

다층적층 조립법을 이용한 은 나노와이어와 폴리아크릴산 전도성 박막의 제조

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Conductive Thin Films Composed of Silver Nanowires and Poly(acrylic acid) Prepared by Layer-by-Layer Assembly

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초록: 최근 나노물질을 실제 응용소자에 활용하고자 하는 시도가 많이 이루어지고 있다. 본 연구에서는 layer-by-layer(LbL) 자기조립 방법을 이용하여 은 나노와이어와 poly(acrylic acid)(PAA)를 전도성 박막으로 제조하였다. LbL 자기조립 과정을 관찰한 결과, 은 나노와이어와 PAA로 이루어진 이중층의 수가 증가함에 따라 최대 흡광도 값이 선형적으로 증가하는 것을 알 수 있었다. 또한 X-ray photoelectron spectroscopy(XPS)를 통해 흡착 과정에는 수소결합과 배위결합 모두 관여한다는 것을 밝혀 내었다. 면저항 수치는 $4.2 \pm 0.6 \Omega/\text{sq}$ 에서 $14 \pm 2 \Omega/\text{sq}$ 범위의 값을 가지는 것으로 측정되었으며, 이는 본 연구에서 제안한 전도성 박막 제조방법이 광전자 소자의 전극제조에 활용될 수 있다는 가능성을 보여준다.

Abstract: Practical use of nanomaterials has drawn significant attention of researchers in the fields of nanoscience and technology. However, the control and processing of nanomaterials are still challenging especially for device applications. In this report, we prepared conducting thin films using silver nanowires (AgNW) and poly(acrylic acid) (PAA) via layer-by-layer (LbL) assembly methods. The AgNW/PAA LbL assembled films exhibited typical adsorption behaviors with a linear increase in the UV-Vis absorbance at the maximum absorbed wavelength with increasing number of bilayers. We utilized X-ray photoelectron spectroscopy (XPS) to investigate the adsorption mechanism. The results revealed that both hydrogen bonding and coordination bonding were engaged in the assembly process. The sheet resistances of AgNW/PAA LbL assembled films were measured within the range of $4.2 \pm 0.6 \Omega/\text{sq}$ to $14 \pm 2 \Omega/\text{sq}$, indicating their potential use as thin film conductors for the fabrication of opto-electronic devices.

Keywords: layer-by-layer assembly, silver nanowire, poly(acrylic acid), conductive thin film.

Introduction

There has been significant progress in the area of nanoscience and technology in the last decade. The fundamental understanding on nanomaterials and their unique characteristics based on the quantum confinement effect have been thoroughly investigated.^{1,2} Commercial products developed using nanotechnologies are already in the markets ranging from daily cosmetic products, food packaging materials and textiles to high technology products, including nanoelectronics, quantum

dot displays, and bio-sensors.^{1,2} However, the processing of nanomaterials is still a major issue and is regarded as being a bottleneck preventing further industrial applications. Among the many issues related to the processing of nanomaterials, preparation of thin solid films is one of the key issues especially for wet-chemistry-based nanomaterials.^{1,2}

Various types of preparation methods have been used for the fabrication of thin films with nanomaterials, including the Langmuir-Blodgett method,^{3,4} dip coating,^{5,6} spin coating,^{7,8} vacuum-filtration⁹ and layer-by-layer (LbL) assembly.^{10,11} The Langmuir-Blodgett method was developed to prepare a monolayer of amphiphilic molecules, and extended to use nanomaterials for monolayer deposition.¹² However, this method cannot be used for the preparation of thicker films or for mass

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production. Dip coating requires precise control of various coating conditions, including humidity and temperature for efficient reproducibility. Spin coating has drawbacks such as the non-uniform film quality due to the formation of stray lines. Also, large amounts of wastes are produced in these methods, which are not favorable with respect to process economics and the environment.¹³ Vacuum filtration is a facile method for the preparation of films made of nanomaterials, which is advantageous due to its efficiency. However, this method has limitations in terms of controllability of film thickness and the contaminations during the detaching process.¹⁴ The LbL assembly method has been used in the preparation of functional thin films for electrical, optical, pharmaceutical, and biomedical applications. This method produces layered structures of nanomaterials via various types of molecular interactions such as electrostatic attraction, hydrogen bonding, coordination bonding, and other physical/chemical interactions. Therefore, various functional moieties attached onto the surface of nanomaterials were utilized as adsorption driving forces in the LbL assembly method.

