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공학석사 학위논문

**Usage of lignin as nature-derived  
organic dopants for tuning  
thermoelectric properties of carbon  
nanotubes**

탄소나노튜브 열전 성능을 조절하는 천연 고분자  
도펀트로서의 리그닌 연구

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지도교수 김 진 영

이 논문을 공학석사 학위논문으로 제출함

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재료공학부

최 유 현

최 유 현의 공학석사 학위논문을 인준함

2022 년 8 월

위 원 장                      장 호 원                      (인)

부위원장                      김 진 영                      (인)

위        원                      장 혜 진                      (인)

## **Abstract**

# **Usage of lignin as nature-derived organic dopants for tuning thermoelectric properties of carbon nanotubes**

Yoohyeon Choi

Department of Materials Science and Engineering

College of Engineering

Seoul National University

The continued application of fossil fuels is causing various environmental problems. Therefore, one of the eco-friendly power generations, a thermoelectric generating has been highlighted as an environmental generation method using waste heat. A thermoelectric generator (TEG) requires both *p*-type and *n*-type semiconductors. Since all are synthetic chemicals based on fossil fuels, they also need to be replaced. Lignin, one of the biopolymers, can be easily obtained as a by-product of various processes. They consist of a phenolic structure which can be a

precursor for various chemical reactions, making it possible to modify the molecular structure as desired. In this study, an eco-friendly biopolymer works as a dopant for CNTs *via* the chemical modification of functional groups in lignin. A microwave-assisted reaction, an eco-friendly process, was conducted on lignin for phenolation and amination. As a *p*-dopant, the phenol groups worked as electron-withdrawing groups (EWGs). In contrast, the diethylamine groups, electron-donating groups (EDGs), were used to synthesize an *n*-dopant. Carbon nanotubes (CNTs) were doped with modified lignins, and their thermoelectric performance was similar or superior to those of conventional synthetic dopants. The doped CNTs were characterized by ultraviolet photoelectron spectroscopy (UPS) and the shifts of the Fermi levels could be directly observed, indicating that the modified lignins successfully act as dopants. As a proof of concept, the thermoelectric generator assembled using lignin-doped CNTs and showed that the eco-friendly biopolymers could be used as dopants and, further, could be applied to eco-friendly power generations.

**Keyword:** eco-friendly, thermoelectric, carbon nanotube, lignin, dopant

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# Chapter 1. Introduction

Heat is closely related to our lives and industries. Therefore, precise control of heat is becoming an important factor in all industries. Since environmental issues are important keywords in various industrial fields, a thermoelectric method is considered an eco-friendly thermal control.<sup>1</sup> Thermoelectric cooling that does not use refrigerant, which is the main culprit of environmental pollution, and thermoelectric power generation produces electricity using wasted thermal energy without carbon dioxide and noise. The thermoelectric devices are based on the thermoelectric effect that conversion of electrical energy into thermal energy or vice versa.<sup>2</sup> When a temperature difference occurs at both ends, a potential difference occurs. Conversely, when a potential difference occurs, a temperature difference occurs at both ends. The former is used for thermoelectric power generation, the latter for thermoelectric cooling.

Thermoelectric performance is expressed by three factors: electrical conductivity, Seebeck coefficient, and power factor. The electrical conductivity increases when the concentration of main carriers is increased by the doping process. The Seebeck coefficient is a numerical value representing the change in potential according to a change in temperature. Since the *p*-type semiconductor indicates a positive value and the *n*-type semiconductor indicates a negative value, only the sign of the Seebeck coefficient can be a tool to confirm the type of the thermoelectric semiconductors.

Carbon nanotubes (CNTs) are used in thermoelectric generators for various

purposes due to their easy processability, low toxicity, and flexibility.<sup>3</sup> Since CNTs exhibit p-type semiconductor properties due to the moisture in the air,<sup>4</sup> various dopants are applied to control the electrical properties of CNTS to fabricate thermoelectric generation (TEG) which requires both p-type and n-type semiconductors.<sup>5</sup> Most dopants are synthetic compounds derived from fossil fuels. They are also not free from the environmental issues. Therefore, materials to replace the fossil fuel-based materials are needed.

Biopolymers are environmentally friendly polymers occurring in nature, such as cellulose, chitosan, and lignin.<sup>6</sup> The lignin is a secondary abundant biopolymer in nature containing abundant aromatic/ aliphatic hydroxyl groups. Since the low solubility of lignin has been hindered to utilize lignin, physical, chemical, and biological modification methods are widely accepted for the valorization of lignin.<sup>7</sup> One of them, the chemical modification is an effective method due to its freedom of design of the lignin structure through various syntheses. The abundant phenolic structure of lignin can serve as a precursor for various substitution and addition reactions in organic chemistry.<sup>8,9</sup>

In this study, an eco-friendly dopant to control the electrical properties of carbon nanotubes is reported by modifying the functional group of lignin. The chemical modification is conducted at organosolv lignin *via* microwave synthesis which is an eco-friendly synthesis method. The two different synthesized lignins acted as p-dopant and n-dopant, respectively. The modified lignin was brush-doped on the CNT films in the form of a solution, and p- and n-type CNT films were obtained. They were confirmed by the thermoelectric effect, especially the Seebeck coefficient. In order to demonstrate the performance of lignin dopants, TEGs

consisting of lignin-doped CNT films were fabricated. As the temperature differences occurred at both ends of the TEG, current flew by potential differences. The 20 PN pairs of CNT films constituted up a series circuit, showing that the lignin dopants stably change the electrical properties of the CNT films. These results demonstrated that lignin, an eco-friendly material, can replace the synthetic dopants for tuning the electrical properties of semiconductors along with eco-friendly energy harvesting.

## Chapter 2. Fundamental Background

### 2.1 Thermoelectric effect

The thermoelectric effect is the direct conversion of thermal energy between electrical energy in thermocouples.<sup>2</sup> The thermoelectric effect include the Peltier effect, the Seebeck effect, and the Thomson effect. The Peltier effect and the Seebeck effect are opposite expressions of the same physical concept, and the Thomson effect is an expanded concept of them.

The Peltier effect is when current flows at a thermocouple, heat is emitted at one junction and absorbed at the other, resulting in a temperature difference at both ends. It is expressed as the Peltier coefficient the amount of heat transferred per unit charge. (Equation 1)

$$\alpha = -\frac{\Delta V}{\Delta T}$$

Equation 1. Seebeck coefficient

In the contrast, the Seebeck effect occurs when a temperature difference generates between junctions of conductive materials, resulting in a potential difference due to the difference in internal energy and entropy of charge carriers in different conductive materials.

In Figure 2.1, electron diffusion occurs from the hot side to the cold side in an  $n$ -type semiconductor, where the main carrier is electrons, resulting in a drift current

in the opposite direction. Conversely, drift current generates in the same direction as diffusion in a  $p$ -type semiconductor where the main carrier is a hole. Figure 2.2 is a schematic diagram of a thermoelectric generator (TEG). When a pair of PN pairs are connected in series, if a temperature difference occurs between the electrodes at both ends, holes are formed in  $p$ -type and electrons are lower in  $n$ -type, respectively. As it diffuses along the temperature gradient, current flows in one direction.

