12,13]. However, most current techniques require a vacuum to produce high quality films and surfaces, which may be a limitation to technological application due to the size and high cost of the vacuum chambers. Gas and powder guns have been introduced to deposit high quality films on bulky structures. However, the use of such techniques to nanomaterials will require a more critical study on environmental and health safety of nanomaterials [14-18]. Therefore, the coating technology using nanomaterials requires a novel strategy to avoid these shortcomings.

This paper suggests a novel coating method that is a modified form of the layer-by-layer (LBL) process. The LBL technique can produce thin films or coatings on solid substrates using nanomaterials, and is one of best methods for handling nanomaterials because all processes are in the solution, mostly aqueous, which is devoid of the environmental issues with gas phase processes [19-22]. With

LBL techniques, most nanomaterials, e.g., carbon nanotubes, quantum dots, cellulose, etc., can be used after simple hydrophilic modification of the surface of selected nanomaterials through a polymeric coating and surface oxidization [19,21-27]. The coating techniques of various nanomaterials can be directly and broadly applicable in sensing, biomedical, electronic industries as well as environmental and aerospace engineering such as unlimited boundaries of application fields. The development of surface modification processes for these nanomaterials is an expected bottleneck in these techniques. However, there have been considerable advances in techniques for modifying the surface of nanomaterials by adequate chemical synthesis [28-31]. This paper reports a desirable example of an LBL bi-layer coating using a representative hydrophobic nanomaterial, multi-wall carbon nanotubes (MWCNT). The surface of MWCNT was modified by acidic oxidation to form negatively charged functional groups such as carboxyl and hydroxyl groups [32-34]. The resulting MWCNTs stabilized with negative charged surface were deposited on a glass substrate with counter electrophilic polymer materials to produce a UV-vis light protection thin film. The substrate was coated homogeneously by the LBL method under ambient conditions in which the light transmittance in the UV to visible ranges was controlled precisely by the concentration and zeta potential of the coating materials as well as the number of coating repetitions. This technique is suitable for the design of high standard devices employing universal coating materials, such as solar cells, and precise semiconductor material control as well as for fabrication of micro-sensing and energy harvesting devices, and UV light protection.

### EXPERIMENTAL DETAIL

#### 1. Surface Modification and Colloidal Stability of Hydrophilic MWCNT

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The counterpart polymers of poly(diallyldimethylammonium chloride) (PDDA) and poly(acrylic acid) (PAA) were purchased from Sigma (Milwaukee, WI, USA) and used without further purification. The homogeneous and stable dispersion from the surface modification of the selected nanomaterial is important in the suggested LBL method. Morphological changes to the nanomaterials, such as

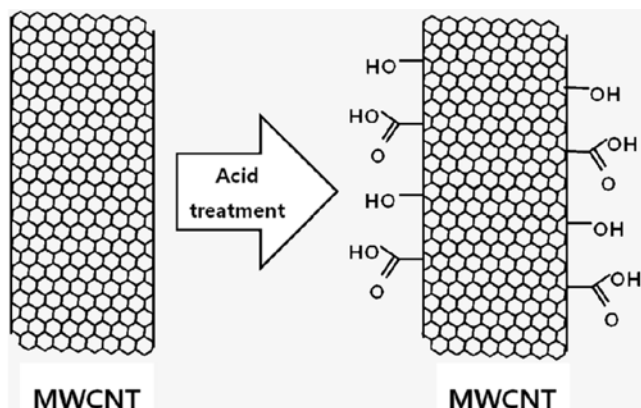


Fig. 1. Schematic view of the surface treatment on MWCNT by using nitric acid.

aggregation and precipitation, should be prevented during the process of surface modification. The MWCNT powder was purchased (CNT Co. LTD., Incheon, Korea). The MWCNT surface was modified by the following process. First, the MWCNT aggregates were dispersed to small sizes (approximately the sub-micrometer scale) by ethanol with vigorous stirring. An acid treatment with nitric acid was then performed to place hydroxyl and carboxyl groups on the MWCNT surface (Fig. 1). In a typical acid treatment, 3.0 mg of CNT was dispersed in 35 ml of nitric acid and boiled under reflux for 1 h. The specimen was then diluted, filtered, and washed repeatedly with 18 M $\Omega$  d.i. water until there was no acidity. The acid treated MWCNT at pH 6.00 was quite stable in the well-dispersed colloidal state for more than two months. The colloidal stability of the dispersed MWCNT was measured by UV-vis absorption spectroscopy, and the zeta potential of the MWCNT was measured with a Zeta sizer (ZS-nano, Malvern, UK).

