

Novel Preparation of Poly(3,4-ethylene dioxythiophene)-Poly(styrenesulfonate)-Protected Noble Metal Nanoparticles as Organic-Inorganic Hybrid Thermoelectric Materials

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Abstract: Here, we describe a novel synthetic method of PEDOT-PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate))-protected Ag, Au and Pd nanoparticles(NPs) by a simple procedure, and thermoelectric properties of the PEDOT-PSS films doped with these NPs. Interestingly, PEDOT-PSS films containing small amount of PEDOT-PSS-protected Ag NPs showed a higher electrical conductivity than that of pure PEDOT-PSS. As a result, the PEDOT-PSS protected Ag NPs system showed a high in-plane power factor ($35.2 \mu\text{W m}^{-1} \text{K}^{-2}$), which was relatively superior to that of conventional metal nanomaterial systems. Thus, we have succeeded in development of high performance organic-inorganic thermoelectric conversion films.

Key words: Conductive polymer, Electrical conductivity enhancement, Metal nanoparticles, Thermoelectric materials

1. Introduction

We depend on the non-renewable energy sources such as fossil fuels; this is essential to life. However, fossil fuel-derived CO_2 is enormous and a factor that promotes global warming. The consumption of fossil fuel is accelerated increasingly with world's population growth in the future, and worldwide demand for renewable energy (*e.g.*, natural heat, sunlight, wind) is expected to expand.^{1,2)} Therefore, new energy production methods without CO_2 emission are required for the realization of a clean energy and sustainable society.³⁾ Recently, development of thermoelectric conversion materials that convert thermal energy into electric energy attracts considerable attention. These materials have the potential to increase energy efficiency and to reduce CO_2 emissions significantly.⁴⁾ Power generation of these materials derive from the Seebeck effect, which is caused by charge carriers (*e.g.*, electrons, holes) in the metal or semiconductor material at the absolute temperature gradient: charge carriers diffuse from hot side to cold side, resulting in a current flow through the closed circuit.⁵⁾ Thermoelectric conversion efficiency is defined as the dimensionless figure of merit ZT value.

$$ZT = (S^2 \sigma / \kappa) T$$

where S , σ , κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Thermoelectric materials with high ZT and Power Factor $PF (= S^2 \sigma)$ are desirable, yet there remains a trade-off between σ and S . Generally, inorganic thermoelectric materials exhibit a large Seebeck coefficient

as well as high electrical conductivity, high ZT values have been obtained (*e.g.*, SnSe ; $ZT = 2.6$,⁶⁾ $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$; $ZT = 2.4$ ⁷⁾). Nevertheless, their weight, rigidity and poor processability have limited widespread application: it is very difficult to scale up large area modules. Meanwhile, a thermoelectric conversion element composed of organic materials with electronic carriers such as conductive polymers^{8,9)} has advantages of light weight, mechanical flexibility, low cost, and is a material with extremely high potential.^{10,11)} Furthermore, large area modules can be formed by the printing method expected to have high productivity.¹²⁾ Since we reported that stretched polyphenylenevinylene derivatives with $ZT = 0.1$ in 2007,¹³⁾ many researchers have been working on the development of organic thermoelectric materials using conductive polymers.^{14,15)} In particular, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) provides a lot of convenience (*e.g.*, high conductivity, transparency, and excellent stability) and has been actively studied in recent years.¹⁶⁾ According to Pipe's study, the doped level optimized PEDOT-PSS film recorded $ZT=0.42$.¹⁷⁾ Cahill and coworkers reported that the in-plane ZT value of this work was about 0.1.¹⁸⁾ In the future, this ZT value needs to be improved to 2.0–4.0; for the effective use of huge unused thermal energy like natural heat and waste heat below 150 °C.¹⁹⁾

Our group has been interested in carbon nanotube or conductive polymer-metal nanoparticles (NPs) hybrid thermoelectric materials.^{20–22)} Hybridization²³⁾ of conductive polymers such as polyaniline (PANi)²⁴⁾ and PEDOT-PSS,²⁵⁾ with inorganic NPs can improve the