Silver nanowires (AgNWs) have been utilized in various applications in electrical and optical devices and, bio/chemical sensors because of their superior properties in terms of electrical conductivity and plasmonic and antibacterial properties.¹⁵ LbL assembly methods were utilized to incorporate AgNWs into thin films. The pair—poly(allylamine hydrochloride) and poly(styrene sulfonate)—was typically used in LbL assembly in most previously reported works.^{16,17} However, there was only a brief mention of the adsorption driving force, that is, electrostatic interaction between poly(allylamine hydrochloride) and AgNWs coated with the stabilizer of poly(vinyl pyrrolidone) (PVP). Besides this study, other pairs of polyelectrolytes or adsorption mechanisms have not been thoroughly investigated yet.

In this work, we utilized the combination of two intermolecular interactions of hydrogen bonding and coordination bonding in LbL assembly of AgNWs with poly(acrylic acid) (PAA). We synthesized AgNWs using PVP as the stabilizer. Also, PAA in an aqueous solution was protonated by adjusting the pH to a value of 3.0 to promote hydrogen bonding between PVP and PAA. AgNWs and PAA were repeatedly adsorbed onto the substrates to prepare (AgNW/PAA)_n LbL assembled films on substrates (where *n* indicates the number of bilayers of AgNW and PAA). The adsorbed amounts of AgNWs linearly increased as the number of bilayers increased similar to the typical LbL assembly system. Moreover, we investigated

intermolecular interactions that are the adsorption driving forces in LbL assembly. Based on the peak shifts observed in C1s and Ag3d spectra, we concluded that both hydrogen bonding and coordination bonding existed, resulting in the effective adsorption of AgNWs and PAA. The electron conductivity of AgNW/PAA LbL assembled films was investigated, and these films show sheet resistances of $4.2 \pm 0.6 \Omega/\text{sq}$ to $14 \pm 2 \Omega/\text{sq}$, which are comparable to those of conductive ITO films. Since the LbL assembly of PAA with metallic nanomaterials has been rarely reported so far, we believe that this approach can be utilized in the preparation of versatile functional thin films with metallic nanomaterials. Furthermore, this method will contribute to the field of nanomaterial processing for advanced applications such as fabrication of electrical and optical devices.

Experimental

Materials. Poly(vinyl pyrrolidone) (PVP) ($M_w = \sim 55000$), poly(acrylic acid) (PAA) ($M_w = \sim 100000$), silver nitrate ($\geq 99\%$), glycerol ($\geq 99\%$) and sodium hydroxide anhydrous pellets were purchased from Sigma-Aldrich. Hydrochloric acid (35.0–37.0%), sulfuric acid (95.0%), hydrogen peroxide (33.0–35.5%) and sodium chloride (99.5%) were used as received from Samchun Chemicals.

Synthesis of Silver Nanowires (AgNWs). 5.86 g of PVP powder was placed in 3-neck flask with 190 mL of glycerol and agitated slowly until PVP were fully dissolved. Then 1.58 g of AgNO₃ powder was added to solution and further agitated until the solution was transparent without precipitates. NaCl solution was separately prepared by mixing 33.5 mg of NaCl with 0.5 mL of DI water and 10 mL of glycerol. NaCl solution was injected into the flask and the flask was heated up to 210 °C in 20 min with gentle agitations. Then the flask was cooled down to room temperature, followed by addition of 200 mL of DI water. Centrifugation was applied to recover AgNWs. Rotation condition of centrifugation was 8000 rpm for 20 min at 20 °C. Typically centrifugations were repeated 3 times with DI water for washing.

