공학석사학위논문

다공성 polydimethylsiloxane–polydopamine 복합체를 활용한 이온전도 및 열전특성에 대한 연구

2023년 2월

부경대학교대학원

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장서현

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지도교수 유성일

이 논문을 석사 학위논문으로 제출함.

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장서현의 공학석사 학위논문을

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장서현

부경대학교대학원 고분자공학과

요 약

열전에너지 발전기는 낮은 등급의 열을 전기로 전환할 수 있다는 점에서 각광받고 있는 해결책 중 하나이다. 이 연구에서는, PEO-NAOH 전해질용액의 열전특성을 PDMS 필름에 복합화 하였다. 도파민 층은 소수성 PDMS의 표면을 친수성으로 바꿔주기 위해 표면 PDMS 기공에 침투시켰다. 마지막으로 도파민의 중합조건, PDMS 필름의 기공크기 등을 조절하여 PDMS 복합체에서 온도조절에 따른 이온이동을 조사하여 이들의 열전성능을 연구하였다.

Ion Transport in Porous Polydimethylsiloxane-Polydopamine Composites for Thermoelectric Application

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Abstract

열전에너지 발전기는 낮은 등급의 열을 전기로 전환할 수 있다는 점에서 각광받고 있는 해결책 중 하나이다. 이 연구에서는, PEO-NAOH 전해질 용액의 열전특성을 PDMS 필름에 복합화 하였다. 전해질용액을 PDMS 스펀지의 기공에 침투시켜 PEO 체인으로 인해 Na이온의 호핑 현상을 향상시켰다. 도파민 층은 소수성 PDMS의 표면을 친수성으로 바꿔주기 위해 표면 PDMS 기공에 침투시켰다. 마지막으로 도파민의 중합조건, PDMS 필름의 기공크기 등을 조절하여 PDMS 복합체에서 온도조절에 따른 이온이동을 조사하여 이들의 열전성능을 연구하였다.

Chapter I. Introduction

I-1. Energy Harvesting

Since most of the energy is imported and used from abroad, we are paying attention to research on alternative energy. Energy harvesting technologies refer to a technology that converts energy such as heat, vibration, light and electromagnetic waves existing aground it into electrical energy. Among them, Energy harvesting technology is already being applied across the industry according to specific uses. Overall, the energy density is still low, but it is shown that conversion efficiency in case of radio frequency energy is the best and the energy density is the lowest in case of using a thermal energy. This study is how efficiently it can be converted into electrical energy with thermal energy

I-1.1. Thermal Energy Harvesting

Harvest power also has various values depending on various energy sources. The thermal energy harvesting uses electromotive force generated by temperature differences on both sides of the material. If thermoelectric performance is higher, electricity can be generated using thermal energy sources existing in nature beyond waste heat recovery. Also, even a very small amount of thermal energy can be recovered. It was attempted to increase thermoelectric efficiency with a polymer and an electrolyte by using such thermoelectric casting. Table 1 shows various energy sources and their conversion efficiency and harvest power. It can be seen that the conversion efficiency of thermal energy is the lowest among them. However, it can convert low-grade thermal energy that exists in daily like into electrical energy, and it is important as a field of eco-friendly energy. So, it will be possible to return the limitations of thermoelectric materials using existing electrical conduction.

Table 1. Comparison of various energy harvesting technologies [1]

Energy Sources	**Conversion Efficiency**	**Harvested Power**	**Technologies/Device**
Solar energy	10-23%	Indoor: 10 μW / cm^2 Outdoor: 10 mW / cm^2	Photovoltaic and thermoelectric generators
Radio frequency energy	52%	0.1 μW / cm^2	Radio frequency generator
Thermal energy	5%	1-15 mW / cm^2	Thermoelectric nanogenerator
Mechanical energy	Source dependent	100 μW / cm^2	piezoelectric and triboelectric nanogenerator

I-2. Porous Polymer

Until now, various studies using porous polymers have been conducted. Porous polymer are materials that simultaneously realize high surface area, which is a characteristic of porous materials, and excellent processability, which is an advantage of polymeric materials, and is subject to various basic and application studies.

In particular, it can be made in various forms such as particles, thin films and sponges, various functional groups can be introduced into the surface or pores through chemical functionalization, and it has advantages of having a low skeletal density. Porous particles can generally be divided into microporous (more than 50 nm), mesoporous (more than 2 nm), and microporous (less than 2 nm) depending on the pore size.

This study increased the thermoelectric effect by inserting a polyelectrolyte into the porous polymer. For example, polyelectrolyte will be inserted into a porous polymer to control ion conduction due to a temperature difference in the polymer material and convert the ion conduction into electrical energy.

I-3. Surface-Initiated Polymerization

I-3.1 Seebeck Effect

A potential difference occurs when two different metal conductive wires are bonded at both sides to form a circuit, and a temperature difference is applied to the bonding part at both ends to create a closed circuit. These thermoelectric phenomena include the Seebeck effect, the Peltier effect, and the Thompson effect. Among them, Seebeck is the effect of generating electromotive force due to the flow of current if a temperature difference is applied to the bonding part after bonding two metal conductors. [2]. So, if the other contact is located at a part where the temperature is to be measured with one contact point as the reference point, the temperature difference is depending on the potential difference. For this system, the temperature is measured by comparing the temperature with the reference point. The Seebeck effect is described as equation. [3]

$$\mathrm{S} = \frac{\Delta V}{\Delta T}[\mu V/K] \quad (1)$$

S is a value called Seebeck coefficient, which means the voltage derived from the unit temperature difference. A higher value of Seebeck coefficient naturally increases the electromotive force occurred by the thermoelectric effect, which makes it a good thermoelectric device. If there is a temperature difference, if the temperature of the low part is T_L, the temperature of the high part is T_H, and the thermal conductivity of the material used thermoelectric effect is K, and the electrical conductivity is σ, ZT is expressed as equation. [4]

$$ZT = \frac{S^2 \sigma T}{K} \quad (2)$$

T is the average temperature between the high temperature part and the low temperature part, that is $T = (T_H/T_L)/2$. ZT is a proportional value to the square of the Seebeck coefficient. For a high thermoelectric effect, it can be seem that the larger the value of ZT, the better. Nyquist plots are important data for understanding the effect of Seebeck effect. The Seebeck effect applied to the Sine Wave waveform to the sample from high frequency to low frequency and measured the amplitude and phase change. According to the Sine Wave in response to the sample, the Seebeck effect analyzed the impedance. It is possible to analyze in various ways along with using the constant current and constant voltage methods based on resistance measurement according to potential through impedance.