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thermoelectric performance of conductive polymers by utilizing the low thermal conductivity of organic constituents and high Seebeck coefficient of inorganic constituents. However, there is no systematic knowledge about the enhancement mechanism. To enhance carrier hopping between conductive polymers, we focus on conductive PEDOT-PSS-protected metal NPs of Ag, Au, and Pd (*i.e.*, noble metal elements) with excellent electrical conductivities^{26,27} and interesting chemical properties,²⁸⁻³⁰ because direct hybridization of PEDOT-PSS with various metal NPs is expected to lead to acceleration of the hopping between PEDOT molecules by direct contact of PEDOT-PSS with metal NPs. In addition, methods for systematically preparing metal NPs protected with conductive polymers have not been reported until now.

Herein, we report on a novel synthetic method of PEDOT-PSS-protected Ag NPs, PEDOT-PSS-protected Au NPs and PEDOT-PSS-protected Pd NPs by a simple procedure of treating noble metal ion in PEDOT-PSS aqueous solution under mild conditions. We also describe the fabrication, thermoelectric properties of PEDOT-PSS hybrid films containing Ag, Au and Pd NPs, and new insights into higher thermoelectric performances than that of insulating poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Ag NPs.

2. Experimental

Materials

Silver perchlorate (AgClO_4) was purchased from Kojima Chemicals Co., Ltd. Hydrogen tetrachloroaurate(III), tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), palladium(II) chloride (PdCl_2), sodium borohydride, hydrochloric acid, nitric acid, sulfuric acid, hydrogen peroxide, silver standard solution (1,000 ppm), gold standard solution (1,000 ppm), palladium standard solution (1,000 ppm), and poly(*N*-vinyl-2-pyrrolidone) (PVP, MW $\approx$ 40000) were purchased from Wako Pure Chemical Industries, Ltd. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) aqueous solution (CleviosTM PH1000; 1 : 2.5 = PEDOT : PSS ratio (w/w)) was purchased from H.C. Starck, the solid content was 1.0–1.3 wt% in water. Polyimide film was kindly supplied by UBE Industries, Ltd., Japan. All chemicals were used without any further purification. Deionized water (18.2 M Ω ·cm) was used for all aqueous solutions.

PEDOT-PSS-protected noble metal NPs

The PEDOT-PSS-protected noble metal NPs were synthesized by a chemical reduction method. The nominal molar ratio (R), PEDOT-PSS (monomer unit of PEDOT-PSS: 657.645 g/mol) / metal precursor, was 1.6. A solution of AgClO_4 (0.132 mmol, 27.4 mg) in 200 mL PH1000/water ($v/v=1/13.6$, 0.207 mmol in PEDOT-PSS monomer unit) was stirred under N_2 atmosphere in an ice-water bath at 0 °C for 1 h. Then, an aqueous solution of NaBH_4 (10 mL, 33 mM, 0 °C) was rapidly injected into the solution, and the mixture was stirred in an ice-water bath at 0 °C for 1 h, then characterized by Ultraviolet-Visible (UV-Vis) absorbance measurement. Thus prepared Ag NPs dispersion was purified by filtration with an ultrafilter membrane (Advantec, Q01000 76E, a cutoff molecular weight:

10000) and by washing with water to remove by-produced ions. The PEDOT-PSS aggregates dispersed in the solution were removed using a glass filter (Pyrex iwaki glass 17G4, pore size: 5–10 μm). The PEDOT-PSS-protected Ag NPs were finally obtained as bulk materials after removal of the solvent by using a rotary evaporator followed by vacuum drying at 40 °C. The PEDOT-PSS-protected Au NPs and PEDOT-PSS-protected Pd NPs were prepared in the similar manner.