## 2. LBL Methods and Fabrication of Automatic LBL Machine

LBL coating method was used to deposit the nanocomposite coating on the glass substrate. Initially, a counterpart polymer solution was prepared with PDDA (0.5 w%, pH 7.60) and PAA (0.5 w%, pH 2.20) in d.i. water. MWCNT (3.5 mg) was dispersed in 100 ml of the prepared PAA solution. Prior to deposition, the glass substrate (76×26×1 mm size of standard microscopic glass) was cleaned

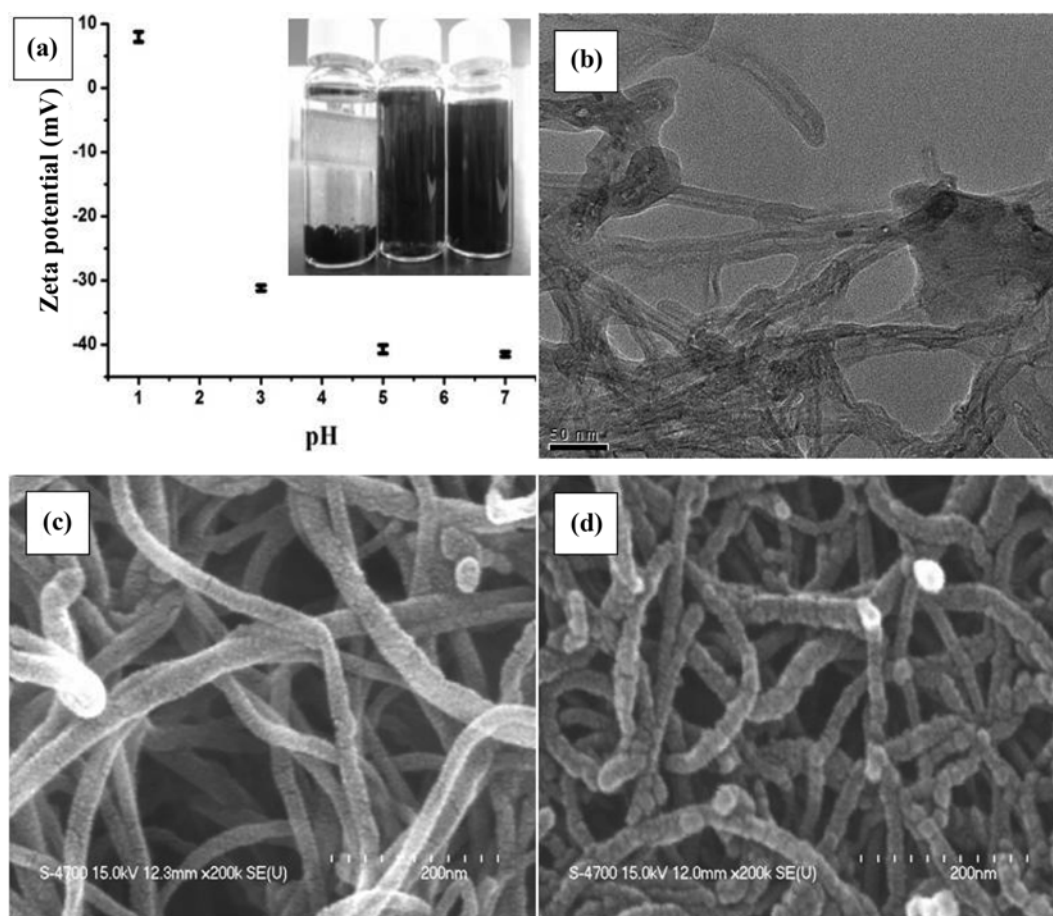


Fig. 2. (a) MWCNT dispersed solutions and their surface potentials depending on the solution pH from pH 1-7, (b) TEM image of the polymer encapsulated MWNT, (c) SEM image of the MWCNT before acid treatment and (d) after the acid treatment and polymer encapsulation.

