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공학석사학위논문

**Stretchable Electrode based on Laterally-  
Combed Vertical Carbon Nanotubes for  
Energy Devices**

에너지 소자를 위한 측면으로 빗질된 수직 탄소  
나노 튜브 기반의 늘어나는 전극

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이 논문을 공학석사학위논문으로 제출함

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## **Abstract**

# **Stretchable Electrode based on Laterally-Combed Vertical Carbon Nanotubes for Energy Devices**

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Electrical power supply to the mobile electronics in general requires a physical connection to the external power sources through a long wire, which causes inconvenience to the users. As the mobile electronics have been miniaturized, their lightweight, thinness, flexibility, and stretchability became the key issues in developing the wearable and epidermal electronic devices. Consequently, their autonomous power generation and storage devices are also necessary to be light, thin, and deformable. In this study, vertically-aligned carbon nanotubes were used to fabricate the stretchable electrodes for triboelectric generator which harvest electrical energy from the human body motion, energy storage devices including supercapacitor and lithium ion battery, and wireless power transmission coil.

Vertically-aligned carbon nanotubes synthesized on the silicon wafer were partially interfused by polydimethylsiloxane ink-jet-printed on it and peeled off to be the stretchable electrode in the desired shape. Then, its electrical conductivity and percolation effect were improved by combing the air-exposed carbon nanotubes to be laterally-aligned and electroplating its surface with nickel metal. As the interconnection between other devices, the electrode could be printed in the serpentine pattern to reduce the uniaxial strain stress while stretched. The pattern in microscale could be realized by using photolithography on the catalyst layer for carbon nanotubes. As the electrode for triboelectric generator, supercapacitor and lithium ion battery, the large area was patterned to accomplish their high output power. The fabricated energy devices maintained their performance within 30% strain stretching, which realized the autonomous power generation and storage system for the wearable and epidermal electronics.

**Keywords: Stretchable electrodes, carbon nanotubes, triboelectric generator, supercapacitor, lithium ion battery.**

**Student number: 2013-23171**

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# 1. Introduction

As the deformable electronic devices have been actively researched for mobile and wearable applications, it is necessary to develop their power system which autonomously harvests and stores its electrical energy. In order to accomplish such power system, the development of flexible and stretchable electrode is required. As the result, many alternatives have been introduced such as conductive elastomeric films containing metals<sup>1,2</sup> or carbon nanomaterials<sup>3</sup>, conductive fabrics<sup>4</sup>, conductive polymer<sup>5</sup>, patterned graphene films<sup>6</sup>, and buckled carbon nanotube microfilms<sup>7</sup>. Carbon nanotubes (CNTs) were spotlighted as one of the promising electronic materials due to their fascinating properties: excellent electrical and thermal conductivity, superior mechanical properties such as strength and flexibility.<sup>8</sup> They have been studied world widely to be applied to various electronic devices including transistors<sup>9</sup> sensors<sup>10</sup>, batteries<sup>11</sup>, and supercapacitors<sup>12</sup>. Practically, CNT yarns<sup>13</sup>, randomly oriented CNT film<sup>14</sup>, and vertically-aligned CNT with polymer matrix<sup>15</sup> have been developed for the flexible energy devices as their electrodes, but they are not stretchable and have relatively low electrical conductivity compared to other metallic conductors and percolation issue. In this study, a noble method to fabricate vertical-CNT-based stretchable electrode for the energy harvesting device is introduced where the low conductivity of CNT was compensated by nickel electroplating on the laterally-combed structure of CNT forest whose microstructure tectonics restrains the rise of resistance upon the uniaxial strain.

To supply power to the mobile electronic devices, connecting a wire from the

conventional outlet would be inconvenient and restrictive to their wide applications. The ideal energy system rather generates electrical power from the naturally occurred mechanical, thermal, or solar energies. Electromagnetic induction generators, piezoelectric generators, and triboelectric generators (TEGs) are the possible options to harvest electrical energy from the human motions.<sup>16</sup> TEG utilizes mechanical friction between two different materials with different triboelectric series. As they repeatedly make a contact between their surfaces and detach from each other, electrons travels back and forth on their surfaces, and electrostatic induction generates electric current. Due to their simple and cost-effective fabrication process and material selection, their stretchable form could be achieved by applying the vertical-CNT-based stretchable electrode. Moreover, since human skin possesses relatively positive triboelectric series, it can easily interact with the single electrode triboelectric generator.<sup>17</sup>

For the energy storage device, recent researches on the stretchable batteries and supercapacitors have been realized using isolated battery cells with serpentine interconnections<sup>18</sup>, buckled Au-coated elastic substrate, stretchable silver fabric, micro-supercapacitors with liquid metal interconnects, and buckled carbon nanotube electrodes. The low energy density of such batteries and supercapacitors except for lithium ion batteries (LIBs) would provide insufficient energy for operating functional devices. Low loading of electrochemically-active materials and ineffective ion transporting channel in the stretchable LIB should be improved for fabricating practically applicable stretchable energy storage devices.