Structural characterization of PEDOT-PSS-protected noble metal NPs

UV-Vis absorption spectra of PEDOT-PSS-protected noble metal colloidal dispersions were measured with a Shimadzu UV-2500PC recording spectrophotometer using a quartz cell with 10 mm of optical path length. Transmission electron microscopy (TEM) images were observed with a JEM 1230 instrument (JEOL, Tokyo, Japan) at accelerated voltage of 80 kV. A colloidal dispersion solution 5 mg/L was obtained by dissolving the resultant bulk materials in water using Sonifier II model 250D ultrasonic homogenizer (Branson Ultrasonic, Emerson, Japan, Ltd.). The TEM sample was prepared by dropping the dispersion solution onto copper grids coated with a thin carbon film. The metal contents of PEDOT-PSS-protected noble metal NPs were determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES, Varian 720-ES). For this purpose, the samples were solubilized in aqua regia (HCl/HNO_3) or piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$). ICP results showed that the metal content of Ag, Au and Pd NPs of the bulk materials were 2.4, 12.9 and 6.0wt%, respectively.

Preparation of PVP-protected Ag NPs

The PVP-protected noble metal NPs were synthesized by a chemical reduction method.^{31,32} The nominal molar ratio, R=PVP (monomer unit of PVP: 114.14 g/mol) / metal precursor was 1.6. A solution of AgClO_4 (0.528 mmol, 109.46 mg) in 800 mL PVP (0.83 mmol in PVP monomer unit) was stirred under N_2 atmosphere in an ice-water bath at 0 °C for 1 h. Then, an aqueous solution of NaBH_4 (10 mL, 132 mM, 0 °C) was rapidly injected into the solution, and the mixture was stirred in an ice-water bath at 0 °C for 1 h, then characterized by UV-Vis absorbance measurement. The mean diameters of NPs were determined from the TEM images to be 3.4 ± 1.2 nm. These results were consistent with the previous report.³¹ The Ag amount was estimated by ICP measurement to be 0.58 mg/mL.

Fabrication and evaluation of PEDOT-PSS-protected noble metal film

The PEDOT-PSS films containing various weight ratios of Ag NPs were prepared by the drop-casted method. PEDOT-PSS aqueous solutions (CleviosTM PH1000) containing 0.01–5.0 wt% of Ag NPs were sonicated (Ultrasonic Cleaner, TAITEC) for 30 min. Homogeneous Ag NPs dispersions with different weight ratios of solids were obtained. One of Ag NPs dispersion (0.8 mL/cm²) was drop-casted on a polyimide sheet, which was placed in a hot plate at 40 °C for 12 h. Then, the surface of the film was covered with a small

amount of ethyleneglycol (0.24 mL/cm^2), dried at 90°C for 12 h and then at 130°C for 30 min,^{33,34} resulting in dry PEDOT-PSS-protected Ag NPs film with a $5.0 \pm 1.0 \mu\text{m}$ thickness. The PEDOT-PSS film, PEDOT-PSS film containing Au NPs, Pd NPs and PVP-protected Ag NPs were prepared in the similar manner. The in-plane thermoelectric properties of the thermoelectric conversion films were measured at least 5 times each with a ULVAC ZEM-3 M8 instrument (ULVAC-RIKO Inc., Yokohama, Kanagawa, Japan) purged with He at 330–390 K.

3. Results and Discussion

Figure 1 shows the UV-Vis spectra of (a) PEDOT-PSS solution, (b) PEDOT-PSS-protected Ag NPs, (c) PEDOT-PSS-protected Au NPs and (d) PEDOT-PSS-protected Pd NPs, respectively. The color of PEDOT-PSS solution as blank sample was royal blue and the absorbance increased in the wavelength range above 500 nm. On the other hand, the solution of PEDOT-PSS-protected Ag NPs showed a peak at around 400 nm, which represents the surface plasmon resonance excitation of Ag NPs.³⁵ Moreover, the PEDOT-PSS-protected Au NPs showed a dominant peak of an absorbance maximum at 540 nm, which is attributed to the plasmon resonance of the Au NPs.³⁶ These observations clearly demonstrate the formation of Ag NPs in the PEDOT-PSS aqueous solution. In the PEDOT-PSS-protected Pd NPs system, no significant absorption peak was found on the spectra of the solution treated with NaBH_4 . However, the absorption in the ultraviolet-visible region increased, suggesting that the Pd NPs were formed.³⁷