Preparation of (AgNW/PAA)_n LbL Films. Slide glasses were used as substrates after piranha treatments using (7:3(v/v) mixture of H₂SO₄:H₂O₂) to remove organic residues. The pH of AgNWs, PVP and PAA solutions was adjusted to 3.0 by diluted HCl and NaOH solutions. First, the base layers of (PVP/PAA)_{2.5} LbL films were deposited onto the slide glasses. The glass substrates were dipped into 1 wt% PVP solution for

4 min. Then the substrates were transferred to the bath of DI water and immersed for 1 min to wash off loosely bound polyelectrolytes. The wash step was repeated two times between deposition of PVP and PAA layers. Then the substrates were immersed in 1 wt% PAA solution for adsorption of PAA layer, followed by two washing steps with DI water. This protocol was repeated 2.5 cycles to fabricate (PVP/PAA)_{2.5} films. After deposition of base layers, (AgNW/PAA)_n LbL films were deposited. The substrates were dipped into 0.2 wt% AgNW solutions for 5 min with Vortex agitation and PAA solution for 4 min.

Characterization

The sheet resistances of the films were measured by 4-point probe station (CMT-SR1000N, AIT Co., Ltd). The surface of the films was examined by X-ray photoelectron spectroscopy (K-Alpha+, Thermo Scientific). The absorbance of the films was measured by UV/VIS spectrophotometer (Optizen POP, Mecasys Co., Ltd). The pH meter (MP220, Mettler Toledo) was used in the preparation of aqueous solutions.

Results and Discussion

AgNWs and PAA were assembled in thin films utilizing the LbL assembly method. The fabrication process is schematically depicted in Figure 1. AgNWs were synthesized by the procedure reported in literature¹⁸ and PVP was used as a stabilizing agent to enable the dispersion of AgNWs in water. The pH of both AgNW and PAA solutions was adjusted to 3.0 to promote hydrogen bonding between carbonyl groups of PVP and protonated carboxylate groups of PAA.¹⁹ Two bilayers of PVP/PAA were adsorbed onto the cleaned glass substrates, forming adhesive layers. Then, AgNWs and PAA were repeatedly deposited over the adhesive-layer coated substrates to prepare (AgNW/PAA)_n LbL films. Instances where n is 0.5 indicate that the final top layer deposited is the AgNW layer.

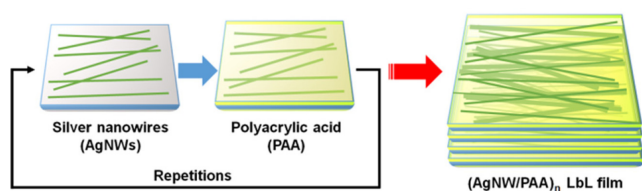


Figure 1. Schematic diagram of the fabrication of the (AgNW/PAA)_n LbL film.

To examine the growth behavior of our LbL assembly, adsorption amounts were investigated by photography and UV-Vis spectroscopy. Figure 2(a) shows the photographs of the films coated onto glass substrates. As the number of bilayers (n) is increased, color of LbL films gradually changes from pale grey to dark grey. Figure 2(b) shows UV-Vis absorbance spectra corresponding to the increase in the number of bilayers (n) from 0.5 to 3.5. We can observe that between the wavelengths 300 to 1100 nm the overall absorbance gradually increases. The absorbance spectra have maximum peaks at 357 nm and are attributed to the transverse mode of plasmonic bands of AgNWs. In addition, maximum absorbance peaks linearly increase with slope of 0.23/bilayers as shown in Figure 2(c), indicating that the adsorbed amounts of AgNWs also linearly increase. Also the transmittance at 550 nm values was monotonically decreased from 90% (n = 0.5) to 30% (n = 3.5)