The electrical conductivity of thermoelectric materials signifies how easily electric current flows through materials and is indicated by carrier concentration ( $n$ ), carrier mobility ( $\mu$ ), and electric charge ( $q$ ) (Equation 2).

$$\sigma = ne\mu$$

Equation 2. Electrical conductivity

Modification of carrier concentration to improve the electrical conductivity is important strategy for electronics and is called doping.

The performance index of a thermoelectric material is expressed as a figure of merit ( $zT$ ) consisted of electrical conductivity, Seebeck coefficient, and the thermal conductivity. (Equation 3)

$$zT = \frac{\alpha^2 \sigma}{\kappa_t} T$$

Equation 3. Figure of Merit ( $zT$ )

Another expression for the Seebeck coefficient along with the carrier

concentration is given in Equation 4.

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

Equation 4. Seebeck coefficient

Comparing electrical conductivity equation with the Seebeck coefficient equation, there is an inverse relationship with the carrier concentration. As the carrier concentration increases, the electrical conductivity increases but the Seebeck coefficient decreases. A figure of merit ( $zT$ ) includes both of the electrical conductivity and Seebeck coefficient at numerator part with the interdependence relation. The thermal conductivity is also affected by the carrier concentration as it expresses electronic thermal conductivity ( $k_e$ ) included electrical conductivity. (Equation 5)

$$\kappa_t = \kappa_e + \kappa_l$$

Equation 5. Thermal conductivity

In addition, the other part of thermal conductivity, lattice thermal conductivity ( $k_l$ ) is an inherent property of a material. In conclusion, the figure of merit ( $zT$ ) is closely related to the carrier concentration and has a maximum point at a certain point.

One of the effective applications of the thermoelectric effect is a tool for determining the type of semiconductor. Generally, the type of semiconductor is identified by using Hall measurements to verify the type of main carriers. However, it is difficult to use the Hall measurements in CNTs from the amorphous structure.

The thermoelectric effect may be used as a simple method for checking the type of semiconductors. Equation 6 represents the formula of the Seebeck coefficient related to fermi energy indicating the type of semiconductor materials.

$$S = -\left(\frac{E_J - E_F}{qT}\right)$$

Equation 6. Seebeck coefficient expressed as fermi energy

The average energy at current flow ( $E_J$ ) of  $p$ -type semiconductors has lower energy than fermi energy ( $E_F$ ) then, Seebeck coefficient has a positive value. The  $n$ -type semiconductors have higher  $E_J$  than  $E_F$ , and the Seebeck coefficient indicates a negative value.



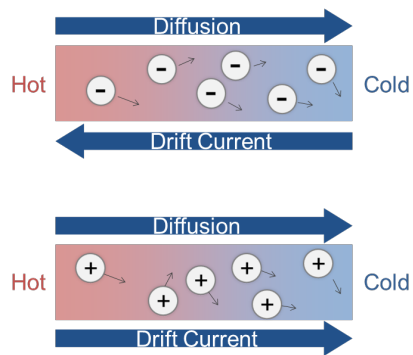


Figure 2.1. Carrier diffusion and drift currents from thermal gradients

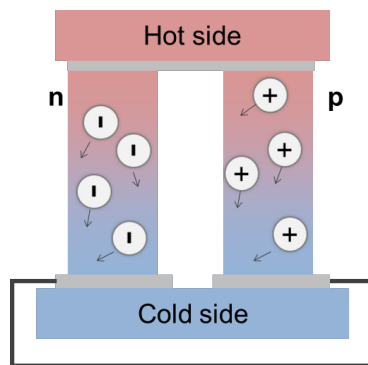


Figure 2.2 Illustration of carrier movement in a thermoelectric generator (TEG)

## 2.2 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are one of the allotropes of carbon, showing excellent electrical, thermal, and mechanical properties. They are a cylindrical nanostructure in which plate-shaped graphene is rolled. The chemical bonding of CNTs is similar to graphene in that carbon atoms form a hexagonal honeycomb structure by covalent bonds. The carbon atoms are  $sp^2$  hybridized and the other pi electrons are perpendicularly conjugated to the surface.<sup>10</sup> These conjugated-pi electrons give high electrical conductivity, and mechanical properties which are unique characteristics of CNTs.

The electrical properties of CNTs are depending on the degree of rolling of plate-shaped graphene which is notated by the roll-up vector. In single-walled carbon nanotubes (SWCNTs), a set of (n,m) indices determines the size and the angle of the roll-up vector as shown in Figure 2.3. When n-m is a multiple of 3, it represents the electrical properties of a metal, but if it is not a multiple of 3, it represents the property of the semiconductor. The roll-up vector represents the electrical properties of SWCNTs decided by their diameter and chirality. In addition, there are double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotube (MWCNTs) depending on the number of walls of CNTs possessing different electrical, thermal, and mechanical properties.

SWCNTs and DWCNTs are used as the thermoelectric materials due to their good Seebeck coefficient and high electrical conductivity. As inorganic materials have been widely used before, their disadvantages of high cost, toxicity, and brittleness, have made limitation of application. In addition, research on thermoelectric

materials based on organic materials shows good flexibility but the low thermoelectric performance. As CNTs possess the advantage of good thermoelectric performance and flexibility as well as mechanical strength, research to improve the thermoelectric performance has been conducting.

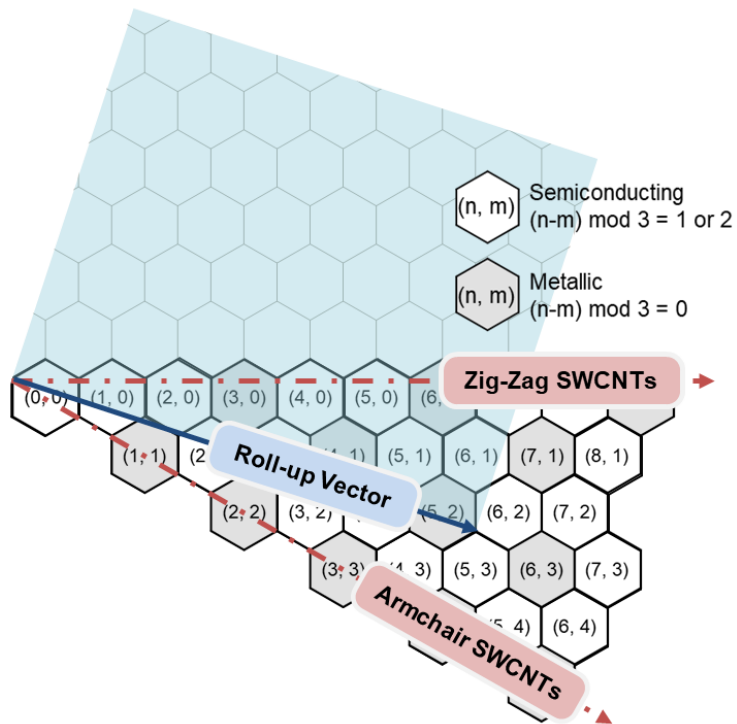


Figure 2.3 Chiral indices  $(n, m)$  and roll-up vector in graphene

## 2.3 Charge-transfer doping

The doping of semiconductors is the key process for electronic devices by manipulating their carrier concentration and electrical conductivity.<sup>11</sup> The doping method includes heteroatom doping, which is a method of directly adding a heterogeneous element to a host material through CVD (Chemical Vapor Deposition) or plasma treatment, and charge-transfer doping in which electron charges are transferred between dopants and hosts. The charge-transfer doping is an important strategy widely used in organic semiconductors and carbon-based semiconductors. It is suitable to tune the electrical properties of those materials from a simple process only putting the dopant in the form of a solution, making less damage to the host material.<sup>12</sup>

In Figure 2.4, the charge-transfer doping process is expressed in a simple schematic diagram. During  $n$ -doping process, electrons transfer from the dopant to the host material, increasing the fermi energy of the host material. Since the dopants contain high electron density, more electrons are provided to the host, shifting the fermi energy closer to the conductive bands. Conversely, electrons transfer from the host material to the dopant material at  $p$ -doping proceeds. The electron density of the host material is reduced, and the fermi energy of host is closer to the valance band. Therefore, the more electron-withdrawing groups (EWGs) contained in the dopant, the stronger shifting the fermi energy.