Size and shape of the PEDOT-PSS-protected noble metal NPs were further confirmed by TEM observation. TEM images of the PEDOT-PSS-protected Ag NPs, PEDOT-PSS-protected Au NPs and PEDOT-PSS-protected Pd NPs in Figure 2 (a)–(c), respectively, showed the formation of spherical NPs with a relatively narrow size dispersion. The mean diameters of the NPs were determined

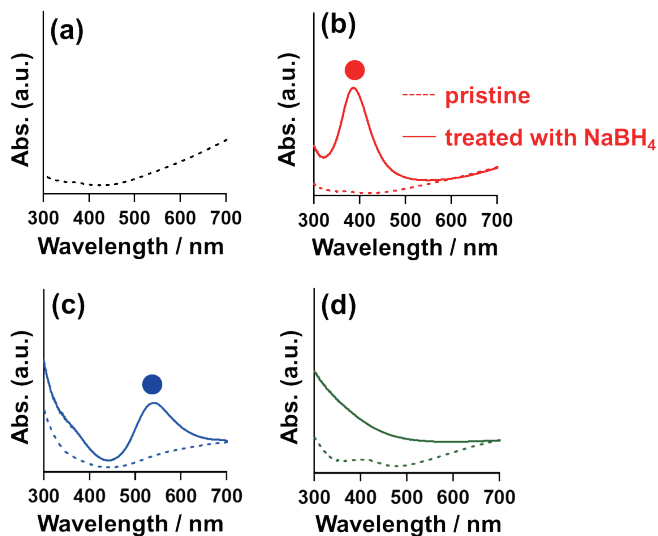


Figure 1 UV-Vis spectra of (a) PEDOT-PSS solution, (b) PEDOT-PSS-protected Ag NPs, (c) PEDOT-PSS-protected Au NPs and (d) PEDOT-PSS-protected Pd NPs dispersion. Broken and solid curves indicate pristine and treated with NaBH_4 , respectively.

from the TEM images to be (d) $3.9 \pm 1.2 \text{ nm}$, (e) $4.5 \pm 1.5 \text{ nm}$, and (f) $3.9 \pm 1.3 \text{ nm}$. These mean diameters were estimated by averaging over 200 particles. There has been no study that tried to systematically prepare conductive polymer-protected metal NPs with a particle diameter on the order of nanometers.^{38,39} In this work, PEDOT-PSS-protected Ag NPs, PEDOT-PSS-protected Au NPs and PEDOT-PSS-protected Pd NPs of single dispersion and the small particle size were prepared by a chemical reduction method.

We investigated the thermoelectric properties of PEDOT-PSS film containing conductive PEDOT-PSS-protected Ag NPs and insulating PVP-protected Ag NPs using Seebeck coefficient / electric resistance measurement system. Figure 3 summarizes (a) Seebeck coefficient S , (b) electrical conductivity σ , and (c) power factor $PF (=S^2\sigma)$ at 345 K of PEDOT-PSS films containing various weight ratios of Ag NPs. All the films exhibited p-type conduction and the Seebeck coefficient of approximately $18.5 \mu\text{V K}^{-1}$ in each Ag NPs concentration region. The electric conductivity value was higher in PEDOT-PSS system than in PVP system for 0.01 to 1.0 wt% Ag NPs concentration. The highest power factor, $32 \mu\text{W m}^{-1} \text{K}^{-2}$ was observed at 0.01 wt% of Ag NPs; the carrier flow within the film accelerated by adding a small amount of conductive PEDOT-PSS protected Ag NPs. On the other hand, thermoelectric characteristics were not improved by the addition of insulating PVP-protected Ag NPs. We previously reported the thermoelectric properties of PEDOT-PSS films containing surfactants or polymer-protected metal nanomaterials (e.g., Au NPs or nanorods and Ag nanowires).^{25,40}