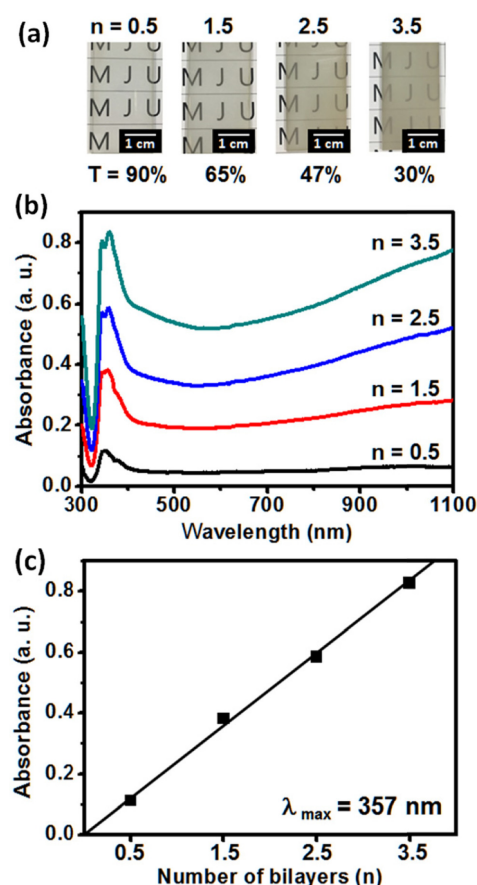


Figure 2. (a) Photographs of the (AgNW/PAA)_n LbL films with n = 0.5, 1.5, 2.5 and 3.5. T is the transmittance at 550 nm; (b) UV-Vis absorption spectra of the (AgNW/PAA)_n LbL films with n = 0.5, 1.5, 2.5 and 3.5; (c) Plot of the UV-Vis absorbance at 357 nm versus the number of bilayers.

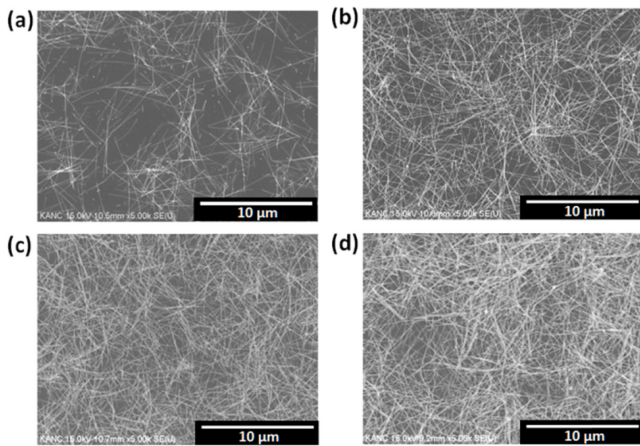


Figure 3. Scanning electron microscopy (SEM) images of (AgNW/PAA)_n LbL films with (a) $n = 0.5$; (b) $n = 1.5$; (c) $n = 2.5$; (d) $n = 3.5$.

(Figure 2(a)).

Surface morphologies of LbL films were investigated by scanning electron microscopy (SEM) and are shown in Figure 3(a-d). The areal number density was calculated by ‘total number of AgNWs divided by the area size’ from SEM images. As the number of bilayers is increased from $n = 0.5$ to 3.5, the areal number density of AgNWs increases from $80/\mu\text{m}^2$ to $195/\mu\text{m}^2$. This result is consistent with our UV-Vis spectroscopy data.

The pristine materials and AgNW/PAA LbL films were examined with X-ray photoelectron spectra (XPS) to investigate the adsorption mechanism for our LbL assembly. C1s spectra were deconvoluted based on the information of peak positions by referring to the literature.^{20,21} C1s spectrum of (AgNW/PAA)_{4.5} LbL film was deconvoluted into four different peaks as shown in Figure 4(c). Peaks numbered with 1 and 2 are mainly attributed to the C-C bonds of the polymer backbone. Peak number 3 (blue dotted line) mainly originated from C=O bond of PVP, which binds onto the surface of AgNWs. The C=O peak for AgNW sample (287.56 eV, Figure 4(a)) is shifted to a higher binding energy of 287.90 eV (Figure 4(c)) for the (AgNW/PAA)_{4.5} LbL sample. Also the COOH peak at 289.05 eV from the carboxylate group of PAA (peak number 4, magenta dashed lines, Figure 4(b)) is also shifted to a higher binding energy of 289.13 eV for the (AgNW/PAA)_{4.5} LbL sample (Figure 4(c)). These shifts indicate that the carbonyl groups of PVP and the carboxylate groups of PAA interacted through hydrogen bonding.²² Also, Ag3d peaks shifted to higher binding energies after LbL assembly (Figure 4(d)). This indicates partial removal of PVP, accompanied by partial adsorption of PAA molecules onto the bare surface of AgNWs