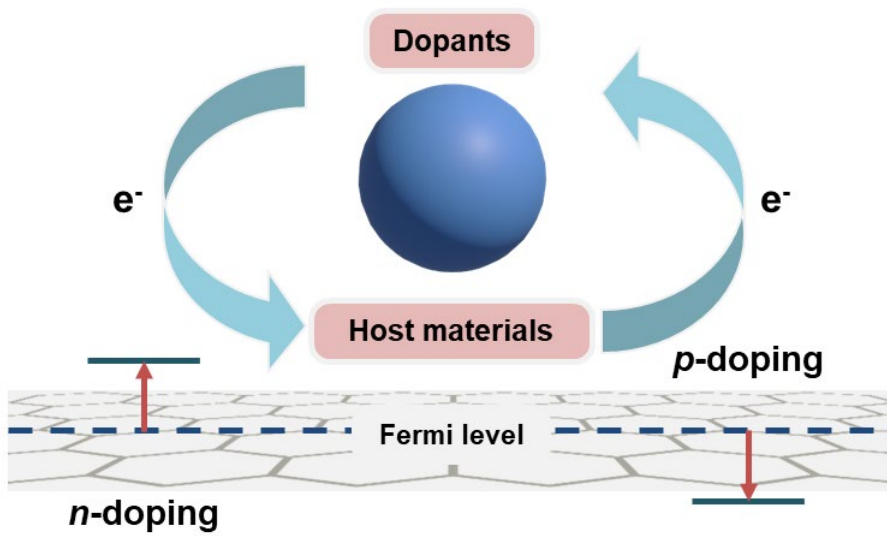


Figure 2.4 Schematic illustration of charge-transfer doping process

## 2.4 Lignin

Lignin is the secondly most abundant biopolymers after cellulose. Mostly, about 50 to 70 million tons of lignin are obtained per year as a by-product of wood biomass or pulp production, but only 2% of this is used for industrial purposes and the rest is incinerated as low-efficiency fuel and discarded.<sup>13</sup> This low industrialization are caused by low solubility of lignin in organic solvents, low purity, and limited structure. To address this issue, some approaches have been considered: (1) physical treatments such as milling, sonication, and extrusion (2) chemical modification to apply various chemicals for handling the chemical bonding (3) biological methods to deform the lignin structure using fungi, enzyme, bacteria and so on.<sup>7</sup> In particular, the chemical modification of lignin is one of the important strategies of lignin-valorization, which has the potential to synthesize the high-purity lignin we needed. Since the lignin included lots of phenolic structures, they have a role in precursors through chemical reactions such as phenolation, amination, nitration, sulfonation.<sup>9</sup> Modified lignin is not only accepted in polymer synthesis, but also in various applications from carbon materials, biofuels, nanomaterials, to energy storage as polymer did.<sup>14</sup>

## 2.5 Previous researches on lignin-based dopants

One research reported that lignin can act as  $p$ -dopant. Mario *et al.* make a report about lignin dopant on carbon nanotube yarns (CNTYs) increasing the electrical conductivity and the Seebeck coefficient.<sup>15</sup> They suggest that thermoelectric materials easily modified using lignin for changing electrical properties. However, none of the studied have been reported using lignin as an  $n$ -type dopant.



## 2.6 Objective

We studied to control the thermoelectric properties of carbon nanotubes by modifying lignin to act as *p*-type and *n*-type dopants through chemical structural changes. (Figure 2.5) Lignin was synthesized to phenolation and amination through microwave-assisted heating method. It is a promising green process that saves in energy and time by instantaneous heating using microwave. Also, it can heat up the reactant homogeneously and only the microwave-sensitive parts be selectively heated with reducing the byproduct. The modified lignins are applied as the organic dopants for charge-transfer doping at the CNTs. They are dissolved in THF solvent and brush-casted at the DWCNT surface in the form of a solution. The doped DWCNT films were characterized by the thermoelectric effect.

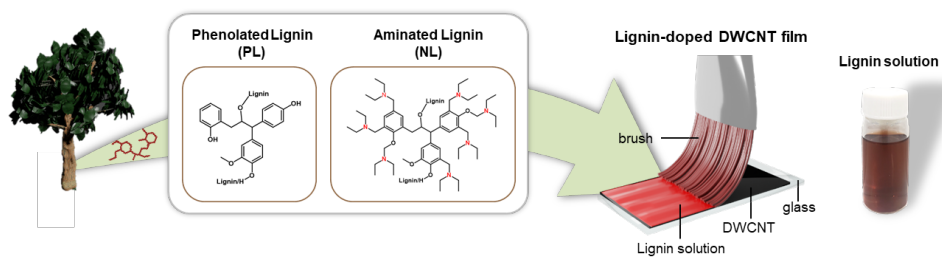


Figure 2.5 Nature-derived polymer for tuning the thermoelectric properties of DWCNT by modifying the lignin structure.

## **Chapter 3. Experiments**

### **3.1 Materials**

#### **3.1.1. Synthesis of phenolated lignin (PL)**

PL was synthesized from organosolv lignin by the phenolation. (Figure 3.1) The phenolation of organosolv lignin was conducted in a 15 mL pressure tube (Ace glass) and heated using a CEM Discover Microwave Synthesizer (power = 150 W, frequency = 2.5 GHz). The 0.15 g H<sub>2</sub>SO<sub>4</sub> catalyst, 2 g of melted phenol, and 1 g of lignin were added to the 15 mL pressure tube, and the reaction was allowed to proceed at 100 °C for 20 min. After completion of the reaction, the product was collected using methanol (15 mL), and recovered by precipitation with acidic water (pH = 1, adjusted using H<sub>2</sub>SO<sub>4</sub>), followed by filtration and washing with deionized (DI) water until the pH of the filtrate became neutral. The precipitate was then dried in a vacuum oven at 50 °C overnight.

### **3.1.2. Synthesis of aminated lignin (NL)**

Aminated lignin (NL) was synthesized by PL with diethylamine. (Figure 3.2) Amination of PL was conducted in a 15 mL pressure tube. It was conducted by 1 g of phenolated lignin, 1 g of diethylamine, 1 g HCHO 30 wt%, 0.2 g acetic acid as catalyst. Those were dissolved in 10 mL dioxane and allowed to react at 60 °C for 1 h. The unreacted reagent and solvent were removed by using rotary evaporation system. The solid was collected and then dried at 150 °C overnight under vacuum conditions. Then, the solid was ground followed by washing with DI water and dried again to remove any remaining impurities.