I-3.2 Surface-Initiated Polydopamine Coating

Recently, functional surface modification techniques using dopamine, a monomolecular material consisting of catechol, an important chemical functional group that exhibits adhesion in the adhesive protein of mussels, have been actively researched. [5]. Dopamine is a monomolecular substance with catechol and amine functional groups, it was reported that the polydopamine coating layer was formed by oxidation of catechol on the surface when the substance to be surface solution under the same basic pH conditions (pH=8.5) as the underwater environment. In addition, the catechol functional group is going to form a covalent bond with the amine functional group as seen in the previous single molecular adhesive force. So various molecules with amine functional groups can be introduced on the surface as secondary surface modification. [6].

In this case, unlike existing basic conditions, there are research in which dopamine is coated under acidic or neutral conditions. Through this method, it was found that polydopamine was formed in an aqueous solution under neutral or acidic pH conditions. [7-10] By adjusting the pH conditions of the oxidizing agent and the solution, depending on the coating time, the thickness diverse surfaces so that the polydopamine surface modification technique can be introduced while controlling it became. Through this, it is possible to maximize the realization of the advantages of various surface adhesion, which is the advantage of polydopamine surface modification. [11]

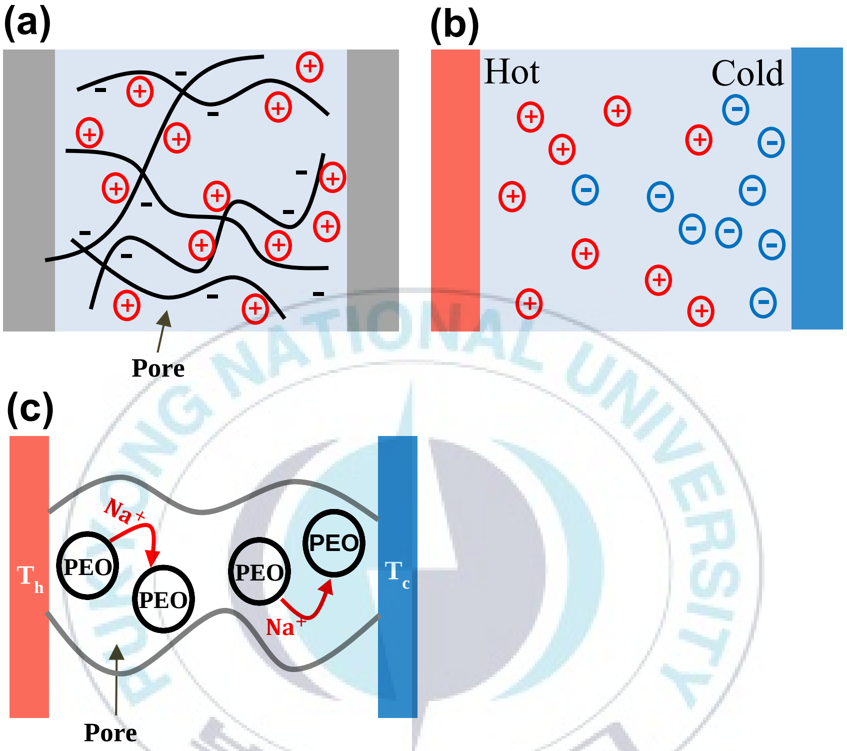

Figure 1. Illustration of ionic thermodiffusion in PDA/PDMS-PE: (a and c) Electrolytes containing simple sodium salt, (b) electrolytes containing anion and small counter cation

Chapter II. Polydopamine Nanoparticles-coated Porous PDMS Composites for Polyelectrolyte with Enhanced Performance

II-1. Introduction

Imposing research efforts have been developed for sustaining the ion conductivity. As a result of chemical potential, ions move spontaneously from other porous PDMS to another porous PDMS. [12-15]. The polyelectrolyte distribution of charges on an PDMS sponge system caused the Seebeck effect. [16-18]. The Seebeck effect allows for selective transmission of cations or anions between porous PDMS sponge. When heat is applied to one contact, current flows due to the potential difference caused by the temperature difference between the two contacts. Generally, the flow of electrons through porous PDMS sponge is defined as a potential difference. [19-21]. Thermoelectric generated from the porous PDMS then is converted into a useful voltage to power the system, or to recharge energy storage devices. [22]. Considering the requirement of thermoelectric efficiency for PDMS sponge, combining polymer and polyelectrolyte are showed to achieve great performance. [23-26].

Currently, various types of nanoparticle are used to improve ion exchange by increasing thermoelectric efficiency applying in contact with porous PDMS sponge. [27-29]. Furthermore, a highly compressible application, especially sponge structure has been reported to porous pores. By making coated PDA NPs of PDMS sponge, they are not maintained only for a certain period of time but are semi-permanent and economical. Also coated PDA properties are not limited to specific surfaces but appeared throughout the volume of porous PDMS. Since polydopamine is formed by spontaneous oxidation of dopamine over time in the solution, the content of the formed coating can be controlled by adjusting the time put in the solution. In order to find the effect of PDA property when coating PDA on a PDMS sponge, a PDMS sponge was manufactured by making a difference by coating time. Furthermore, dopamine is that no additional additives are required other than dopamine, and the reaction takes place in an aqueous solution at 25 ℃, so additional equipment for coating is not required. [30]. Compared to recent reports, there are still not many research on porous PDMS and the ion exchange of electrolyte in its pores, particularly in sponge structured based. [31-33]. In this regard, modification of PDMS/PDA sponge with polyelectrolyte (PE) have been designed as an effective thermoelectric. The porous PDMS sponge has been fabricated by using sugar templates. And it was determined that the porous PDMS sponge would be easy to move the electrolyte because it consists of dense pores. Furthermore, we will find out the effect of pore size on electrolyte transfer, various types of pore size were fabricated. A simple method for surface modification in which self-polymerization of polydopamine through a dipping coated method has been applied in this work. [34]. So, PDA nanoparticles can chemically be attached to the pore of PDMS sponge. With the existence of catechol and amine groups, polyelectrolyte can move easier because hydrophilicity changes to hydrophobic. For comparison, the coated PDA with PDMS sponge and PDMS sponge without coated PDA were fabricated. Because of the polydopamine, the PDA NPs can be made good process to transfer electrolytes easily. Polymer electrolytes (PE) are dissolved in water and have a positive or negative charge. [35-38]. A polymer electrolyte has advantages of a low-temperature mass production process and lightness but has a problem of low ion conductivity at room temperature. In addition, when polymer electrolytes (PE) are ionized, charges may not be completely dispersed in the solution and may be bound by chemical bonds.