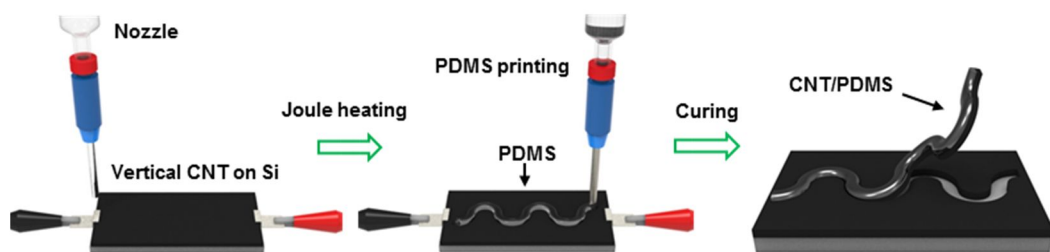
Discontinuous and insufficient power generation of TEG limit its application as the sole power source to the wearable electronics. Practically, the power generation from

TEG could postpone the discharging time of the storage devices.<sup>19</sup> Therefore, wireless power transmission is required to fully charge the storage devices, and the deformable wireless power transmission coil is realized by patterning the CNT forest. Successful integration of those deformable energy devices sharing the CNT-based stretchable electrode would realize the autonomous power system for wearable mobile electronics.

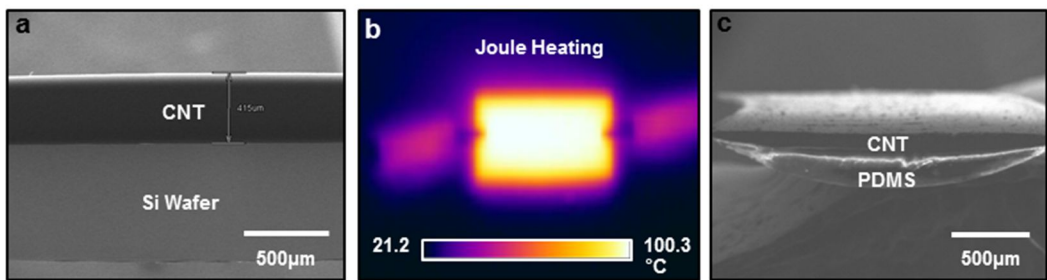
## **2. Stretchable electrode based on vertically-aligned carbon nanotubes**

### **2.1 PDMS inkjet printing on vertically-aligned CNT**

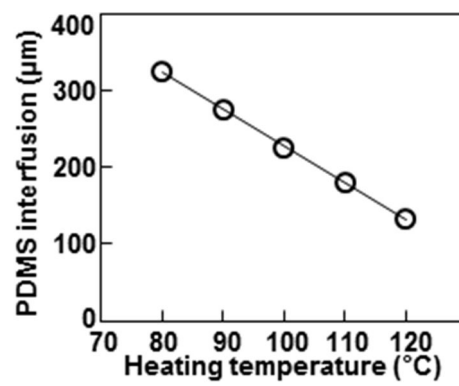
The chemical vapor deposition (CVD) synthesis of single-walled CNT was stimulated by introducing a trace amount of water vapor to the reactor.<sup>20</sup> This catalytic reaction unitizes ethylene gas and Fe nanoparticles as the precursor and catalyst, respectively. As described in Scheme 1, vertically-aligned CNT forest grown on silicon wafer generates heat by joule heating which stimulates polymerization of polydimethylsiloxane (PDMS) printed on it. It prevents the full submergence of CNT into the elastomer, so the air-exposed CNT remains its electrical conductivity after the pattern of CNT-PDMS composite is peeled off. The height of the CNT forest was measured from the cross sectional SEM image (Figure 1a), and the heating temperature was controlled by monitoring the infrared temperature camera (Figure 1b) and adjusting the applied voltage. Once the PDMS became fully solidified, it was peeled off with CNT embedded. As shown in Figure 1c, there is the air-exposed part of CNT on top of the elastomer. The height of the air-exposed CNT forest was subtracted from its original height to calculate the PDMS interfusion depth at different heating temperature, and its reversely proportional relationship is shown in Figure 2.



**Scheme 1. PDMS printing on joule-heated CNT and peeling off the CNT/PDMS electrode.**



**Figure 1. Optical images of the vertically-aligned CNT forest. (a) SEM image of the cross section of vertical CNT on Si wafer. (b) IR camera image while joule heating CNT forest. (c) SEM image of the cross section of peeled-off CNT/PDMS electrode.**

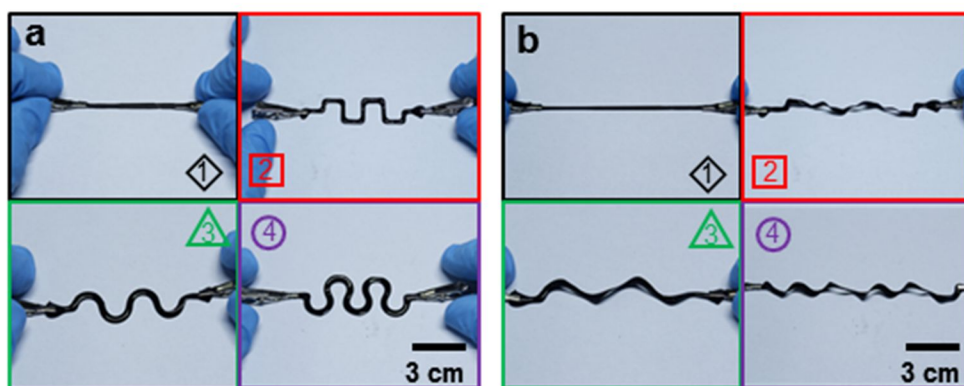


**Figure 2. PDMS interfusion depth into CNT forest depending on the joule-heating temperature.**



## 2.2 Serpentine effect of the printing designs

In Figure 3a, different designs of PDMS/CNT electrodes were patterned using inkjet printer. Design 1 is a simple line pattern, and design 2 is a Peano curve. Design 3 and 4 replace the sharp bends of the curve with arc sections with  $180^\circ$  and  $270^\circ$ , respectively. Figure 3b shows the deformation of each electrode at 100% strain stretching. Those fractal designs of space-filling structures enhance the stretching performance of electronic materials. As the serpentine pattern reduces the strain on the CNT array, the resistance retention was improved within 100% strain stretching (Figure 4a). According to Figure 4b, as the electrode (design number 4) was stretched to 100% strain and released back,  $R/R_0$  kept increased up to 110% in the rearrangement region. After 100 stretching cycles, the resistance retention became stabilized.