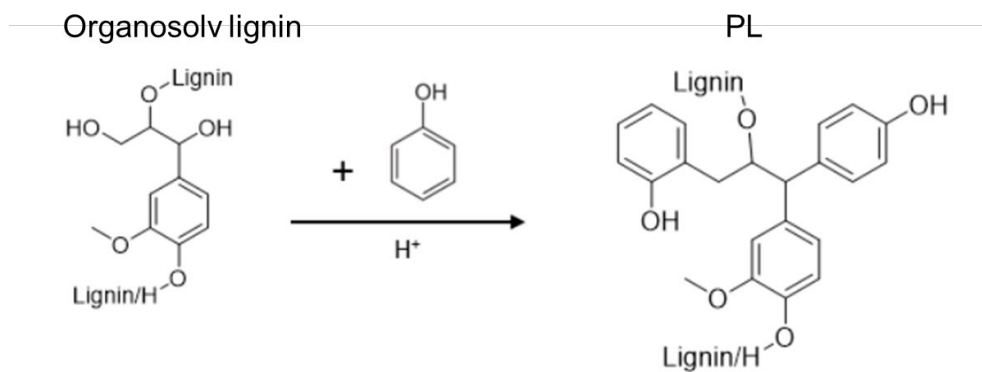


Figure 3.1. Synthesis of phenolated lignin (PL)

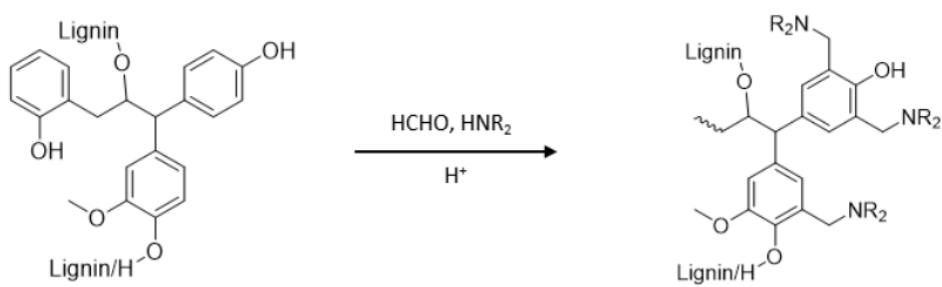


Figure 3.2. Synthesis of aminated lignin (NL)

### **3.1.3. Preparation of lignin solutions**

375 mg two types of lignin. PL and NL, were dissolved in 5 mL of anhydrous tetrahydrofuran (THF, anhydrous,  $\geq 99.9\%$ , inhibitor-free, Sigma-Aldrich) each, making 75 mg/mL lignin solutions. The solutions were treated by bath sonication for 10 min. (Figure 3.3)

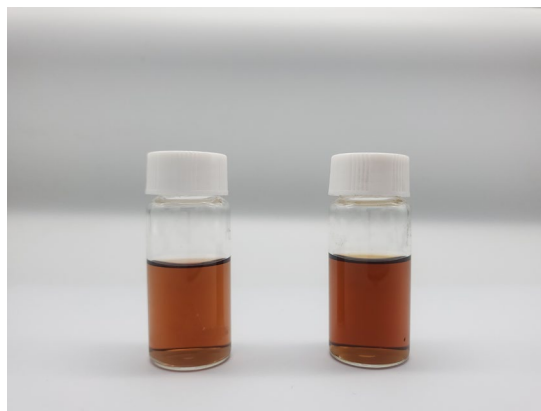


Figure 3.3. Lignin in THF solution: PL(left) and NL(right)

### **3.1.4. Preparation of free-standing DWCNT films**

50 mg of double-walled carbon nanotube (Nanoshel) was dispersed using the tip sonicator for 1h (VCX-750, 750 Watts Ultrasonic Processor) with 50 mL ethanol. The DWCNT dispersion was piled on the PVDF membrane during vacuum filtration, followed by drying at 100 °C for 2 days under the vacuum conditions.



### **3.2. Fabrication of lignin-doped DWCNT films**

The free-standing DWCNT films were prepared to cut into the 2 cm × 1 cm on the glasses. Two different brushes for *p*- and *n*-type dopants were dripping at the lignin solution and brushed softly on DWCNT films. The wetted DWCNT films were dried at the 40 °C on the hot plate for 5 min, which process was repeated twice. The third-doping process was conducted at the same method, except drying at 70 °C which is higher temperature than boiling point of THF. (Figure 3.4)

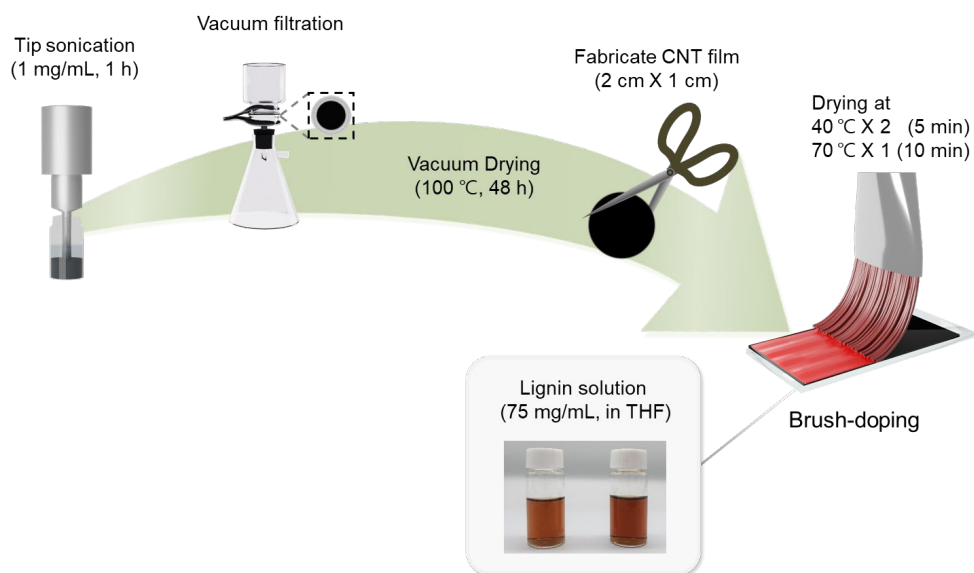


Figure 3.4. Fabrication process of lignin-doped DWCNT films

### 3.3. Analysis

X-ray photoelectron spectroscopy (XPS) was conducted to analyze the types of chemical bonds of C1s, N1s, O1s and their contents in materials. (XPS, ThermoFisher, K-Alpha X-ray Photoelectron Spectrometer) The surface morphology of lignin-doped DWCNT films was characterized by scanning electron microscopy (SEM, Sigma 300, ZEISS). Also, selective mapping of specific elements in the sample was characterized by energy dispersive x-ray spectroscopy analysis (EDS, BRUKER, XFlash 6|60). TGA analysis was performed to observe the change in weight caused by chemical and physical changes of the sample according to time and temperature. (Q50, TA instruments) The content of lignin contained in the doped film was calculated by comparing the reduced weight. The electrical conductivity was calculated with Semi-auto Rs/Res measurement system (CRESSBOX, NAPSON Co.) A thickness of films is measured using micrometer. The Seebeck coefficient was measured using four-point probe system. (TEP 600, Seepel instrument) A temperature difference was provided using a Peltier device above and below the thermoelectric device, and the voltage, current, and resistance at each point was measured by tracking the temperature difference in real time.