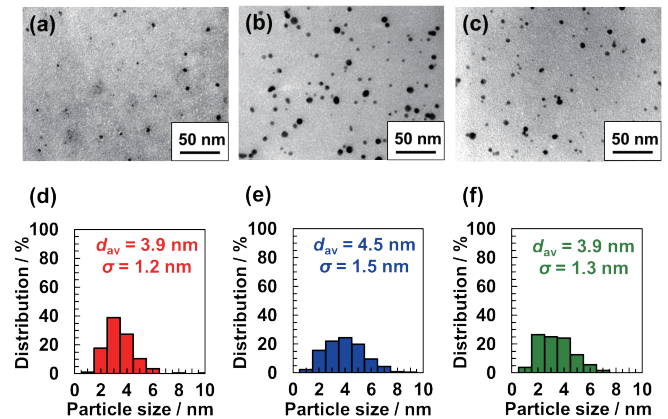


Figure 2 TEM image and size distribution histograms of PEDOT-PSS-protected Ag NPs (a and d), PEDOT-PSS-protected Au NPs (b and e) and PEDOT-PSS-protected Pd NPs (c and f), respectively.

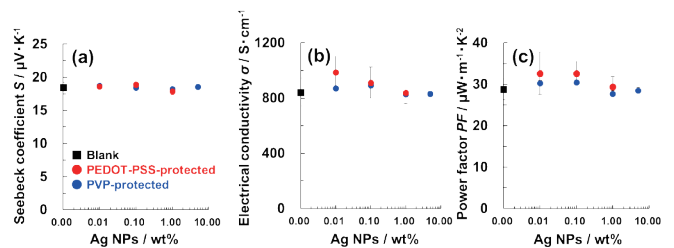


Figure 3 (a) Seebeck coefficient, (b) electrical conductivity and (c) thermoelectric power factor at 345 K of PEDOT-PSS film (black) and PEDOT-PSS film containing various weight ratio Ag NPs with PEDOT-PSS (red) or PEDOT-PSS film including Ag NPs with PVP (blue).

The Seebeck coefficient of films containing the metal nanomaterial with the insulating layer decreased with increasing metal concentration, while the electrical conductivity increased, *i.e.*, power factor improved. This suggested that the insulating protective agents on the metal surface prevent contact of the metal nanomaterial with PEDOT conductive polymers. On the basis of these results, higher thermoelectric performances are also expected to be realized by employing the conductive polymer-protected nanomaterials.

We next prepared the PEDOT-PSS film containing various amount of Ag NPs and investigated their thermoelectric performance testing. Seebeck coefficient, electrical conductivity, and power factor at 330–380 K of PEDOT-PSS films containing Ag NPs of various weight ratios are shown in Figure 4 (a)–(c), respectively. The Seebeck coefficients of these films gradually increased with the temperature up to around 390 K. The electrical conductivity of these sample slightly decreased *i.e.*, negative slope in σ vs. T . This is an indication of metal-like behavior, as evident from the previous reports.^{41–43} The electrical conductivity dramatically increased from 827 to 1002 S/cm with the increase of Ag NPs content from 0.0 to 0.01wt% at 380 K. As a result, the power factor of PEDOT-PSS film containing 0.01wt% Ag NPs was around 12% higher than that of pure PEDOT-PSS film ($35.2 \mu\text{W m}^{-1} \text{K}^{-2}$). Surprisingly, the thermoelectric properties were greatly improved by adding only a small amount of Ag NPs to PEDOT-PSS film. However, when the Ag NPs concentration further increased to 1.0wt%, the electrical conductivity rather decreased and thermoelectric power factor thereby decreased. We think that an increase in Ag NPs content hinder the packing of the PEDOT molecules necessary for keeping the electrical conduction of the polymer film.