By adding NaOH to the PEO solution, ion is transformed to terminate alcohol groups (-C-OH) into anionic alkoxide end groups (-C-O^{-}Na^{+}). To complement for these disadvantage NAOH, which can be easily moved in the PEO chain, was added. PEO weight molecular is high with alcohol groups (Mw = 200,000g/mol) as the electrolyte, because PEO can withstand relatively high temperature (<100℃) and the higher concentration is easy to ion movement, potential or conductivity is also improved. When temperature difference is applied, sodium ions move easily in the PEO chain. [39-40]. Furthermore, it was investigated whether the concentration of electrolytes also affects ion exchange. By making of various types of concentration of polyelectrolyte, it indicated whether the potential and ion conductivity were improved, and sodium ions moved more efficiently. It was determined that the higher the concentration, the more dense the polymer chains in the electrolyte, making it easier for sodium ions to move. However, as the concentration increased, the physical properties did not increase and found the appropriate concentration. [41]. The higher performance of porous PDMS sponge was showed in sponge with coated PDA and PE, compared to PDMS sponge without coated PDA. The optimum outcome of PDA/PDMS/PE sponge can achieve thermoelectric correspond with potential and conductivity about 98mV and 0.182 S/cm, respectively.

II-2. Experimental Section

II-2.1. Materials

Poly(dimethylsiloxane) SYLGARD 184 Silicon Elastomer base and the thermal curing agent were obtained from Sigma-Aldrich. Dopamine hydrochloride (98%), Polyethylene oxide (Mw=200,000g/mol), Sodium hydroxide beads (98%) were obtained from Sigma-Aldrich.

II-2.2. Procedure

II-2.2.1. Fabrication of PDMS Sponge

The commercial sugar was mixed by adding DI water and casted onto a specific size (2cm x 0.5cm) of cylinder mold. After the sugar was dried 3 days, the sugar template was peeled away from the cylinder mold, The mixture of base and the curing agent was poured in a weight ratio of 10:1 on a petri dish. Sugar templates were placed into a petri dish containing total 3 grams mixture of PDMS. Further, the PDMS mixture was degassed in a vacuum oven at 25 °C for 4 hours. The PDMS mixture can infiltrate into the sugar templates. The absorbed PDMS in sugar templates was cured at 80 °C for 2 hours. After that, the sugar templates were dissolved to use DI water for 2 times following by washing for 12 hours. Therefore, the sugar was removed from the PDMS sponges. The PDMS sponges were dried at room temperature for 2 days (Figure 2).

II-2.2.2. Synthesis of Polydopamine Nanoparticle

Firstly, a 20 mL ethanol and a 45mL di water was mixed, and a 2.8 mL ammonia solution was added. Dopamine hydrochloride (0.25 g) was added a 10 mL DI water. And then, dopamine solution was injected into above mixture solution. The mixture was stirred for 48 hours at very slowly and keep the time accurately. Because the particle size changes easily depending on the time or pH. Secondly, the mixture was centrifuged at 13500rpm, 15 min and washed Di water 3 times. The centrifugation-based purification was repeated thrice. The precipitate was freeze-dried for 48 h to obtained PDA NPs in a powder.

II-2.2.3. Modification of PDMS Sponge

The PDMS sponge was surface modified by dipping in dopamine solution.

the PDMS sponge was immersed into dopamine solution (2mg/mL) in 10 mM Tris buffer (pH 8.5) for different periods of time (0, 5, 10, 15, 24 h), which allowed the oxidative polymerization of polydopamine (PDA) on the porous surface of PDMS sponges. (Figure 3). The prepared PDA-coated PDMS sponges with polyelectrolytes will be denoted as PDA(x)-PDMS/PE, at which x denotes the polymerization time of PDA. Then polydopamine layer was introduced onto the surface PDMS pores to covert the hydrophobic PDMS surface into hydrophilic one. As the PDMS pores are reformed to be hydrophilic, the movement of the PEO-NaOH electrolyte becomes to facilitate.

II-2.2.4. Insertion of PDMS Sponge with Polyelectrolyte

The modified PDA/PDMS sponge was infiltrated polyelectrolyte. Polyelectrolyte was synthesized by the Poly(ethylene oxide) (PEO) and Sodium hydroxide beads (NaOH). 10 mL of PEO solution (1.4 g in 10 mL) was added to NaOH beads (4 wt% in 10 mL). NaOH beads were conducted by various concentrations, but 4 wt% had the highest potential. The viscosity of polyelectrolyte was high, there is a limit to immersing it in an electrolyte solution. Instead of immersing, it was inserted at room temperature under reduced pressure for 4 hours using a vacuum oven. Comparing the cross section of the PDMS sponge when after immersed and inserted, it was confirmed that the electrolyte was better appeared into the cross section of the inserted PDMS sponge.

II-2.3. Measurement

To measure thermovoltage, PDA(x)-PDMS/PE composites was inserted inside coin cells. The coin cell was placed between two Peltier modules, which can apply temperature different between the top and bottom surfaces of coin cells. Both the temperature and electric potential differences between the top and bottom surfaces of coin cells were recorded by a thermocouple and voltmeter (Keithley 6514). Ion conductivity was measured by impedance spectroscopy using a Bio-Logic VSP-300 operating over a frequency range of 10^1 to 10^7 Hz at an amplitude of 20 mV to examine conductivity of PDA(x)-PDMS/PE. Thermal conductivity was analyzed by LFA 467. The microstructure of the porous PDMS was analyzed by field-emission scanning electron microscopy (FE-SEM) with the TESCAN(VEGA II LSU) instrument operating at 2.0 kV. Fourier Transform Infrared (FTIR) spectra were obtained by using a JASCO FTIR 4100 spectrometer. X-ray Photoelectron

Spectrometer (XPS) was analyzed by AXIS SUPRA made KRATOS Analytical Ltd.