## Chapter 4. Results and Discussions

### 4.1. Characterization of modified lignin

Phenolation and amination were performed through microwave-assisted synthesis, in which the reaction was carried out by heating with microwave irradiation at Organosolv lignin. Microwave-assisted synthesis is a promising green process that selectively applies energy to react only a desired material, so it produces almost no by-products and is environmentally friendly as it is a dry process. It has the advantage of being able to homogeneously heated in a short time, resulting in saving times and energy.

For the quantification of the phenolation and amination, the X-ray photo-emission spectroscopy (XPS) analysis was performed. (Figure 4.1) The XPS survey spectra of NL show an additional peak near 400 eV representing N(1s). PL and NL have a distinct difference in the  $\sigma$  bond at C that appear as the additional peak at 288.7 eV in the C(1s) graph, which exhibits a C-N bond at the linkage between the amine and PL. This is represented that amine is connected to the lignin backbone after amination. The other two peaks commonly contained at both PL and NL arose from the benzene and aliphatic C bonds (C-C, C=C); and C-O bonds of hydroxyl and ether. The former peaks are from the monatomic carbon bonds (C-C, C=C) at 285.7 eV and 285.3 eV. The latter peaks are from the oxygen-containing bonds (C-O), consisting of hydroxyl and ether groups, at 287.2 eV and 286.2 eV of PL and NL, respectively. The formation of the C-N bond by amination was represented by the existence of the N-C bond at 401.3 eV in the N(1s) graph. O(1s) graphs about PL

and NL showed a similar shape. The XPS graph illustrated that PL did not include any nitrogen inside, and amination was successfully added to the formation of C-N bonding.

The amount of nitrogen which performs to electron donating part is important information thereby quantitative analysis, CHNS combustion analysis, was performed. (Figure 4.2) When comparing PL and NL, it was confirmed that about 7% of nitrogen was newly contained after the amination process.

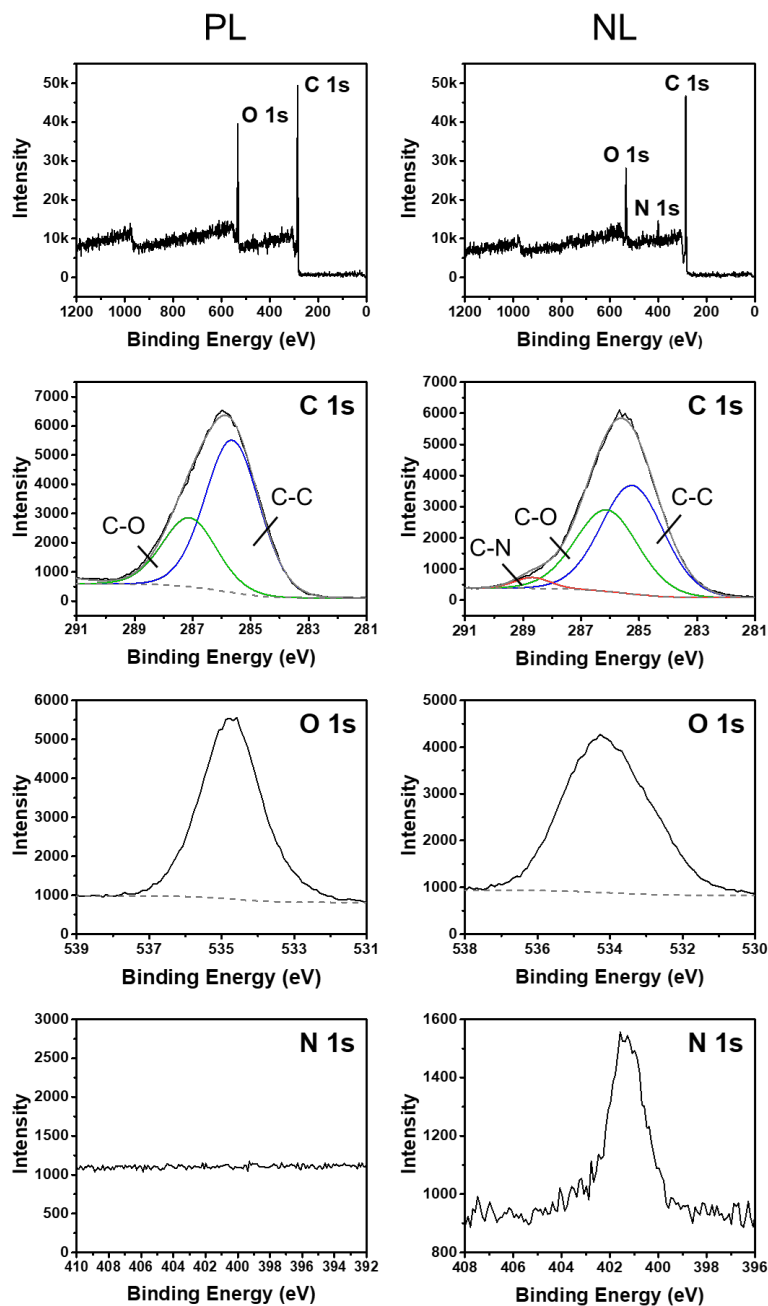


Figure 4.1. XPS spectra of PL and NL: survey scan, and C(1s), O(1s), and N(1s)

peaks

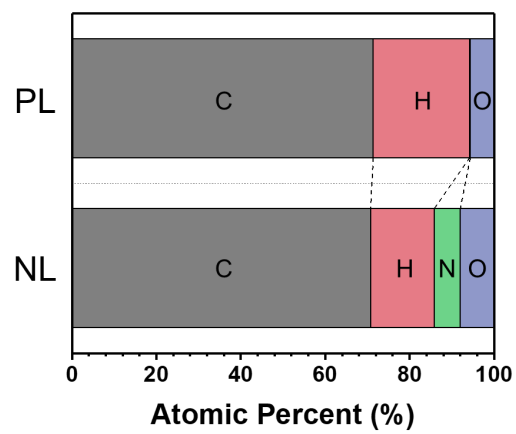


Figure 4.2. CHNS analysis of PL and NL

## **4.2. Morphology of lignin-doped DWCNT films**

SEM images were obtained to observe the morphology of the pristine DWCNT film and the NL-doped DWCNT film (NLCNT). The images of DWCNTs show that after the doping process, a thin layer of the polymer film is formed on the DWCNT strands. In addition, the EDS image for N composed of amines in NL is indicated by yellow dots, indicating uniform doping through uniform tracking along the film (Figure 4.3). It can be confirmed that lignin is not lost even after doping and adheres well to the DWCNT strand.