Furthermore, we investigated the temperature dependence of thermoelectric performance for PEDOT-PSS film containing 0.01wt% of Au NPs with PEDOT-PSS and PEDOT-PSS film containing 0.01wt% of Pd NPs with PEDOT-PSS. Figure 5 shows (a) Seebeck coefficient, (b) electrical conductivity and (c) thermoelectric power factor for the prepared films. The Seebeck coefficient decreased only slightly with metal NPs. The electrical conductivity of PEDOT-PSS film dramatically increased with Ag NPs or Au NPs. The electrical conductivities of PEDOT-PSS films containing 0.01wt%, 0.1 wt%, and 1.0 wt% of Au NPs at 345 K were 919 S/cm, 874 S/cm, and 853 S/cm, respectively. In the addition of Au NPs, the same tendency was observed in the case of PEDOT-PSS film containing Ag NPs, as shown in Figure 4 (b). Meanwhile, when Pd NPs

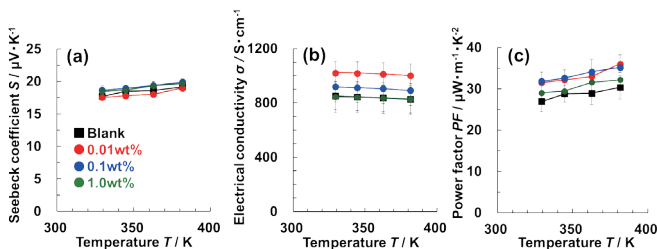


Figure 4 Temperature dependence of (a) Seebeck coefficient, (b) electrical conductivity and (c) thermoelectric power factor for PEDOT-PSS (black) and PEDOT-PSS films with 0.01wt% (red), 0.1wt% (blue), 1.0wt% (green) Ag NPs, respectively.

were added, the increase in electrical conductivity was small. Namely, the electrical conductivity of PEDOT-PSS film increased with metal NPs in the order of $\text{Ag} > \text{Au} > \text{Pd}$. This order corresponds well with the order of the electrical conductivity of these metals, *i.e.*, $\text{Ag} > \text{Au} > \text{Pd}$. This result showed that the properties of the metal in the PEDOT-PSS-protected metal NPs contributed to the increase in electric conductivity of the PEDOT-PSS film. Temperature dependent conductivity measurements were the most direct way to study experimentally the thermoelectric properties and conduction mechanism in a conjugated polymeric materials. The charge transport in the ethyleneglycol-treated PEDOT-PSS film is identified as a one-dimensional variable range hopping (1D VRH) model.⁴⁴⁾

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/2}] \dots (1)$$

In equation (1), σ_0 is the conductivity at infinite temperature, T_0 is the energy barrier between localized states. The temperature dependent electrical conductivity in the range of 330 K < T < 380 K were fitted by 1D VRH model, the Figure 6 shows the plots of $\ln(\sigma)$ vs. $T^{-1/2}$ for pure PEDOT-PSS film and PEDOT-PSS film containing 0.01wt% of Ag NPs film. According to the analyses of the data, the T_0 value of pure PEDOT-PSS film and PEDOT-PSS film containing 0.01wt% of Ag NPs film are 63 K and 28 K, respectively. Because these results implies that the carrier hopping barrier decreases, *i.e.* the electrical conductivity increases,⁴⁵⁾ in the Ag NPs system, PEDOT-PSS-protected Ag NPs entered between the PEDOT molecules promoted one-dimensional carrier conduction within PEDOT-PSS film.

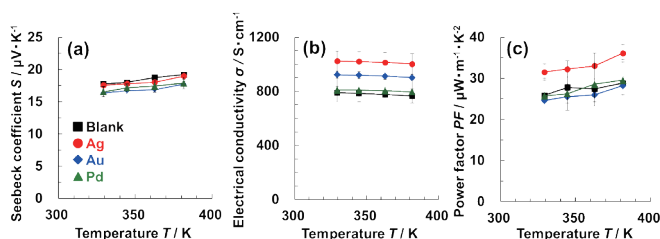


Figure 5 Thermoelectric parameters as a function of temperature for PEDOT-PSS film including 0.01wt% Ag NPs (red), PEDOT-PSS film containing 0.01wt% Au NPs (blue) and PEDOT-PSS film including 0.01wt% Pd NPs (green): (a) Seebeck coefficient, (b) electrical conductivity and (c) thermoelectric power factor, respectively.