by immersion into a “piranha” solution ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  mixture of 3 : 1 volume ratio) at  $80^\circ\text{C}$  for 1 h, followed by rinsing with copious amounts of d.i. water. The piranha solution reacts vigorously with organic materials with the release of possibly toxic vapors. Therefore, special caution, particularly for the skin and eyes, is required during the experiment! A typical LBL process was as follows. A base layer of  $(\text{PDDA}/\text{PAA})_1$  was prepared on the surface of the glass substrate to reduce the surface roughness and enhance the chemical bonding interaction. The number under the parenthesis shows the bi-layer of two different polymers. The LBL process of  $(\text{PDDA}/\text{MWCNT in PAA})_n$  was then performed. The coated bi-layer can be controlled, depending on the final transmittance of the glass. The glass substrate was immersed in a polymer solution for 5 min, rinsed with d.i. water and dried with compressed air for 1 min. The same process was continued with the MWCNT in PVA. Hence, one bi-layer was deposited on the glass slide. This process was repeated until the desired transmittance was obtained [21].

### 3. Optical and Morphological Properties of LBL Coating

The optical properties of the MWCNT coated glass were examined by UV-vis spectrophotometry (SCINCO, Korea), and the morphology of the thin film was observed by scanning electron microscopy (SEM, Hitachi-S4700, Japan). The surface potential of the MWCNT was measured with a Zeta sizer (ZS-nano, Malvern, UK) in order to optimize the colloidal stability.

## RESULTS AND DISCUSSION

Homogeneous and stable dispersity of MWCNT in an aqueous solution is the most important factor for obtaining high quality coatings using the LBL method. The MWCNTs were acid-treated to place hydrophilic functional groups on their surfaces, which increased their solubility and dispersity through repulsive interactions between functional groups in the aqueous solution. However, one should also essentially consider maintaining the innate structural properties of the CNT during the acid treatment. Fig. 2(a) shows the MWCNT dispersed solutions and their surface potential depending on pH, where the pH of the solution was varied from pH 1-7. The zeta potential of the MWCNT was changed from +8 to -42 mV when the pH was changed from 1 to 5. This means that the functional groups, mostly hydroxyl and carboxyl groups, on the surface of CNT changed from  $\text{H}_3\text{O}^+$  to  $\text{OH}^-$  and  $\text{COO}^-$  groups during the changes in pH. The repulsion energy between the negatively charged groups of the surface of MWCNT increased the dispersion of the CNTs in the aqueous solution, and the well-dispersed solution remained stable for more than two weeks (Fig. 2(a) insert). This well-dispersed CNT solution allowed the subsequent coating steps to be carried out. The surface morphology of the acid-treated CNT was observed by SEM (Fig. 2(c) and (d)). The surface roughness of the MWCNT was increased by the acid treatment, but its diameter and length were rel-