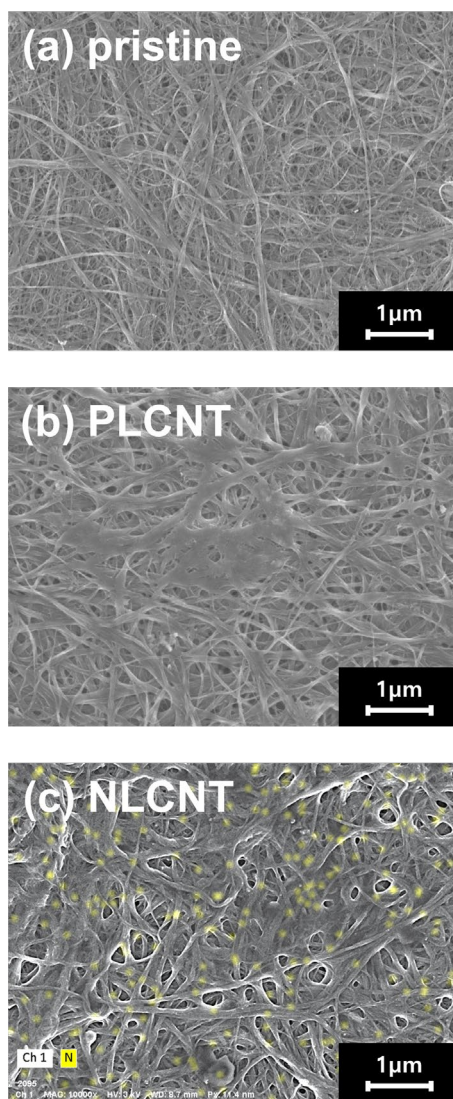


Figure 4.3. SEM and EDS images of (a) pristine DWCNT, (b)PLCNT and (c)NLCNT

### **4.3. TGA analysis of lignin-doped DWCNT films**

TGA analysis was performed for quantitative analysis of the amount of lignin inside the doped DWCNT films. (Figure 4.4) PL doped DWCNT films (PLCNT), NL doped DWCNT films (NLCNT), and pristine DWCNT films remained the residual weights of 67.1 wt%, 62.4 wt%, and 80.6 wt%, respectively. Therefore, PLCNT included almost 14.4 wt% of PL as well as NLCNT and the NLCNT did 11.4 wt%. When compared with the PL and NL graphs indicated by dotted lines, it can be confirmed that the sudden change in the slope at 200 °C is caused by the thermal decomposition of lignin. It can be seen that the change in the slope of PLCNT is larger than that of NLCNT near 350 °C because the change in slope of PL is larger than that of NL. Therefore, it can be seen that the difference in the residual weight of CNT, PLCNT, and NLCNT at 700 °C is caused by the thermal decomposition of PL and NL.

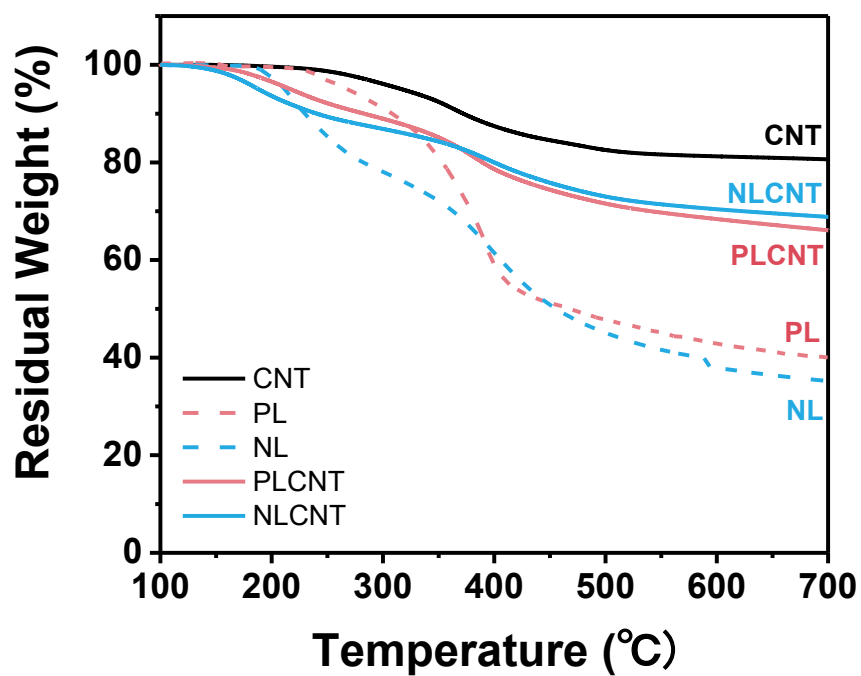


Figure 4.4. TGA analysis of pristine CNT, PL, NL, PLCNT, and NLCNT

#### 4.4. Thermoelectric properties of lignin-doped DWCNT

Thermoelectric (TE) properties were used to study the electrical properties of lignin dopants (Figure 4.5). Three thermoelectric properties are used to define the performance of a TE: conductivity, Seebeck coefficient, and power factor. Among them, the Seebeck coefficient indicates the type of semiconductor through a positive sign in *p*-type and a negative sign in *n*-type, respectively. The conductivities of PL and NL increased until the concentration of the lignin solution reached 75 mg/mL, a value of 347.2 S/cm and 246.0 S/cm, respectively, and then decreased with both types of dopants. The graph indicates that the conductivity decreases by overdoping of lignin after progressive doping of DWCNTs with concentrations of carriers such as holes and electrons from the maximum to 75 mg/mL. Meanwhile, the Seebeck coefficient of PLCNTs started at a positive value of 53.5  $\mu\text{V/K}$  and peaked at 75 mg/mL, whereas NLCNTs showed -48.0  $\mu\text{V/K}$ . The Seebeck coefficient of PLCNT showed an almost constant value through the doping process, whereas the Seebeck coefficient of NLCNT was completely converted to a negative value. The power factor indicates the performance of the lignin-doped DWCNT film. The maximum value of the power factor of PLCNTs is 111.2  $\mu\text{W/K}^2\text{m}$ , which is a 130% improvement in performance compared to raw DWCNTs, and 58.2  $\mu\text{W/K}^2\text{m}$  in NLCNTs. According to the thermoelectric properties, PLCNTs consistently have *p*-type semiconductor properties and much higher electrical conductivity, which contributes to the successful conversion of NLCNTs to *n*-type semiconductors.

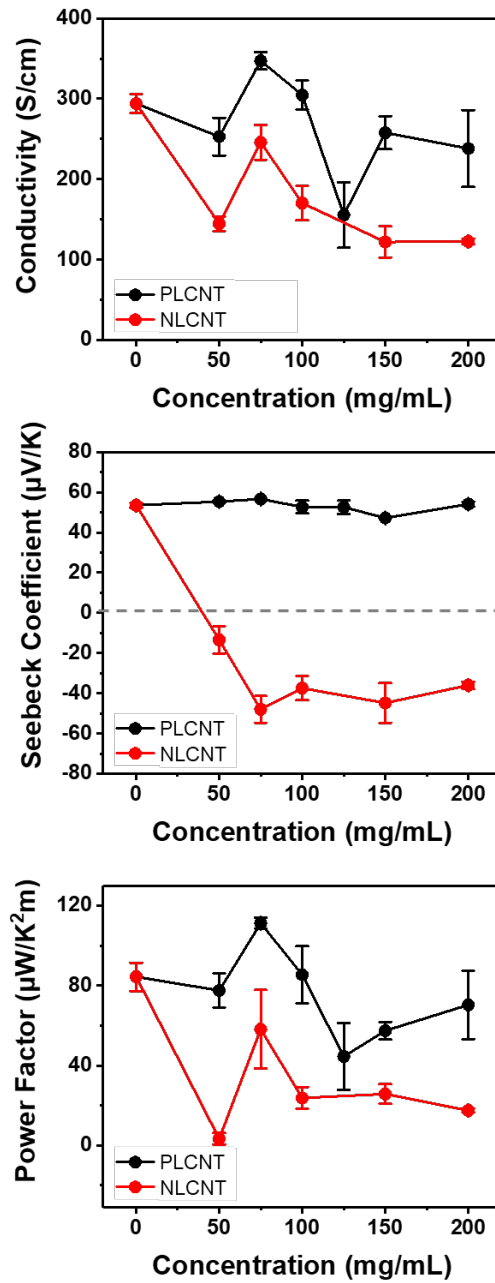


Figure 4.5. Thermoelectric properties of PLCNT and NLCNT

#### **4.5. Comparison of performance with other organic dopants**

The performance of a dopant showing high performance among commonly used synthetic polymer dopants and synthetic organic dopants and lignin, an eco-friendly polymer dopant, was compared. PL showed almost similar or better performance compared to 4-hydroxycarbazole and 7,7,8,8-Tetracyanoquinodimethane (TCNQ). (Figure 4.6) NL showed almost similar values when compared to polyethylenimine (PEI) and 1,3-Bis(diphenylphosphino)propane (dppp). (Figure 4.7) This result shows that the dopant used only as a synthetic chemical can have sufficiently similar or better performance using an eco-friendly dopant.