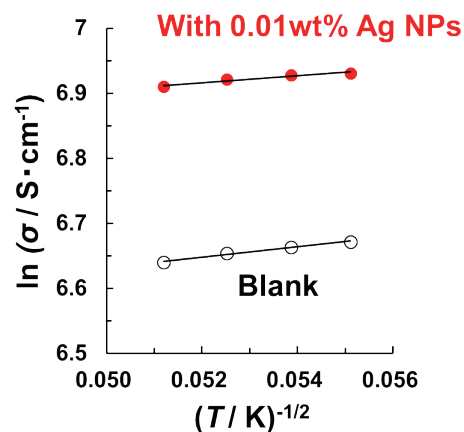


Figure 6 Dependence of natural logarithm of conductivity versus T for PEDOT-PSS (black) and PEDOT-PSS with 0.01wt% Ag NPs (red).

Additionally, the thermoelectric performances in this works were compared with that of PANi system. The electrical conductivities at 325 K for PEDOT-PSS or PANi-metal NPs system in this and previous studies are summarized in Figure 7. As in the case of PEDOT-PSS system, addition of conductive polymer-protected metal NPs (*i.e.*, PANi-protected Au NPs) promoted current-flow in the conductive polymer film also in the PANi system. This indicates that the utilization of the hybridization of conductive polymer films and conductive polymer-protected metal NPs probably achieve higher electrical conductivity. From these results, the conductive polymer-protected metal NPs could be expected to function as charge transport promoter between the conductive polymer chains within organic thermoelectric conversion film. In this study, we designed a suitable metal-conductive polymer interface within thermoelectric conversion film and realized smooth carrier transport by using a small amount of PEDOT-PSS-protected Ag NPs.

4. Summary

In conclusion, we have succeeded in the fabricating an organic-inorganic hybrid thermoelectric materials consisting of PEDOT-PSS molecules and PEDOT-PSS protected noble metal NPs, *i.e.* Ag, Au and Pd, prepared by simple and convenient method. The electrical conductivity of PEDOT-PSS film significantly increased by adding PEDOT-PSS-protected Ag NPs, while thermoelectric power factor was enhanced. Surprisingly, we have demonstrated the optimized fabrication and interfacial carrier transport of metal nanomaterial-PEDOT-PSS hybrid films with high performance. That is, fabrication of conductive polymer-metal NPs hybrid material is a promising method for improving the thermoelectric performance of conductive polymers. These results present an important example for the control and understanding of carrier transport within organic thermoelectric conversion materials, and provides a guiding principle of the improved thermoelectric devices for the realization of sustainable society.

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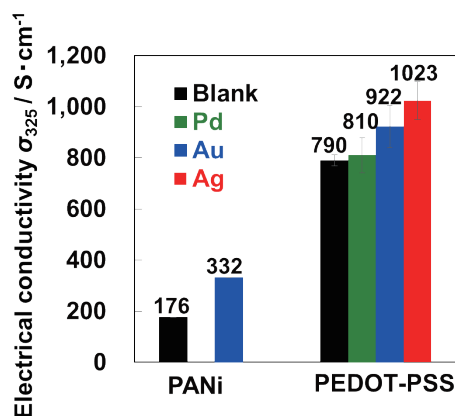


Figure 7 Electrical conductivity at 325 K of PANi or PEDOT-PSS (black) films with 0.01 wt% Ag NPs (red), PEDOT-PSS film with 0.01 wt% Au NPs (blue) and PEDOT-PSS film with 0.01 wt% Pd NPs (green), respectively.

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