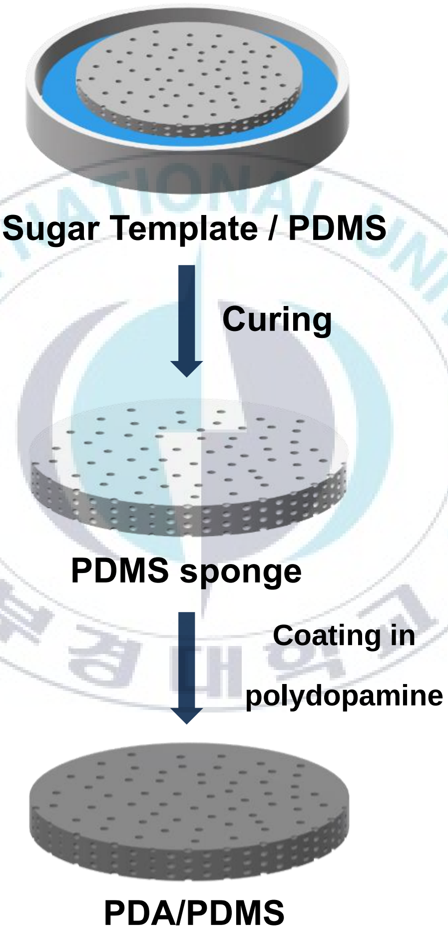

Figure 2. Schematic illustration for the fabrication process of the PDA/PDMS sponges from sugar templates.

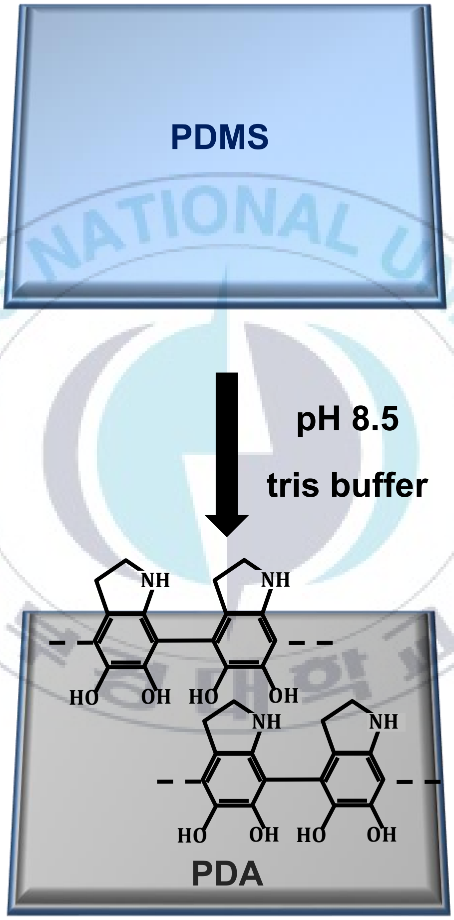

Figure 3. Schematic diagram of coating PDA with PDMS sponge.

II-3. Result and Discussion

II-3.1. Characteristic of PDMS sponge and PDA Nanoparticle

The process of fabricating the PDA/PDMS/PE sponge is described. The dipping method was used for coating polydopamine and polyelectrolyte onto the PDMS sponge. The sugar templates from commercial sugar powder were used to make the porous PDMS sponge. In the production of PDMS sponge, it is remarkable that the sugar templating process is one of the fast and easy production that only needs a few hours in the process. Furthermore, it has a potential for large scale production that can be make it easier. [42].

Before fabricating of PDA/PDMS sponge, the coating of PDA was used as a simple step in system. As a using curing agent, polydopamine can be spontaneously polymerized into polydopamine under pH 8.5. The dopamine concentration in the coating solution has an important part in controlling the coating rate and the roughness of the coated surface. And then, Under the pH conditions of the coating solution, the coating thickness formed increased as the pH increased between pH 5-8.5. [44]. When synthesizing polydopamine, various buffer solutions can be used.

In the case of Tris solutions, tris molecules with amine functional groups react with catechol and unintentionally intervene in polydopamine, which can affect the physical and chemical properties of polydopamine. By taking advantage of tris buffer, pH 8.5 at alkaline condition can initiate self-polymerization of dopamine. The PDA/PDMS sponge washed by DI water 3 times to remove an attached dopamine and dried a day. After that, the PDA/PDMS sponge was inserted the electrolyte into the sponge using a vacuum oven for 4 hours. In figure 4a, the color of PDMS sponge changes from white (i) to light gray after 5 h dipping in polydopamine solution (ii). The color of PDMS sponge becomes darker after dipping in dopamine solution. (iii-v). Hereafter, In the figure 4b-c, there were the plan view of SEM images of PDMS sponge with dipping time for 0 hours and 24 hours. When comparing to coated dopamine before and after, it was observed that the color became darker. And it was confirmed that the thickness of the pores became thicker after the dopamine coating. Figure 5a shows the FTIR peak of PDMS and PDA(24)/PDMS. 1502 cm^{-1} is shown N-H shearing vibration of the PDA nanoparticle. Figure 5b shows the typical XPS survey spectra of PDMS sponge without coated dopamine and PDMS sponge with coated dopamine at 24 hours. Both samples exhibit a Si 2s peak at 94.3 eV and an Si 2p peak at 156.7 eV. C 1s peak was found at 293.2 eV, respectively. The PDMS sponge with coated dopamine at 24 hours had nitrogen peak. The N 1s peak located at 537.7 eV was detected on the PDMS sponge surface with dopamine and disappeared in the PDMS sponge spectrum. This evidences that dopamine was successfully attached to the PDMS sponge pores during the dipping-coated process. This indicates that the nitrogen species of polydopamine was completely covered by the PDMS pores. Also, the XPS Si 2s and 2p peak had the low content of PDA/PDMS sponge, compared with the PDMS sponge, it can be seen that the Si element of PDMS sponge was attached to the dopamine with C=O groups. However, the existence of sulfur can be easily confirmed by the corresponding.