**Figure 3. Photographs of 4 different designs of CNT/PDMS electrodes with (a) 0% strain and (b) 100% strain stretching.**

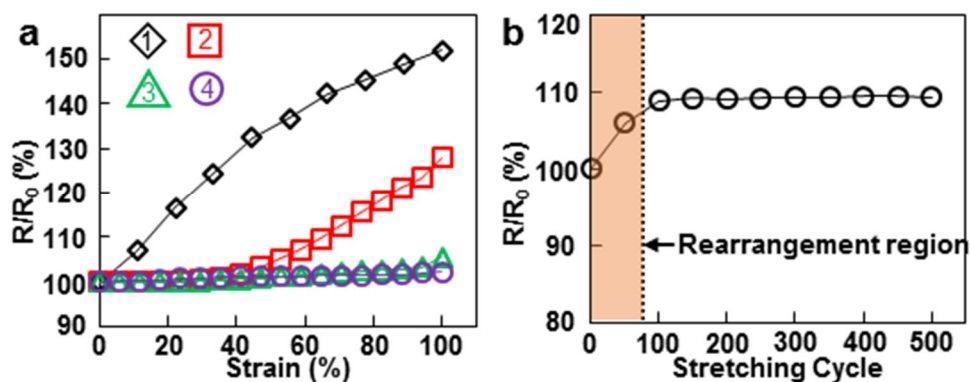
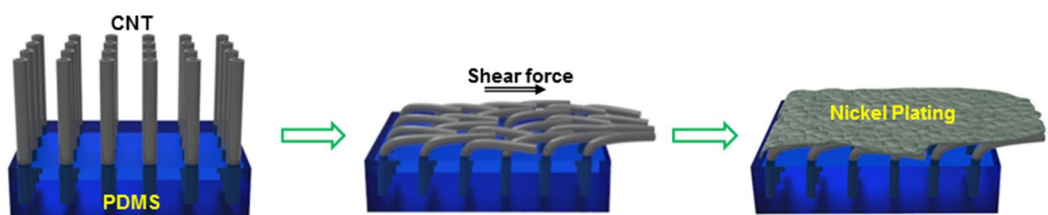


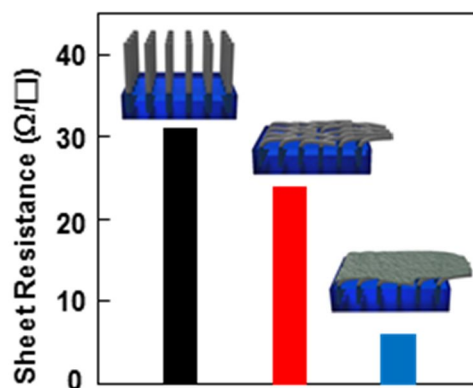
Figure 4. Resistance retention of (a) each design of electrodes depending on uniaxial strain and (b) design number 4 electrode depending on 100% strain stretching cycles.

## 2.3 Shear-pressing CNT and Ni electroplating

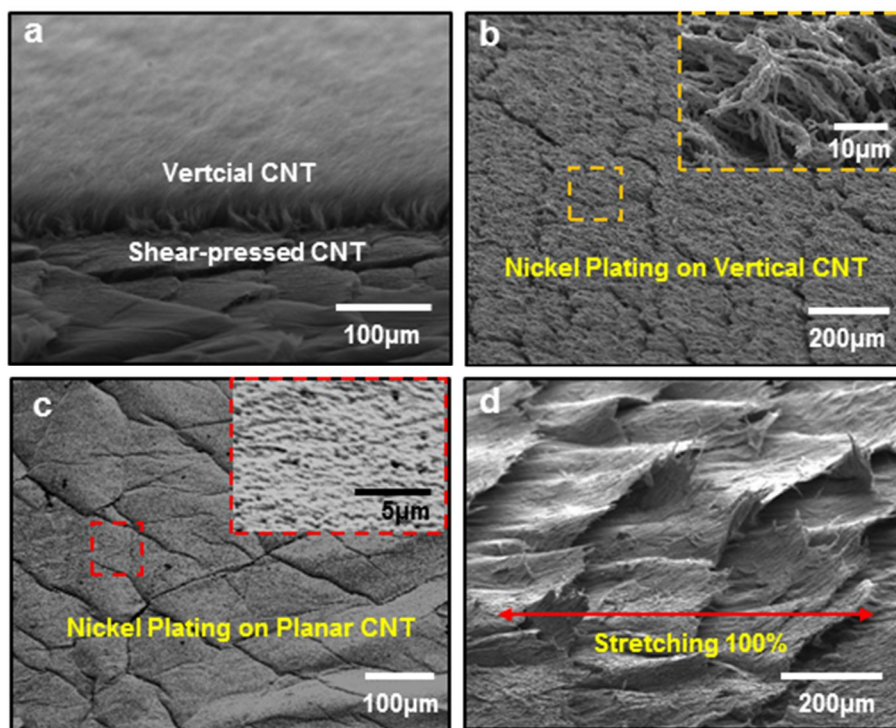
However, the conductivity of the CNT/PDMS electrode is still not enough to be used as the practical electrodes in the stretchable electronics. In order to utilize the percolation effect as the electrode is stretched, the air-exposed CNTs were shear-pressed to be aligned in a planar fashion, then they were electroplated with nickel to improve the low conductivity of CNT (Scheme 2). Figure 6a shows the surface morphology of air-exposed CNTs and shear-pressed CNTs. According to Figure 5, the sheet resistance of the vertical CNT/PDMS electrode was measured to be 30  $\Omega/\text{sq}$ , which should be reduced to improve the device performance. As the vertical CNT was forced to become planar, the sheet resistance slightly declined to be 26  $\Omega/\text{sq}$ . Finally, the nickel electroplating provides the electrode with metallic sheet resistance (7  $\Omega/\text{sq}$ ). Figure 6b and c show the surface morphology of electroplated vertical-CNT and planar CNT, respectively. Since nickel particles were homogeneously covered on the surface of each CNT, thin film-like metal layer was formed on the planar CNT surface where the contact resistance is reduced. Figure 6d shows how the electrode surface deforms as it was stretched. Its scalelike deformation maximizes the contact between the scales of nickel metal to maintain the current path.