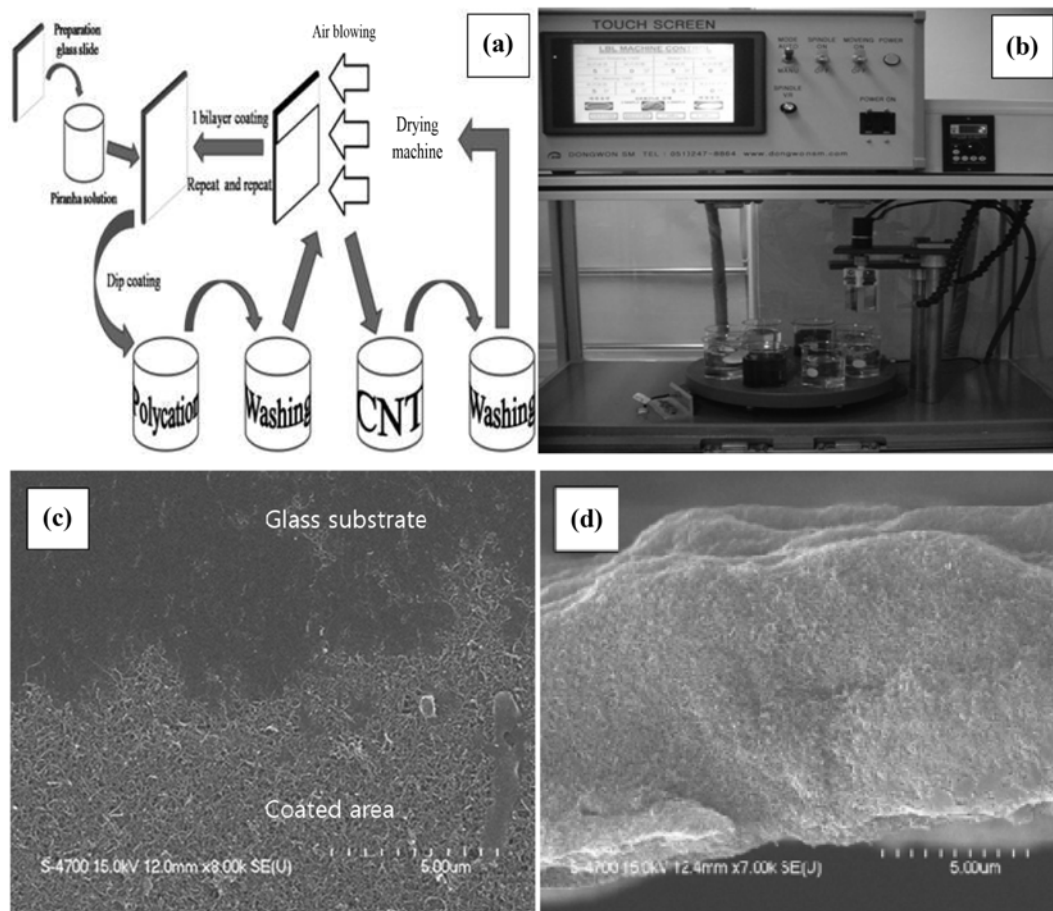


Fig. 3. (a) schematic diagram of the LBL process, (b) a home-made automatic LBL machine, SEM image of (c) the surface morphology and (d) cross-section.

actively unchanged, which results in the structural properties of the acid-treated CNT were not altered. The counterpart polymers were homogeneously coated on the surface of the MWCNT. The transmission electron microscopy (TEM) images (Fig. 2(b)) show that the MWCNTs were encapsulated with polymeric materials and linked with other CNTs via the polymers, which maintained the optical and chemical stability of the deposited film.

Fig. 3(a) gives an example of a typical LBL process. For this LBL process, a home-made automatic LBL machine was manufactured, which was composed of several parts, such as a rotating stage, sample holder, water basket, air blower and control box (Fig. 3(b)). The rotating stage consisted of eight slots. The sequence of the above described LBL process can be adjusted automatically with the control box. The optical properties of a thin coating could be controlled with high precision and reproducibility through repeated deposition of the monolayer. SEM images of the surface and cross section morphology of the film show that the monolayer stacking-up method ensures long-term photostability from strong UV radiation because the nanoscale structure of the coating film is ultimately entangled via covalent and electrostatic interactions between the surface functional groups on the MWCNT and the polymers. No aggregation or CNT islands were observed on the coated area, which confirmed

that a homogeneous dispersion of a colloidal solution of acid-treated MWCNT produced a high quality film (Fig. 2(c) and (d)). A thermogravimetric analyzer (TGA N-1000, SCINCO) was used to compare the qualitative composition of the mixture. The results showed that the thin coating film consisted of 60 wt% CNT and 40 wt% of the counter polymer.

Fig. 4(a) and (b) show an atomic force microscopy (XE-100, Park SYSTEMS) image of the MWCNT coating film with ten bi-layers, and the cross sectional profile of a designated area, respectively. The results show that the surface morphology of the coating film was homogeneous and the mixture of CNT and polymer was well distributed in the designated area. The height of the cross section indicated that a single layer of MWCNT ( $d=20\text{--}30\text{ nm}$ ) had been coated by one cycle of the LBL process, which suggests the possibility of precise control of the light transmittance for high quality film fabrication. Fig. 4(c) shows a full area image of the LBL coating film, where the number of LBL operation running cycles from the left slide was 0, 10, and 15, respectively. An obvious change in transmittance was observed. Fig. 4(d) shows the UV-vis light transmittance of the films on the glass substrate with up to 40 bi-layers. The reference was a piranha solution cleaned glass substrate. The transmittance of the coated glass substrate increased with increas-