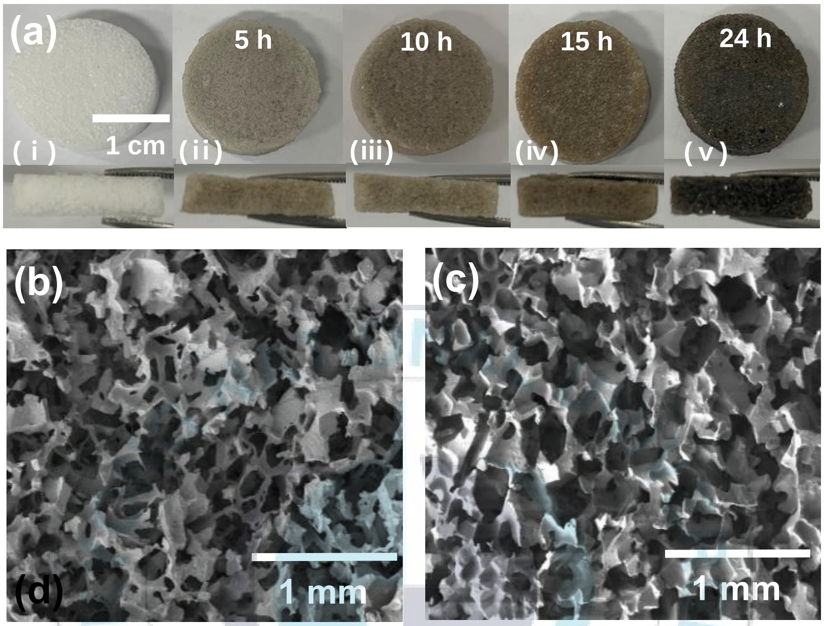

Figure 4. (a) Digital photo of PDMS sponge (i), the PDMS sponge coating dopamine at 5 hours (ii), 10 hours (iii), 15 hours (iv), 24 hours (v)**.** The SEM image of PDMS sponge for 0 hours (b), and for 24 hours (c).

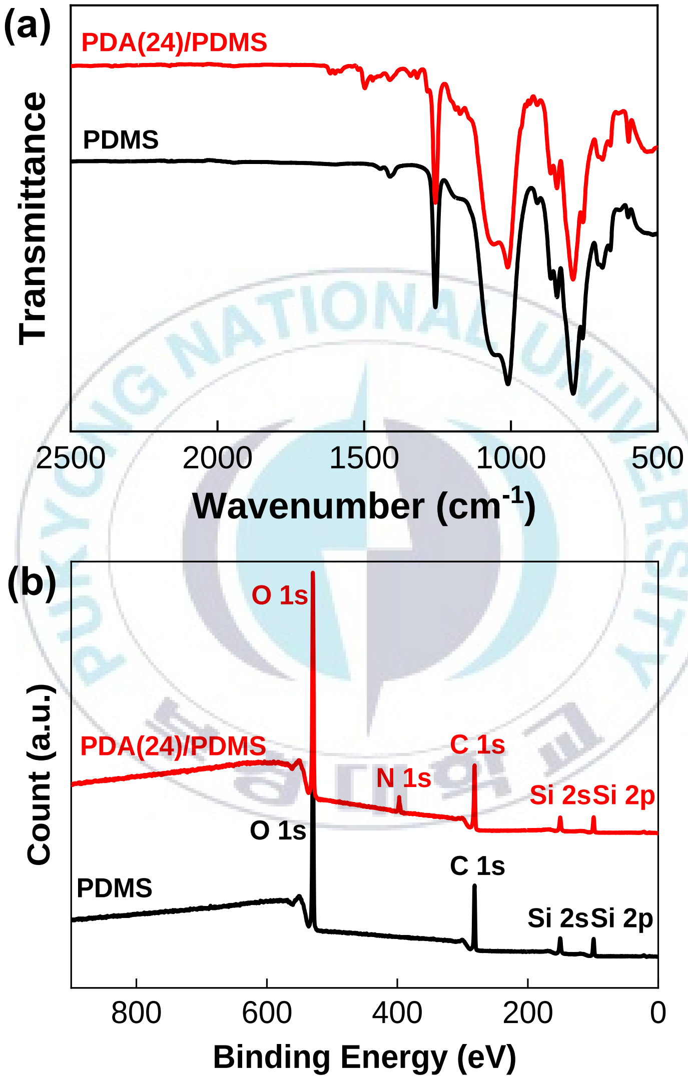

Figure 5. FTIR peak and XPS spectrum of the PDMS and PDA/PDMS.

II-3.2. Characteristic of PDMS Sponge for Pore Size

When fabricating the porous PDMS sponge, the pore size was fabricated to be 170 μm approximately. We investigated whether the size of the pores affects the physical properties of the PDMS sponge. When preparing the PDMS sponge, the difference in pore size was made using various particle sizes of sugar. Scanning Electron Microscopy (SEM) in the figure 5 exhibits the various pore of PDMS sponge. As a result, the average pore sizes of various PDMS sponge are 698.8 μm, 162.54 μm, 145.65 μm. (Figure 6a-c). Also, the average pore size confirmed from the SEM images were 53 μm, 135 μm, and 250 μm, respectively (Figure 6d-f). After that, the potential of various pore sizes was measured by having temperature difference (Figure 7a), and conductivity also was measured (Figure 7b). As a result, as the size of pores is smaller, the penetration of ions could move more densely along the polymer chain, so the voltage and ion conductivity were further increased. [45].

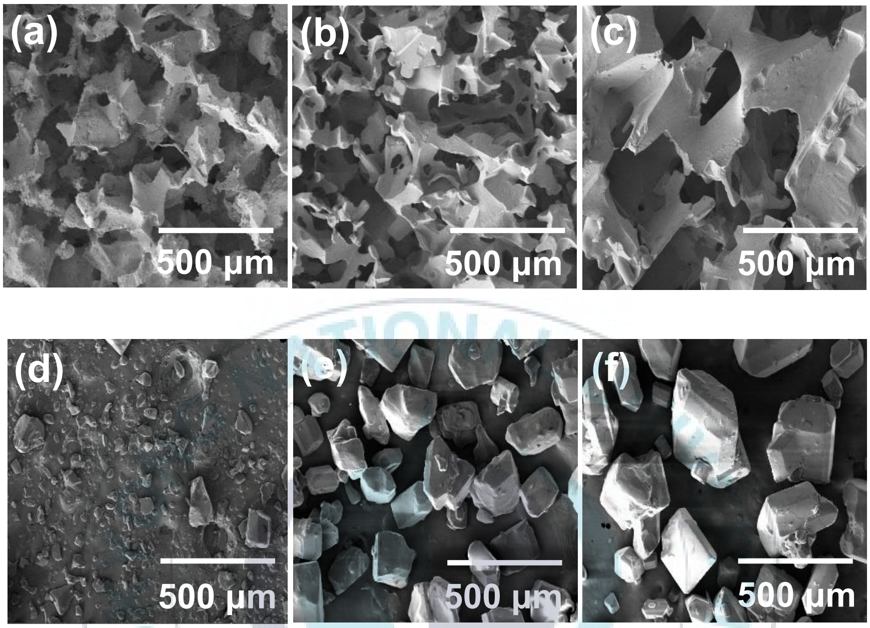

Figure 6. Morphology of PDMS sponges for (a) large, (b) medium, (c) small pore sizes. SEM images of the sugar particles. (d) large (e) medium (f) small size of sugar particles.