**Scheme 2. Nanoscale illustration of shear-pressing the air-exposed vertical CNT and Ni electroplating on it.**



**Figure 5.** Sheet resistances of the vertical CNT/PDMS electrode (black), laterally shear-pressed CNT/PDMS electrode (red), and Ni plated lateral CNT/PDMS electrode (blue).



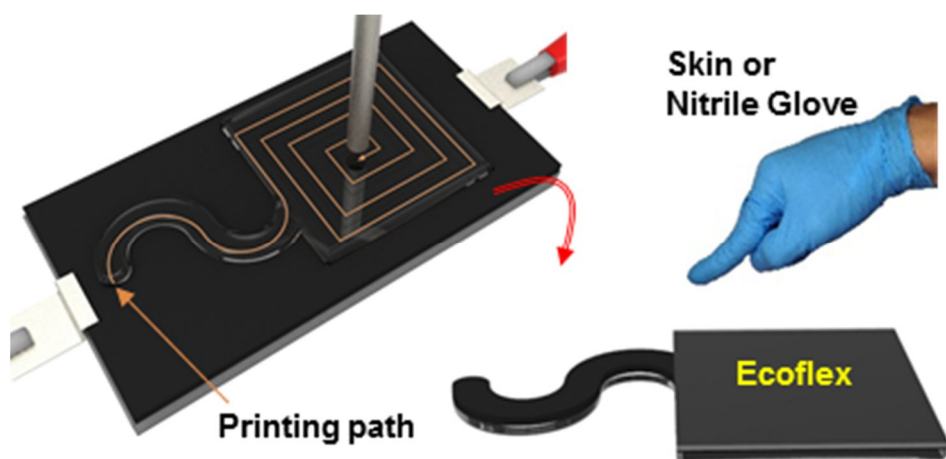
**Figure 6. SEM images of the surface morphology of CNT/PDMS electrodes. (a) The top half is air-exposed vertical CNT and the bottom half is shear-pressed CNT. (b) Ni plated on the vertical CNT. (c) Ni plated on the laterally shear-pressed CNT. (d) Ni plated lateral CNT/PDMS with 100% strain stretching.**

### **3. Stretchable triboelectric generator**

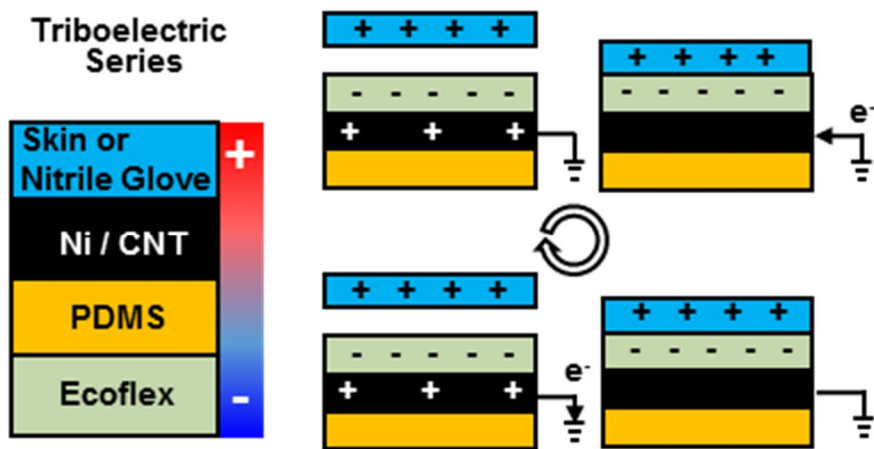
#### **3.1 Triboelectric generator fabrication and mechanism**

Using the fabricated electrodes, a single-electrode TEG was designed. Scheme 3 demonstrates how the electrode was printed, and the silicone-based elastomer (Ecoflex)-coated TEG generates electrical energy by interacting with human skin or nitrile glove. Triboelectrification occurs when two materials with different triboelectric series make contact with each other. Electrons tend to move one to another to satisfy the lowest electron states of two materials.<sup>16</sup> Typical insulating materials preserve such changes of charges mostly on their surfaces, while conducting materials can move the deviated charges from the contact surface to external connection owing to their free electron carriers. Unique utilization of an insulator and a conductor may achieve the triboelectric generation via electrostatic induction process. Such mechanism of the TEG is applied to our device, which is illustrated in Scheme 4. Since human skin or nitrile rubber is mostly insulating materials with relatively positive triboelectric series, the top surface of the stretchable electrode was designed to be Ecoflex with negative triboelectric series. The contact between nitrile rubber and Ecoflex results in charge separation for positive charges on nitrile rubber and negative ones on Ecoflex. A relative distance between above materials can make electric field around, which drives the attraction or withdrawal of electrons in the electrode. The Ni-plated CNT/PDMS electrode coated with Ecoflex plays a role of conducting electrode for transportation of electrons. Ecoflex is selectively chosen for its higher output in TEG and stretchability instead of PDMS.