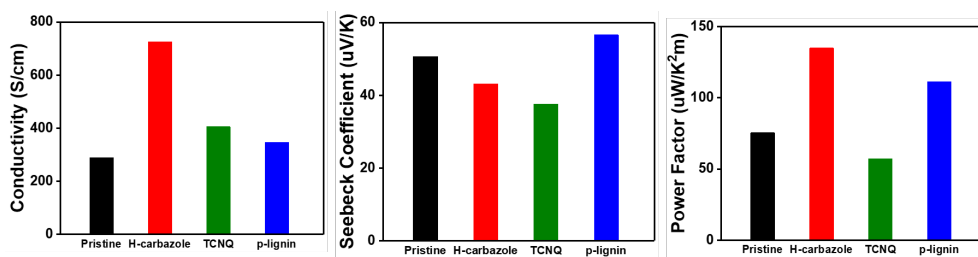


Figure 4.6. Comparison of thermoelectric performance of *p*-type dopants with PL

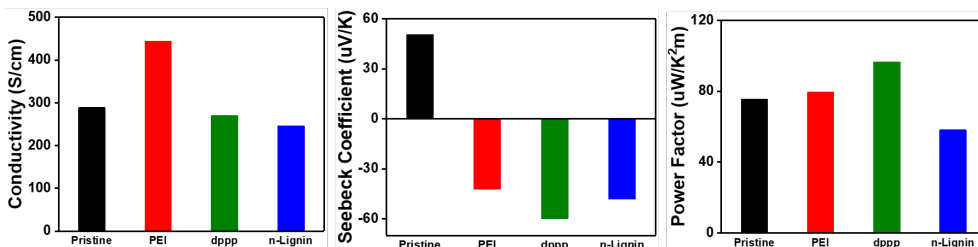


Figure 4.7. Comparison of thermoelectric performance of *n*-type dopants with NL

## 4.6. UPS analysis of lignin-doped DWCNT

To check the energy level difference through the doping process, the work function was measured using UPS (Ultraviolet photoelectron spectroscopy). Figure 4.8 shows the changes in slope and work function of PLCNTs, NLCNTs and, pristine DWCNT. More detailed data are in Table 4.1, the work function of PLCNTs increased by 0.05 eV compared to pristine DWCNTs, which is a result of increasing the concentration of charge carriers through charge transfer doping with PL. In contrast, the work function between NLCNTs and pristine DWCNTs decreased by 0.55 eV from 4.55 eV to 4.00 eV. The significant change in work function between NLCNTs and pristine DWCNTs may not be direct evidence of *p*- and *n*-type characters, however, the Seebeck coefficients for NLCNTs should be used to indicate the conversion of carrier types. According to the thermoelectric properties and UPS graph, PL by phenolation to induce phenol in lignin can certainly act as a *p*-type dopant, and similarly, NL by amination acts as an *n*-type dopant.



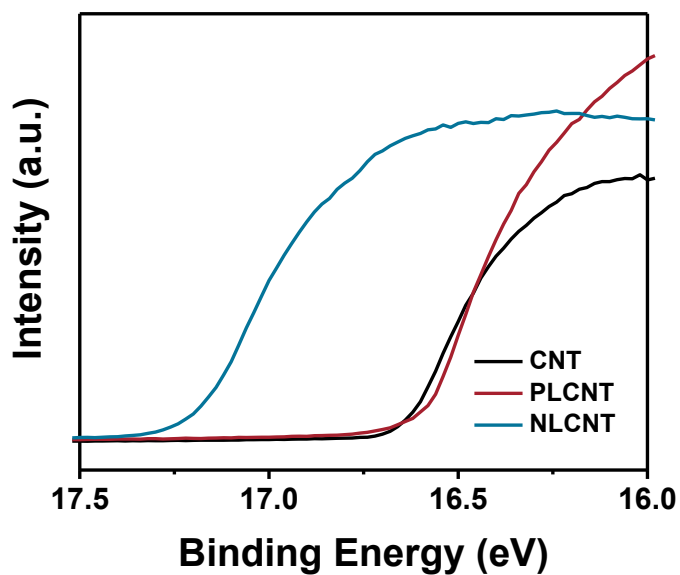


Figure 4.8. UPS spectra of DWCNT, PLCNT, and NLCNT

Sample	h $\nu$ (eV)	cut off	E <sub>F</sub>	Work func.
DWCNT	21.20	16.65	0	4.55
PLCNT	21.20	16.60	0	4.60
NLCNT	21.20	17.20	0	4.00

Table 4.1 UPS data of DWCNT, PLCNT, and NLCNT

## 4.7. Doping mechanism

A schematic diagram of the doping process is shown in Figure 4.9. For easy representation. Schematic diagram of the charge-transfer doping process of PLCNTs and NLCNTs. For PLCNTs, the H of the hydroxyl group attached to the aromatic ring acts as an electron-withdrawing group (EWG), driving force of charge-transfer from the DWCNT to the PL. Aromatic H has higher acidity than aliphatic H, resulting in a higher partial positive charge on H. NLCNTs act as electron-donating groups (EDGs) by lone pair electrons contained in nitrogen atoms of NL. Therefore, occurring charge-transfer from NL to DWCNT is *n*-doping.

To determine whether this doping is due to the backbone of lignin or functional groups contained in lignin, the thermoelectric effect of organosolv lignin without phenolation, PL, which is phenolated lignin, and phenol was respectively compared. (Figure 4.10) Phenol showed a high doping effect by itself but resulted in a decrease in the Seebeck coefficient. In the case of organosolv lignin, the addition of a non-conductive polymer decreased the carrier concentration, resulting in a decrease in electrical conductivity and an increase in the Seebeck coefficient. In PL, both of these results occurred and the electrical conductivity increased due to doping, but the Seebeck coefficient did not decrease and the power factor increased.