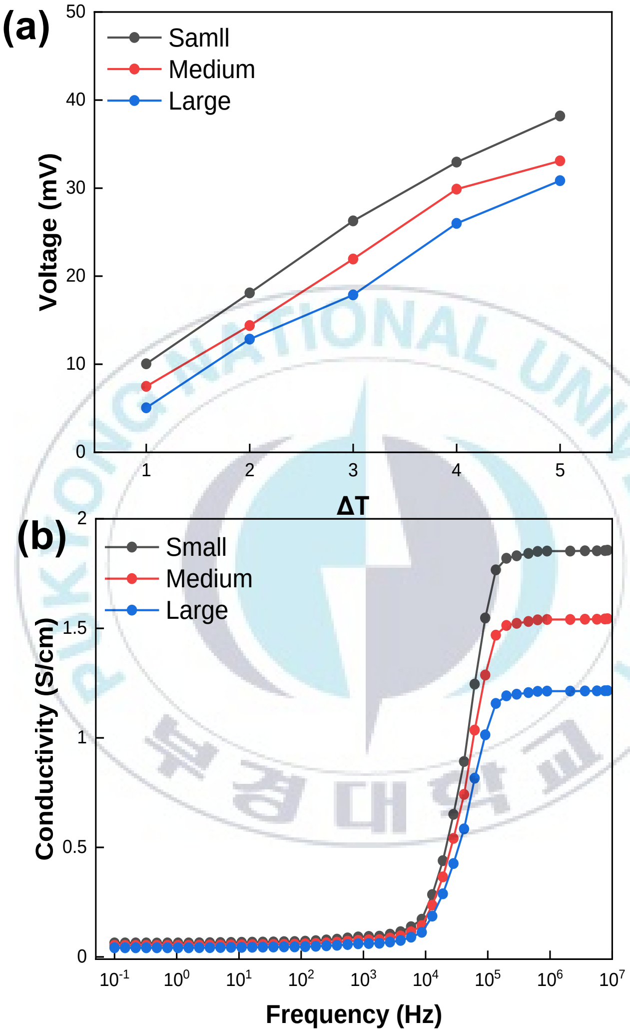

Figure 7. The potential (a) of PDMS sponges and ion conductivity (b) for large, medium, small size of sugar particles.

II-3.3. Thermoelectric Effect of PDA/PDMS/PE Sponge

The enhanced thermoelectric effect was investigated by inserting an polyelectrolyte into the PDA/PDMS sponge. [46]. Thermoelectric effects were induced by coating polydopamine on PDMS/PE sponge samples with temperature difference and polyelectrolyte concentration. [47]. Firstly, thermal conduction characteristics in the existence or nonexistence of polyelectrolyte in the PDA/PDMS sponge was examined. In figure 8, the potential of PDA/PDMS sponge and weight transition for with polyelectrolyte and without polyelectrolyte. The difference in the existence or nonexistence of polyelectrolytes had a great influence on the potential. When the temperature difference is 5 ℃, the potential of PDA/PDMS sponge without polyelectrolytes had 6.09 mV and PDA/PDMS sponge with polyelectrolyte had 38.04 mV. Furthermore, the weight transition of PDA/PDMS/PE sponge was big difference. PDA/PDMS sponge before inserted polyelectrolytes had 0.84 g and PDA/PDMS sponge after inserted polyelectrolytes had 1. 47 g. It can be found that the electrolytes are well inserted into the pores of the porous PDA/PDMS sponge.

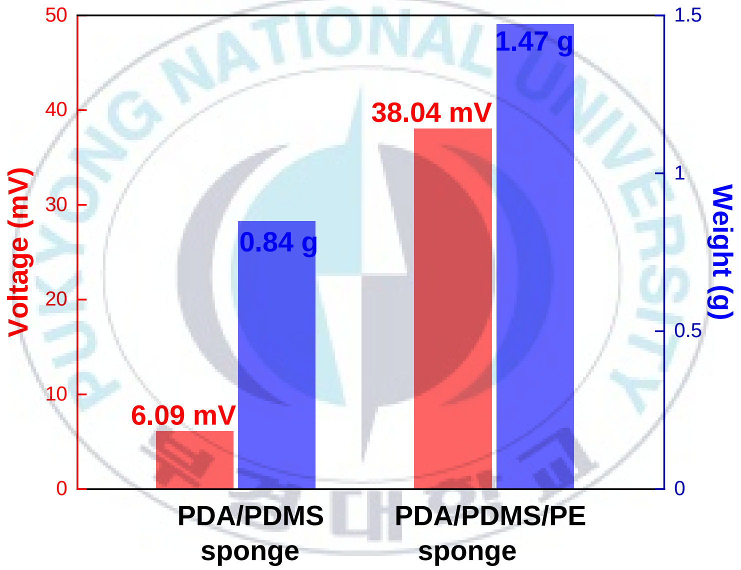

Figure 8. The potential of PDMS sponges and weight transition for with polyelectrolyte and without polyelectrolyte.

Polydopamine nanoparticles were added to the polyelectrolyte to measure whether the conductivity was improved. Firstly, the conductivity of various solutions was measured. In figure 9, the conductivity according to the dopamine coating time was measured at PDMS/PE sponge. It was shown that the longer the time of dipping in polydopamine, the better the conductivity value. The reason why the conductivity was increased as the dipping time is that the content of polydopamine on the surface was increased, so that the polyelectrolyte ion becomes easily moved. In order to analyze the effect of dipping dopamine time, polydopamine nanoparticles (PDA NPs) were prepared. As shown in the Scanning Electron Microscopy (SEM) image (Figure 10a), PDA particle size was approximately between 141 nm and 143 nm. It had an average diameter of 141 nm by calculating various particle sizes. The DLS of PDA NPs was measured by dispersing in DI water at 0.1 wt%, and the PDA diameter size has 141nm (Figure 10b).