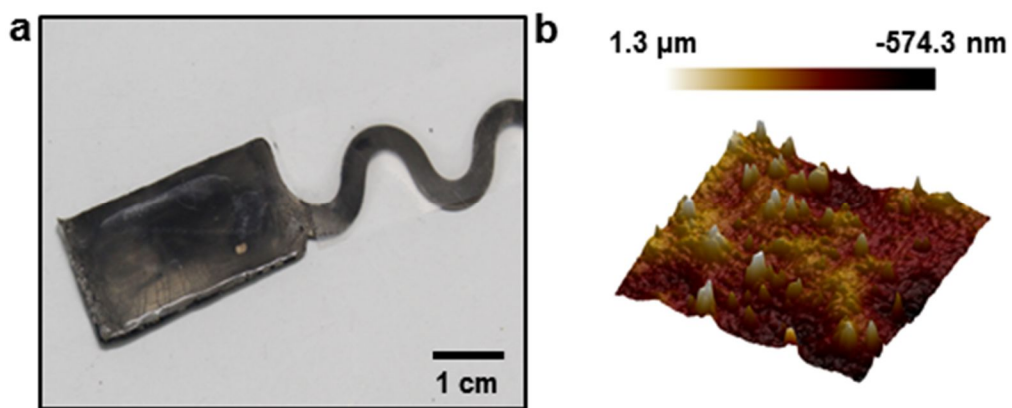
**Scheme 3. Stretchable single electrode TEG fabrication procedure and operation illustration.**



Scheme 4. Triboelectric series of the materials and the TEG mechanism.

### 3.2 Triboelectric generator analysis

The photograph of the TEG is shown in figure 7a, and its surface morphology is in figure 7b. Figure 8 shows the dependence of current and voltage loads on the resistance, providing the optimized power output of the stretchable TEG. The optimum power density of 33.5 mW/m<sup>2</sup> was obtained when the resistance was 350 M $\Omega$ . Figure 9a and b show the short-circuit current and open-circuit voltage, respectively, obtained while a nitrile glove repeatedly contacts to and move away from the TEG with a resistor of 350 M $\Omega$  attached. As shown in Figure 10 the power generation performance of the device maintained when the device was stretched up to 30% indicating the fabricated electrode realized the stretchable TEG. In stretching measurements, the area of contact between nitrile rubber and Ecoflex maintained the identical, which implies our stretchable TEG has much room for high performance by increasing area of nitrile rubber contacted to Ecoflex.



**Figure 7. (a) Photograph and (b) AFM surface morphology of TEG.**

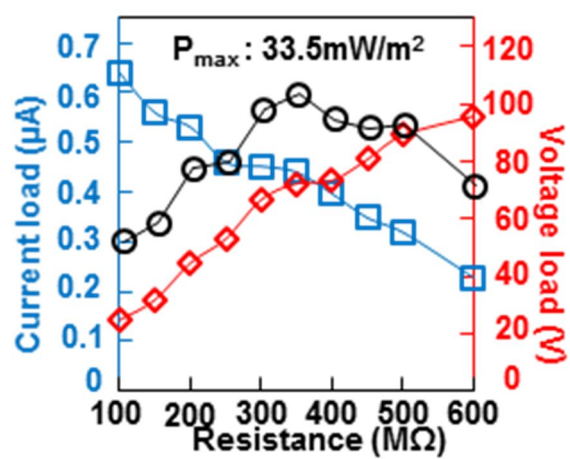


Figure 8. Power optimization of TEG depending on external resistance.