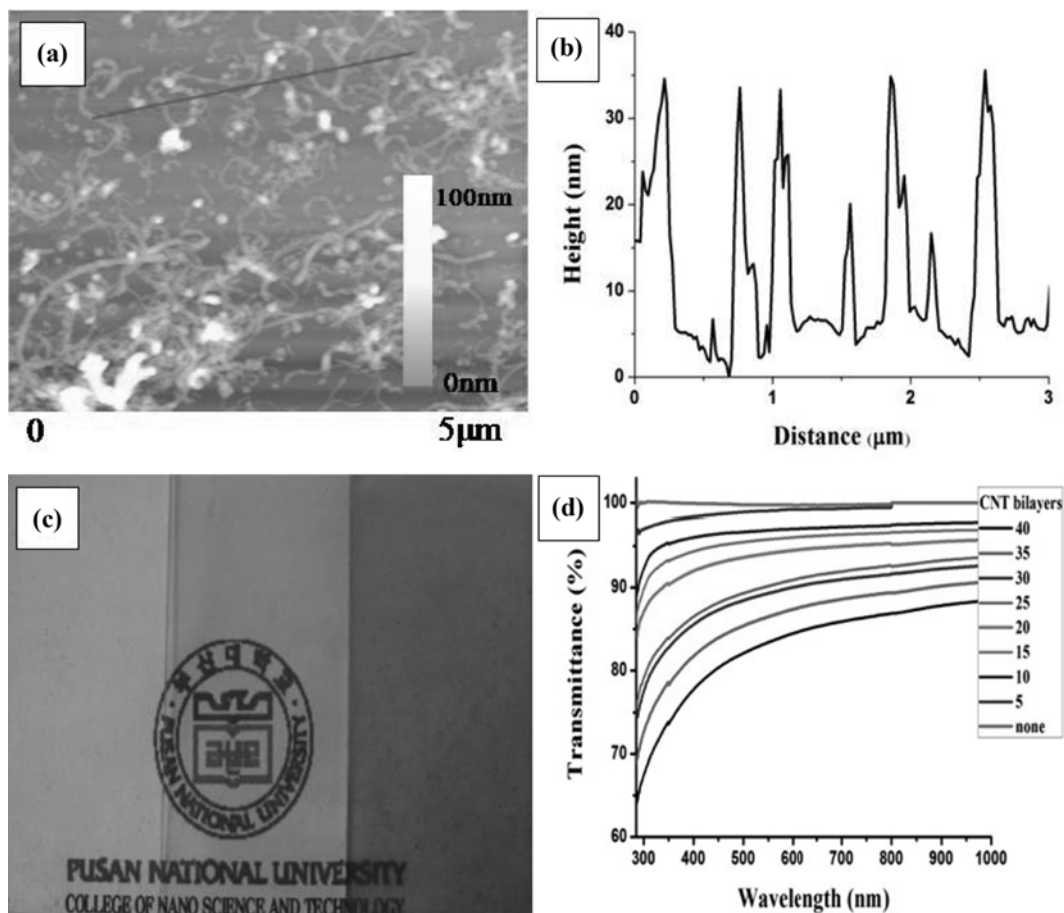


Fig. 4. (a) AFM morphology image of the LBL-treated surfaces on glass substrates (10 bi-layers), (b) a cross section profile at the designated area (a line on the left AFM image), (c) The full area image of the LBL coating film where the LBL operation running cycle was altered 0, 10, and 15 times, respectively, from the left slide, (d) UV-vis light transmittance data of the automatic LBL processed coating film on a glass substrate until 40 bi-layers.

ing number of coated bi-layers. The transmittance at 400 nm could be controlled in approximately 1% increments per bi-layer. This can easily be changed by controlling the concentration of the dispersed CNTs solution and counter polymers. The films deposited by using the LBL method had similar or superior film quality to that obtained by vacuum deposition.

## CONCLUSION

LBL bilayer coating containing multi-wall carbon nanotubes (MWNT) was deposited to produce a UV-vis protection coating. The substrate was coated homogeneously by the LBL method under ambient conditions in which light transmittance from UV to the visible range was controlled precisely by controlling the concentration, zeta potential of the coating materials and number of repetitions of the coating process. This universal technique is applicable to the design of high standard devices employing universal coating materials, such as solar cells, precise semiconductor material control, and biomedical and aerospace applications for fabrication of micro-sensing and energy harvesting devices, and UV light protection.

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