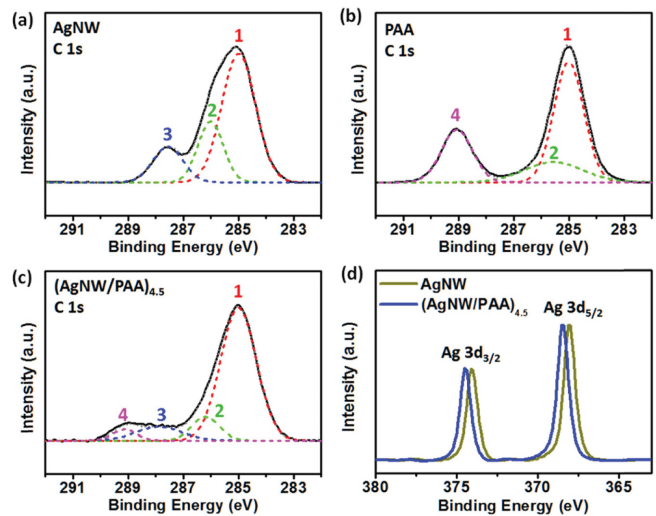


Figure 4. X-ray photoelectron spectra (XPS) for pristine materials and AgNW/PAA LbL films. C1s peaks of (a) AgNW; (b) PAA; (c) (AgNW/PAA)_{4.5} LbL film. Experimental data (black lines), cumulative data from deconvoluted curves (grey dotted lines), deconvoluted C-C curves (1 and 2, red and green dash lines, respectively), C=O (3, blue dash lines), C-OOH (4, magenta dash lines); (d) Ag 3d peaks for AgNWs and (AgNW/PAA)_{4.5} LbL film.

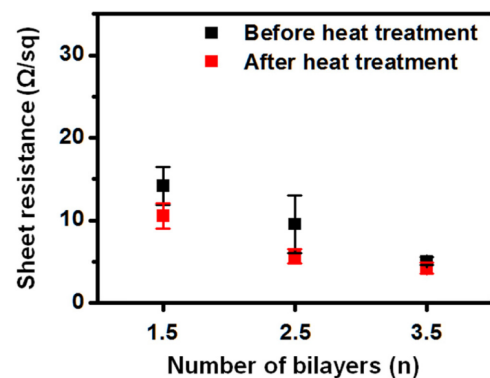


Figure 5. Sheet resistances before and after heat treatments for (AgNW/PAA)_n LbL films with $n = 1.5$, 2.5 and 3.5. The average of at least five measured values was used, and the error bars show the standard deviation.

via the formation of coordination bonds.^{23,24} Based on the XPS measurements, we assume that both hydrogen bonding and coordination bonding can be utilized in the LbL assembly of AgNWs and PAA.

The electrical conductivity of AgNW/PAA LbL films was investigated using a four-probe station by measuring sheet resistances of thin films (Figure 5). As the number of bilayers is increased, we can observe that the sheet resistance is reduced from $14 \pm 2 \Omega/\text{sq}$ ($n = 1.5$) to $5.1 \pm 0.5 \Omega/\text{sq}$ ($n = 3.5$).

For the $n=0.5$ samples, we could not obtain reliable results due to lack of interconnections between AgNWs. It is assumed that more conducting paths were formed as the areal density of AgNWs increased with the number of bilayers (n). In addition, sheet resistances were further reduced to $11\pm 2 \Omega/\text{sq}$ for $n=1.5$ and $4.2\pm 0.6 \Omega/\text{sq}$ for $n=3.5$ after heat treatments at temperature of 120°C for 20 min. We attributed this to the partial melting of AgNWs resulting in the reduction of contact resistances as reported elsewhere.^{25,26}

Conclusions

We prepared AgNW/PAA LbL thin films based on the combination of two intermolecular interactions of hydrogen bonding and coordination bonding. PAA interacts with the PVP coated onto AgNWs via hydrogen bonding. In addition, carboxylate groups in PAA can partially coordinate to the bare surface of AgNWs with the removal of the PVP coating. The conductivity increased as the number of bilayers was increased, and the sheet resistances were further reduced by heat treatments. We believe that this approach for the fabrication of conducting thin films can be used in various applications such as flexible conducting electrodes, anti-static coatings, and platforms for bio-sensors.

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