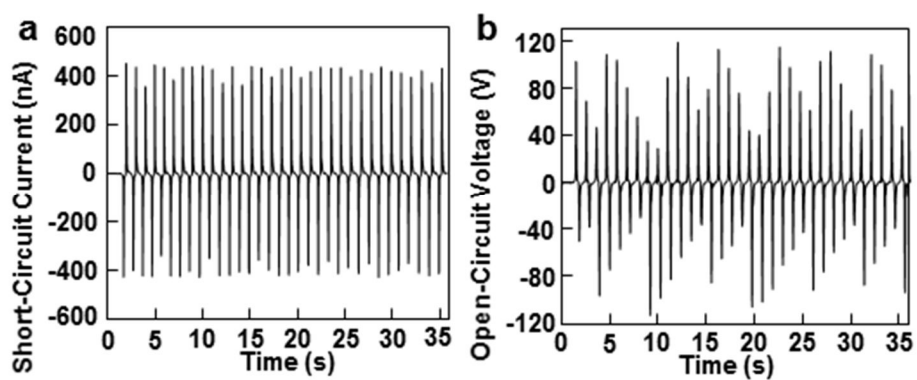


Figure 9. (a) Short-circuit current and (b) open-circuit voltage signals

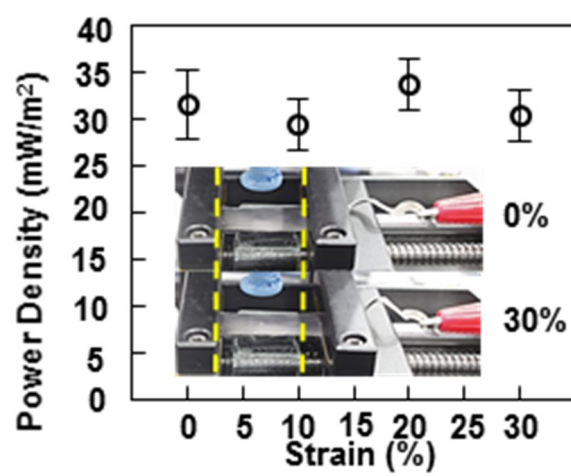


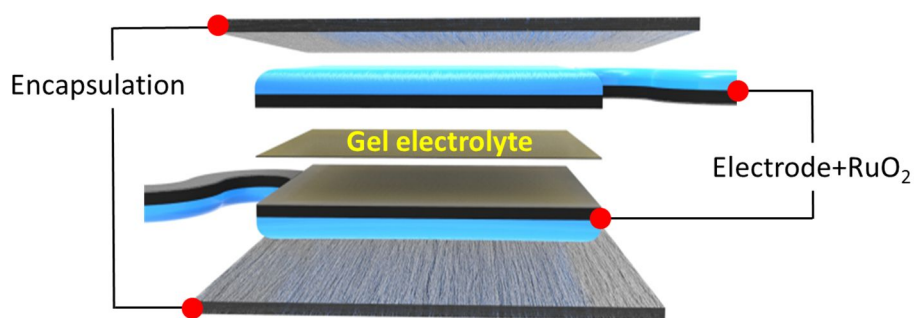
Figure 10. Power density depending on strain stretching of TEG

## 4. Stretchable energy storage devices

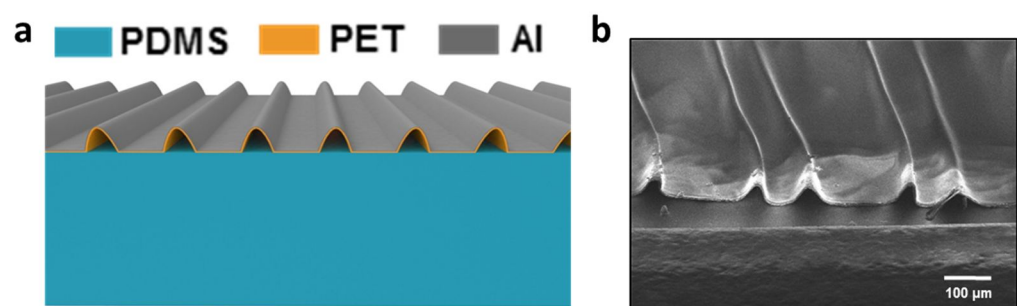
### 4.1 Supercapacitor

Supercapacitors have been established themselves as the promising energy storage devices as their energy capacity is improved up to that of lead-acid batteries.<sup>21</sup> flexibility and biocompatibility. Moreover, the all-solid-state supercapacitor is likely to be flexible, environment-friendly, and safe with high power density and long cycle life.<sup>19</sup> In order to enhance the pseudocapacitive performance, RuO<sub>2</sub> nanoparticles are decorated on the surface of the fabricated stretchable electrode. As shown in scheme 5, the poly(vinyl alcohol) (PVA)-H<sub>3</sub>PO<sub>4</sub> gel electrolyte is sandwiched by two of the modified electrodes to fabricate the stretchable supercapacitor. The encapsulation layer consists of the stretchable PDMS substrate and the buckled PET-Al layer on top of it (Figures 11a and b). The cyclic voltammetry curves at different scan rates (5mV/s to 100mV/s) show the typical semi-rectangular shapes of supercapacitors (Figure 12a) and the galvanostatic charge-discharge curves are obtained at the current density from 50  $\mu\text{A}/\text{cm}^2$  to 500  $\mu\text{A}/\text{cm}^2$  (Figure 12b). As shown in figures 13a and b, the stretchable supercapacitor was stretched up to 30% strain, and it maintained its areal capacitance of 11.4mF/cm<sup>2</sup>.

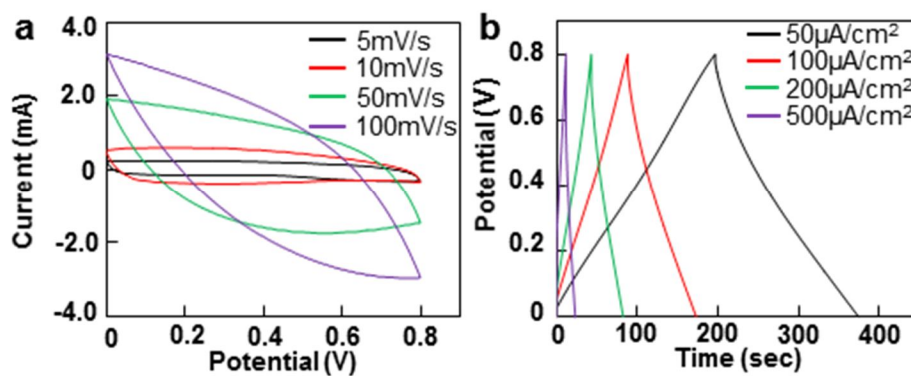




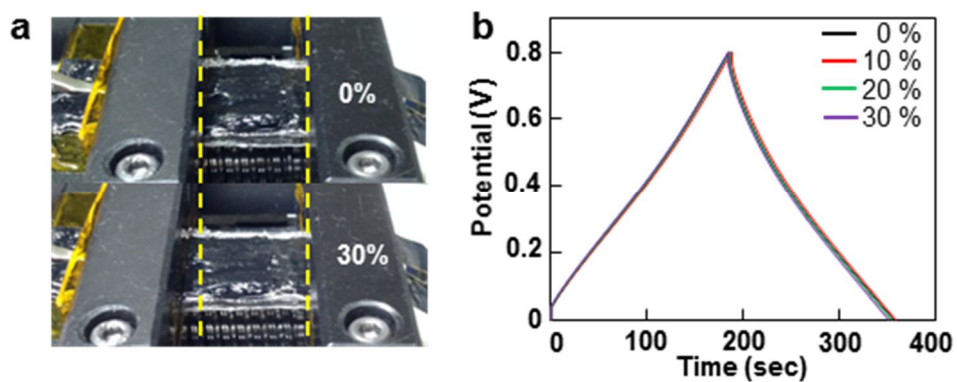
**Scheme 5. Exploded description of stretchable supercapacitor**