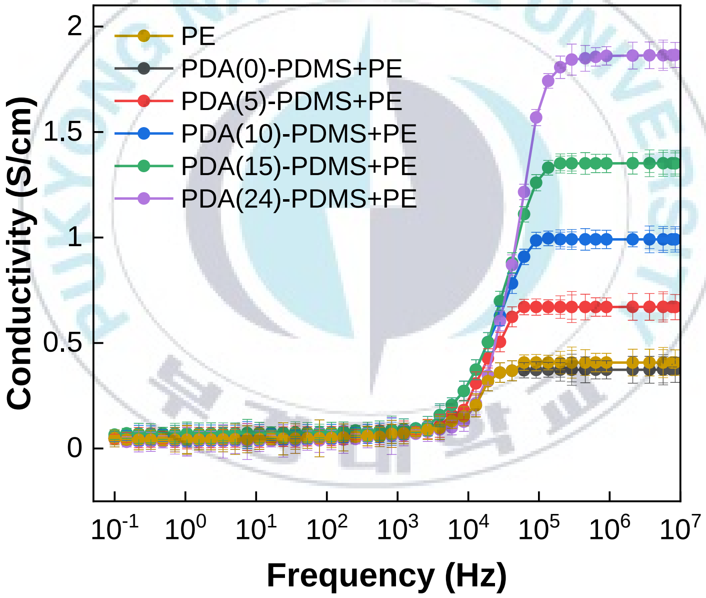

Figure 9. The conductivity depending on coating PDA NPs from PDMS/PE sponge.

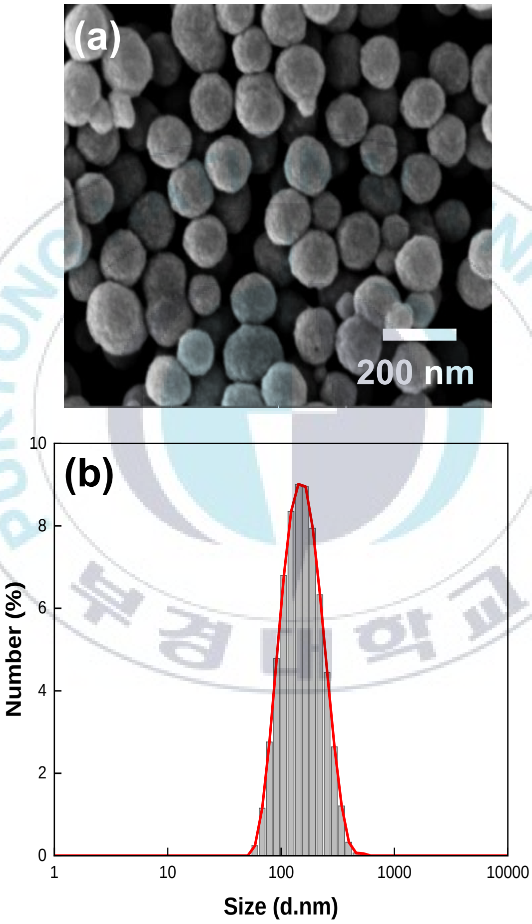

Figure 10. The analysis of Polydopamine (PDA) NPs by (a) SEM image, (b) DLS histogram.

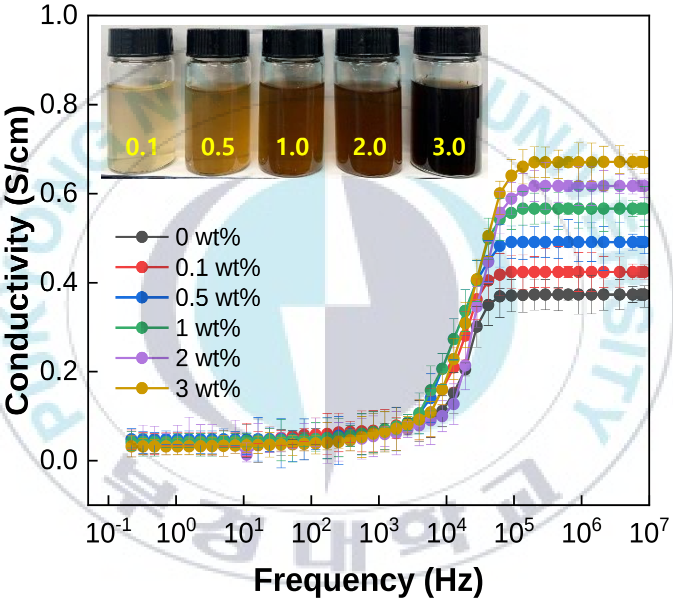

Figure 11. The conductivity of polyelectrolytes with Polydopamine NPs.

The thermal conductivity of the PE, PDA/PDMS sponge and PDA/PDMS/PE sponge was shown in Figure 12. In the thermal conductivity measurement method, a sample was placed between two plates (hot and cold plate), and the amount of heat passing through the sample is measured by a calibrated heat flux transducer. For the high performance of thermoelectric materials, the thermoelectric material must have a high electrical conductivity and a high Seebeck coefficient and a low thermal conductivity. The thermal conductivity was measured at room temperature, and the the PDA/PDMS/PE sponge was the 0.6726 W/mK, the PDA/PDMS sponge was 0.1973 W/mK, the PE was 1.3736 W/mK. As the thermoelectric performance of the PDA/PDMS/PE sponge was the lowest, it was confirmed that the thermal conductivity was the highest.