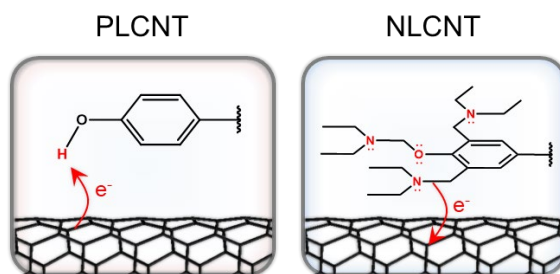


Figure 4.9. Schematic illustration of charge-transfer doping process of PLCNT and NLCNT

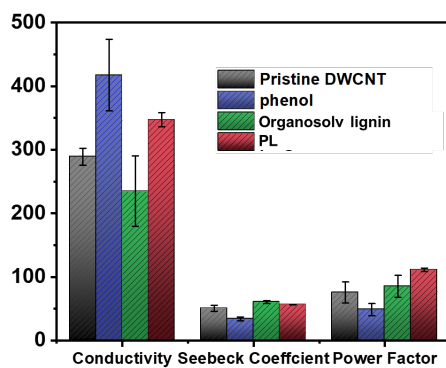


Figure 4.10. Thermoelectric properties of DWCNT, phenol, organosolv lignin, and PL

#### 4.8. Performance of thermoelectric device

Doping of two types of lignin-doped DWCNT films, *p*- and *n*-, was successfully carried out, and thermoelectric devices were fabricated to check whether the thermoelectric material was functioning normally. In the thermoelectric element, 20 PN pairs are connected in series and each is connected with an aluminum electrode. (Figure 4.11) A single circuit was formed by connecting the electrode and the film with silver paste. When a temperature difference is applied to the top and bottom of the device, the main carrier is spread from the bottom to the top, and a potential difference occurs at both ends, which causes the current to flow in one direction. Figure 4.12 shows the output voltage generated by TEG. The output power at  $\Delta T = 30$  K was  $1.2 \mu\text{W}$ , which was about 30% of the calculated voltage. The calculated voltage was calculated as in Equation 7 using the values of PLCNT and NLCNT measured in the form of films.

$$V = n(|S_p| + |S_n|)\Delta T$$

Equation 7. Output voltage formula related with Seebeck coefficient

The low power generation is caused by the long vertical distance between the Peltier device that changes the temperature differences and lignin-based TEG. Heat received from the Peltier device was dissipating in the air making few temperature differences we intended. Also, the voltage differences were decreased as the contact resistance between the device and the electrode occurred.

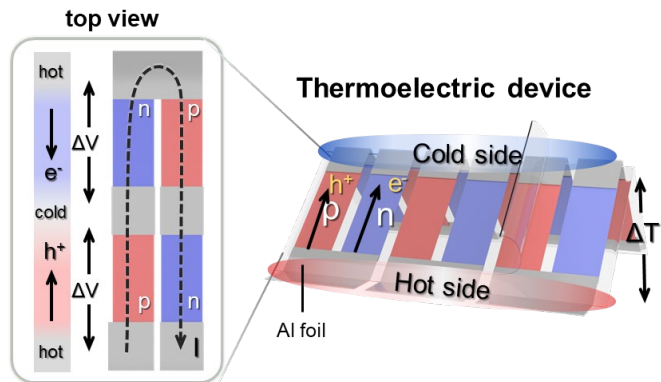


Figure 4.11 A TEG made from *p*-type and *n*-type DWCNT films

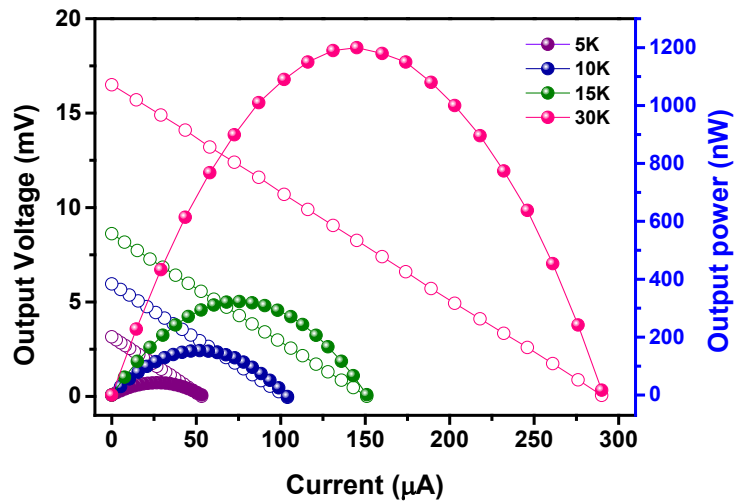


Figure 4.12. Output power measurement of the TEG

## Chapter 5. Conclusion

In summary, we proposed eco-friendly biopolymer-based dopants obtained by modifying the functional groups of lignin which is a biopolymer *via* the green process. As many dopants applied in the industry are synthetic compounds based on fossil fuels, they cannot be freed from various environmental issues. Therefore, dopants should be replaced with eco-friendly materials for a real green process. Lignin is the second most abundant natural polymer including many phenolic parts, easy to change by chemical modification. In this work, the functional groups of organosolv lignin were modified through phenolation and amination. The two types of modified lignin were dissolved in solution and acted as the dopant by transferring electrons between dopants and DWCNT, called charge-transfer doping. The doping performance was characterized by the thermoelectric effect that was clearly notified by the Seebeck coefficient and electrical conductivity. Also, the shifting of the fermi energy is detected in UPS analysis, in which PL tuning the fermi energy increased indicating *p*-doping and NL represented *n*-doping by decreasing the fermi energy. In addition, the thermoelectric device was fabricated to demonstrate whether the lignin dopants were well applied and operated. In this work, the organic dopants from biopolymer prove that the use of fossil fuels can be reduced by replacing the synthetic compounds to perform as *n*-dopant successfully. It presents the important frontier of a new application method for natural-based polymer for electronic usage.

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## 국문 요약

지속적인 화석연료의 사용은 여러 환경문제를 일으키고 있다. 열전 발전은 버려지는 폐열을 이용한 친환경 발전 방법으로 강조되어 오고 있다. 열전 발전을 위해서는 *p*-타입과 *n*-타입의 반도체가 모두 필요한데, 기존에 사용되던 도펀트는 모두 화석연료 기반으로 합성된 chemical 이기 때문에 친환경 generator를 위해서는 이러한 합성 고분자 역시 대체 되어야 한다. Biopolymer 중 하나인 리그닌은 여러 공정의 부산물로서 손쉽게 얻을 수 있을 뿐 아니라 다양한 화학반응의 precursor가 될 수 있는 페놀 구조를 포함하고 있기 때문에 분자의 구조를 원하는 대로 변형 할 수 있다는 장점이 있다. 따라서 본 연구에서는 리그닌을 이용하여 친환경 과정인 microwave-assisted synthesis 을 통해 charge-transfer doping 으로 CNT에 도펀트로 사용될 수 있는 친환경 고분자 도펀트를 제시하였다. 리그닌의 작용기를 변화하여 electron-withdrawing groups (EWGs) 인 페놀을 첨가함으로써 *p*-dopant로 사용하였고, electron-donating groups (EDGs) 인 다이에틸 아민을 첨가하여 *n*-dopant 로 사용하였다. 리그닌으로 도핑 된 carbon nanotubes (CNTs) 의 열전 성능은 기존에 사용되던 합성 도펀트와 거의 비슷하거나 더 나은 수치를 보였다. 또한 UPS 를 통해 일함수를 분석하였을 때 페르미 레벨의 변화를 직접 관찰할 수 있었고, 이는 리그닌이 도펀트로 잘 역할을 하였다는 것을

보여준다. 최종적으로 리그닌과 CNT만을 이용하여 조립된 열전 발전기는 자연친화적인 열전발전기를 제작할 수 있다는 가능성을 보여주었다.

주요 어: 친환경, 열전, 탄소나노튜브, 리그닌, 도펀트

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