**Figure 11. Encapsulation layer. (a) Schematic illustration of the cross section of the encapsulation layer. (b) SEM image of the buckled PET-Al film on PDMS substrate.**



**Figure 12.** Electrochemical analysis of supercapacitor. (a) Cyclic voltammetry curves at different scan rates. (b) Galvanostatic charge-discharge curves at different current density.



**Figure 13.** Stretchable supercapacitor stretching performance. (a) DSLR pictures of supercapacitor with 0% strain (top), and 30% strain (bottom). (b) Galvanostatic charge-discharge curves at different strain stretching.

## 4.2 Lithium-ion battery

In order to compensate the low energy density of supercapacitor, LIB is required in the energy system to supply enough energy to other devices. The structure of LIB is similar to that of supercapacitor as shown in scheme 5 except RuO<sub>2</sub> nanoparticles are replaced with lithium iron phosphate (LFP) for cathode and lithium titanate oxide (LTO) for anode. Each active materials are coated on the stretchable electrode, and their first charge-discharge cycles (0.2 C) as half-cell are shown in figures 14a and b. Further study on the realization of full cell LIB and its stretching test would be required.

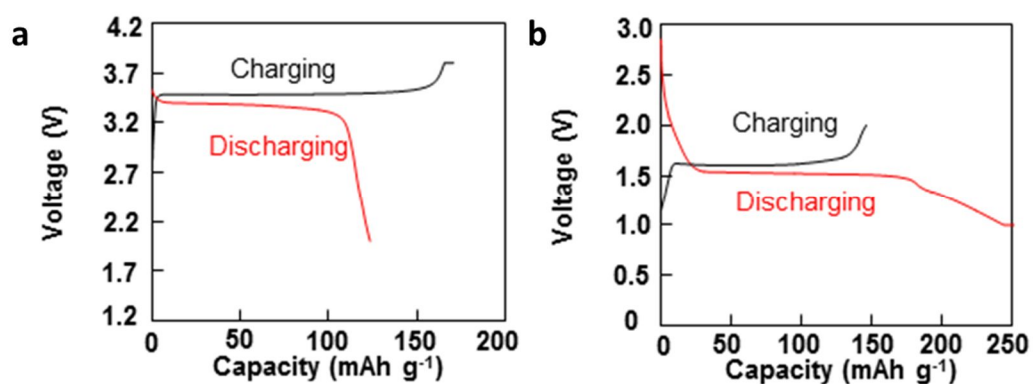
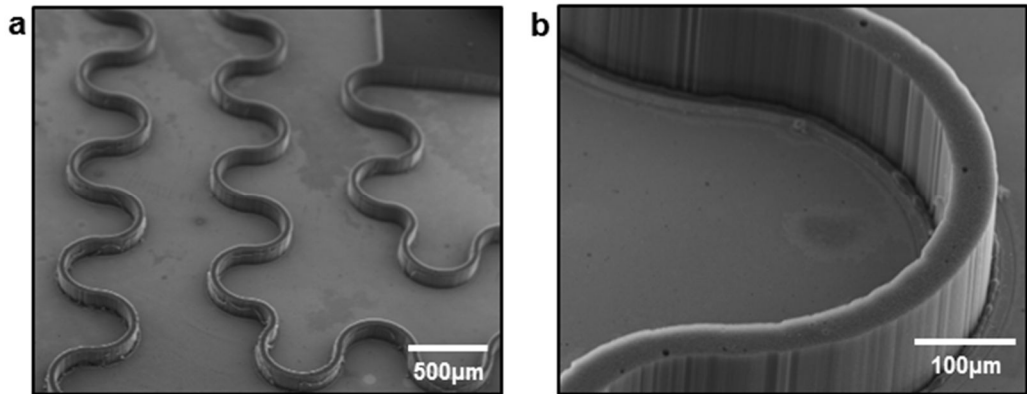


Figure 14. First charge-discharge cycle of LIB. (a) Half-cell test of cathode (LFP).  
(b) Half-cell test of anode (LTO)

## **5. CNT-based wireless power transmission coil**

Since the power generation from the TEG is still not high enough to charge the LIB, stretchable wireless power transmission coil is designed to be integrated in the energy system. The coil is also based on vertical CNTs, but its line width is only 0.1 mm which is too thin for PDMS printing. To address the issue, Fe catalyst layer is patterned using photolithography, and CNT forest grows in the coil shape as shown in figures 15a and b. The CNT coil would be transferred on the PDMS substrate. Additional combing and Ni electroplating would accomplish the stretchable CNT coil for wireless power transmission.



**Figure 15. SEM images of CNT forest for wireless power transmission coil. (a) Low magnification. (b) High magnification.**



## **6. Experimental section**

### **6.1 Vertically-aligned carbon nanotubes synthesis**

The adhesive aluminum metal layer of 10nm was deposited on the Si wafer using thermal evaporator, followed by iron catalyst layer of 3.5 nm. The sample is placed in 1 inch quartz tube with 100 ppm Ar gas, 2 ppm Ar with a trace amount of water. The furnace is heated up to 730C, and 100ppm of H<sub>2</sub> and 75 ppm of ethylene was applied to the tube.