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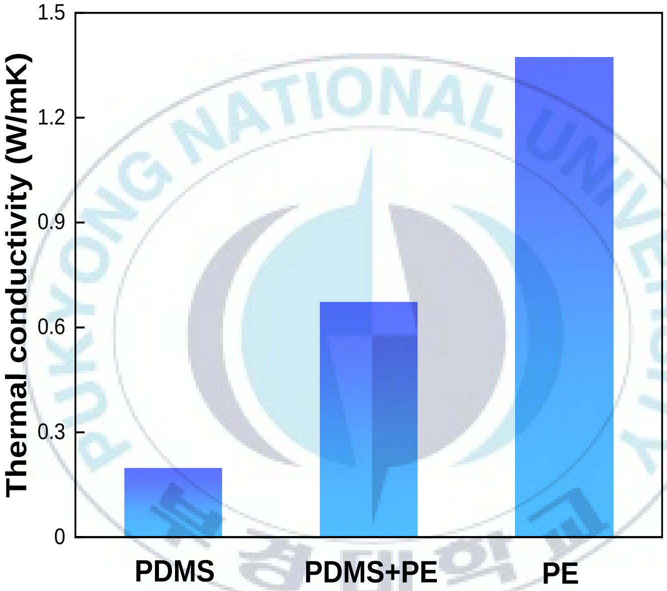

Figure 12. The thermal conductivity of PE, PDA/PDMS sponge and PDA/PDMS/PE sponge.

We introduced the method when measuring the potential during having the temperature difference. In figure 13, the Keithley was used to measure potential and conductivity. The power supply maintained the cold block temperature, thermocouple reader was recorded the temperature and the Keithley was applied voltage. Here, as the voltage was adjusted and increased, a temperature difference occurred due to the potential difference. After putting the PDA/PDMS/PE sponge between the two electrodes where the temperature difference occurred and measured the potential. [48]. As a result, the PDA/PDMS/PE sponge according to dopamine coating time was measured. It showed that the volatility steadily increased over time (Figure 14a). In figure 15b, it was the potential over time from Δt=0 ℃ to Δt=5 ℃. As the temperature difference increased, the potential rapidly increased linearly. The values of thermoelectric characteristics measured up to this study were summarized in a table 2. In order to increase thermoelectric characteristics, the ion conductivity and the Seebeck coefficient must be high, the thermal conductivity must be low. So the ZT value must be high too. In table 2, it can be seen that the ZT value improved as the dopamine coating time increased.

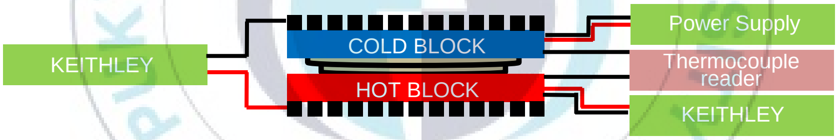

Figure 13. Schematic diagram of measurement potential.

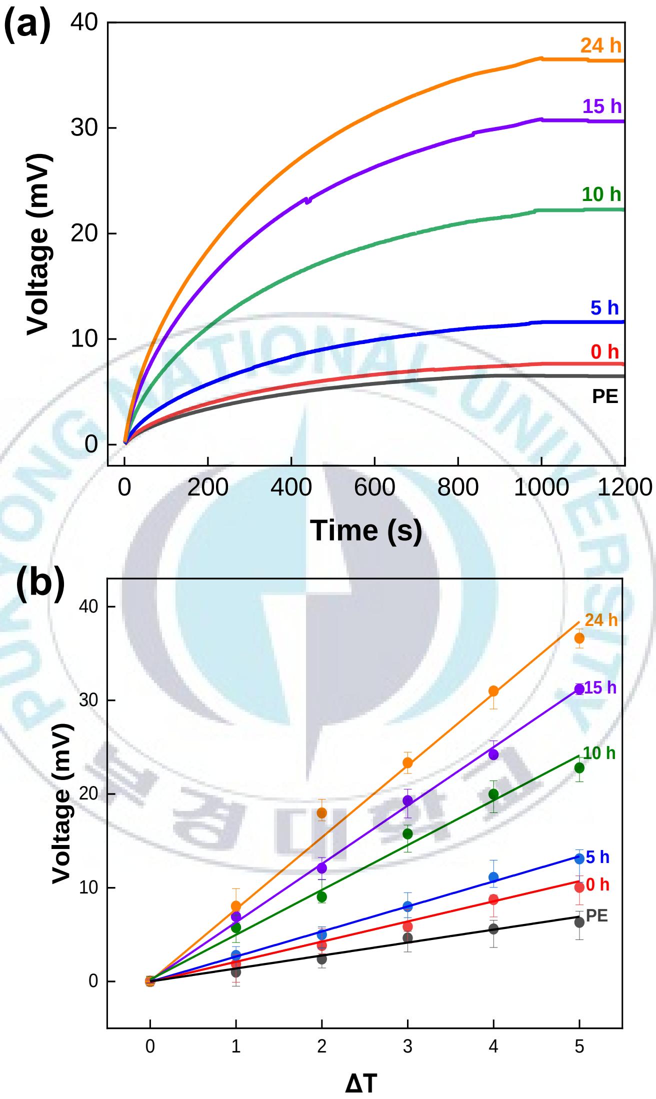

Figure 14. Output performance of PDMS sponge with increasing dipping time in PDA NPs solution: (a) Potential of PDMS with difference of coating PDA, (b) potential with temperature difference from 0 °C to 5 °C.

Table 2. The thermoelectric readings depending on coated PDA NPs time.

Sample	Ion conductivity (S/cm)	Thermal conductivity (W/mK)	Seebeck coefficient (mV/K)	ZT
PDA(0)/PDMS/PE	**0.042**	**0.109**	**2.020**	**0.009**
PDA(5)/PDMS/PE	**0.075**	**0.101**	**2.410**	**0.023**
PDA(10)/PDMS/PE	**0.109**	**0.097**	**4.203**	**0.136**
PDA(15)/PDMS/PE	**0.143**	**0.076**	**6.401**	**0.317**
PDA(24)/PDMS/PE	**0.183**	**0.058**	**7.580**	**0.587**

II-4. Conclusion

In this study, we prepared the PDMS-based sponge, coated with dopamine, and inserted a polyelectrolyte into the pores. The pores in PDA/PDMS sponge were acted to facilitate ion movement of the electrolyte. The polymer chain of the PEO electrolyte serves as a bridge, and the nitrogen ions and sodium ions could be easily moved because polydopamine coated on the surface of the PDMS sponge. The thermoelectric characteristics were examined by applying a temperature difference to both sides of the sponge and become stronger as the temperature difference increased. Furthermore, the concentration of the polyelectrolyte and the dopamine coating time also had an effect on the thermoelectric characteristics. To improve the performance of the device, we will change the kinds of the polyelectrolyte and various surface modification.

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