### **6.2 Stretchable electrode fabrication**

A certain voltage power is applied to the CNT forest on the Si from the power supply. The voltage was adjusted to have the desired temperature of Joule heating while the temperature was monitored using infrared temperature camera. The polydimethylsiloxane precursor and the curing agent was mixed with the mass ratio of 10:1. The solution is contained in a syringe and printed on top of the CNT forest using the inkjet printer. After the PDMS is fully solidified, the patterned PDMS/CNT composite film was carefully peeled off from the wafer. A slide glass was placed on top of it and shear-pressed to make the air-exposed CNTs laterally-aligned. Its surface was hydrophilized by O<sub>2</sub> plasma using RIE before Ni electroplating. Ni Electroplating solution was prepared by mixing 300g/L of nickel sulfate, 150 g/L of nickel chloride, and 52g/L of boric acid in DI water. The solution bath was heated up to 50 °C, and 3

electrodes (CNT/PDMS, Pt, and Ag/AgCl in NaCl as working, counter, and reference electrodes, respectively) were placed in it. A constant current was applied to the electrodes while the CNT/PDMS electrode was slowly lifted upward to help the uniform plating over the electrode.

### **6.3 Stretchable supercapacitor fabrication**

RuO<sub>2</sub> electroplating solution was prepared by mixing 5 mM ruthenium(III) chloride hydrate, 0.1 M potassium chloride, and 0.01 M hydrochloric acid in DI water. The pH of solution was adjusted to become 2.0 by adding 3M sodium hydroxide. The plating solution was heated to 50 °C, and the fabricated electrode was placed with a Pt counter electrode and an Ag/AgCl reference electrode in NaCl. A potentiostat was used for cyclic voltammetry between -0.2V and 1.0V at a 0.05mV/s scan rate.

The electrolyte was prepared by adding 6 g of PVA and 9 g of H<sub>3</sub>PO<sub>4</sub> to 60mL of DI water. The mixture was constantly stirred at 104 °C until it became a clear solution. It was then dehydrated in a petri dish to become a gel electrolyte.

### **6.4 Stretchable lithium-ion battery fabrication**

The active materials (LFP and LTO) were mixed with carbon black and PVDF binder with the mass ratio of 7:2:1 in NMP solvent. The mixture was then evenly spread on the surface of the Ni coated stretchable electrode. The solvent was dried in the vacuum oven at 70 °C.

## **7. Conclusion**

In summary, vertically-aligned CNT was modified in various ways to be utilized as the stretchable electrodes for TEG and supercapacitor. Its various application could be realized by photolithographic patterning of the iron catalyst and polymer printing while joule heating. Once the desired shape of CNT forest was obtained, its electrical conductivity was enhanced by metal plating, and its unique surface tectonics and improved percolation effect enabled its application as the stretchable electrodes for those energy devices. If the complete study of stretchable LIB and full integration of each devices are accomplished, the energy system based on CNT could be widely applied for other wearable or epithermal electronics to supply electrical energy.

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## 요약(국문초록)

### 에너지 소자를 위한 측면으로 빗질된 수직 탄소 나노 튜브 기반의 늘어나는 전극

휴대용 전자기기에 필요한 전기적 에너지를 공급하기 위해서는 보통 외부 전력 공급원과 긴 선을 이용하여 기계적으로 연결을 해야 하는 불편함이 있다. 휴대용 전자기기의 소형화가 이루어지면서 가볍고 얇으면서 구부러지거나 늘어날 수 있는 능력이 웨어러블 소자나 피부 부착형 소자들의 개발에 큰 관심거리가 되었다. 그러므로 자발적으로 에너지를 생산하고 저장할 수 있는 가벼우면서 얇고 변형이 가능한 에너지 소자들이 필요하다. 본 연구에서는 수직으로 배열된 탄소 나노 튜브를 이용하여 늘어나는 전극을 만들고 이를 이용하여 사람의 신체 운동으로부터 전기 에너지를 생산하는 마찰전기 발전기와 슈퍼커패시터와 리튬이온 전지와 같은 에너지 저장 매체, 그리고 무선 충전 코일을 만들었다. 실리콘 웨이퍼 위에 수직으로 자라난 탄소 나노 튜브 위에 유연성 고분자인 PDMS를 잉크젯 인쇄하여 탄소 나노 튜브를 부분적으로 고정하고 패어뎀으로써 원하는 모양의 늘어나는 전극을 만들었다. 이 전극의 전기전도성과 나노 튜브 간의 뭉치는 효과를 향상하기 위해 공기 중에 노출된 탄소 나노 튜브를 측면으로 빗질하고 그 위에 니켈금속을 전기도금 하였다. 소자들 간의 연결을 위하여 전극을 구불구불하게 만들어 단축으로 늘어날 때 전극의 부담을 감소시켰다. 마이크로 단위의 패턴은 탄소 나노 튜브의 촉매 층을 증광식각 하여 구현하였다. 마찰전기 발전기와

슈퍼커패시터, 리튬이온 전지의 경우 넓은 면적으로 만들어 높은 출력을 얻었다. 이렇게 만들어진 에너지 소자들은 성능을 유지하면서 30%까지 늘어날 수 있었으며 이를 통해 웨어러블 소자나 피부 부착형 소자들의 자발적인 에너지 생산 및 저장 시스템을 구현하였다.

주요어 : 늘어나는 전극, 탄소 나노 튜브, 마찰전기 발전기, 슈퍼커패시터, 리튬 이온 전지

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