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Organic Thermoelectric Materials Composed of Conducting Polymers and Metal Nanoparticles

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Organic thermoelectric materials consisting of conducting polymers have received much attention recently because of their advantages such as wide availability of carbon, easy syntheses, easy processing, flexible devices, low cost, and low thermal conductivity. Nevertheless, their thermoelectric performance is still not good enough for practical use. To improve their performance, we present herein new kinds of hybrids of organic conducting polymers and metal nanoparticles (NPs). Since hybridization of polyaniline with poly-(*N*-vinyl-2-pyrrolidone) (PVP)-protected Au NPs decreased the electrical conductivity of polyaniline films from 150 S cm^{-1} to 50 S cm^{-1}, we carried out direct hybridization of polyaniline with Au NPs without PVP in this study. Direct hybridization improved the electrical conductivity to as high as 330 S cm^{-1} at 50°C while keeping the Seebeck coefficient at 15 $\mu\text{V m}^{-1}\text{ K}^{-2}$. Poly(3,4-ethylenedioxythiophene) (PEDOT) is another promising conducting polymer. Here, we used hybrid films of PEDOT with Au NPs protected by two kinds of ligands, terthiophenethiol and dodecanethiol (DT), revealing that the hybrid of PEDOT with DT-protected Au NPs showed better thermoelectric performance than pristine PEDOT without Au NPs. Addition of DT-protected Au NPs improved the electrical conductivity of the PEDOT films from 104 S cm^{-1} to 241 S cm^{-1} and the thermoelectric figure of merit from 0.62×10^{-2} to 1.63×10^{-2} at 50°C.

Key words: Hybrid thermoelectric materials, organic thermoelectric materials, Au nanoparticles, conducting polymer, polyaniline, PEDOT

INTRODUCTION

Conjugated polymers are attracting attention as promising materials for electronic devices due to their photophysical properties and electrical conductivity. In comparison with other polymers, conjugated polymers exhibit conducting or semiconducting behavior and thus serve to develop materials for light-emitting diodes, photovoltaics, and thermoelectrics.[1,2]

Organic thermoelectric materials composed of conjugated conducting polymers have advantages of high flexibility and low cost due to their easy processing and the wide availability of carbon. In contrast, poor thermoelectric performance is a weak point of organic thermoelectric materials. A decade ago, the dimensionless thermoelectric figure of merit ZT was 10^{-4} for polyanilines,[3–5] 4 years ago, 0.1 was achieved by us for polyphenylenevinylene,[6,7] and in the last year, hybrid films of polyaniline and bismuth(III) telluride nanoparticles (NPs) were reported.[8] In addition, an increasing number of reports on the thermoelectric performance of conducting polymers[9–12] and their hybrids[13–20] have been published recently. Here, we propose for the first time that the combination of conducting polymers, polyanilines or polythiophene derivatives, with gold (Au) NPs could offer improved thermoelectric performance.

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EXPERIMENTAL PROCEDURES

Preparation of Hybrids of Polyaniline and Au NPs

A redox reaction of aniline and $HAuCl_4$ was carried out by dropwise addition of aqueous solution of a designed amount of $HAuCl_4$ into 50 mL 1 mol/L HCl solution containing 50 mmol purified monomeric aniline in a 100-mL flask in an ice bath. After addition of $HAuCl_4$, aqueous solution of ammonium peroxodisulfate [$(NH_4)_2S_2O_8$, 62.5 mmol] was added dropwise to the mixtures at 0°C to complete oxidative polymerization of the residual aniline. The produced precipitates were separated by filtration, and washed with diluted ammonia to produce an emeraldine base of polyaniline containing Au NPs. The yields were more than 90% based on the charged amount of aniline. The contents of Au were measured by atomic absorption analysis and found to be nearly the same as the charged amounts.

Poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Au NPs were prepared by reduction of $HAuCl_4$ (0.66 mmol/L) with ethanol in mixed solution (ethanol/water = 8/2) in the presence of PVP (3.3 mmol/L in monomer unit). The reduction was started by refluxing the mixtures at 80°C for 5 min. After addition of 0.1 mol/L NaOH aqueous solution (keeping the molar ratio of $NaOH/HAuCl_4 = 4$) to the mixtures, the reaction was completed by continuing refluxing at 80°C for 2 h. The obtained PVP-protected Au NPs were purified by filtration and washing with ethanol by using a ultrafilter and dried under vacuum. Hybrid films of polyaniline and PVP-protected Au NPs were obtained by mixing these two powders with camphorsulfonic acid and casting the mixtures on glass substrates.

To obtain film of polyaniline or its hybrid, camphorsulfonic acid (0.29 g) and polyaniline or its hybrid with Au NPs (0.25 g) were placed in an agate mortar and mixed with a pestle at first. After adding *m*-cresol (24.8 g), the mixture was well ground with a pestle. The resulting mixture in a sample tube was sonicated at 50°C for 3 h. A part of the clear supernatant was placed on a glass substrate and heated on a hot plate at 50°C for 18 h to remove the solvent *m*-cresol. The prepared film of polyaniline or its hybrid was dried at 60°C under vacuum.

Preparation of Hybrids of Poly(3,4-ethylenedioxythiophene) (PEDOT) and Au NPs

Thiol-protected Au NPs were first prepared as follows:[21] Aqueous solution (60 mL) of $HAuCl_4{\cdot}4H_2O$ (0.6 mmol) was at first mixed with tetraoctylammonium bromide (TOAB, 1.2 mmol) solution in toluene (20 mL). After addition of toluene (120 mL), the mixture was vigorously stirred for 24 h. The yellow aqueous layer became colorless, and the toluene layer turned orange as a result of the formation of complex of $[AuCl_4]^-$ with tetraoctylammonium cations. After mixing the solution with the freshly prepared thiols, dodecanethiol (DT) or terthiophenethiol (TSH), in toluene (200 mL) for 10 min at room temperature, freshly prepared aqueous solution (60 mL) of sodium tetrahydroborate ($NaBH_4$, 6 mmol) was added to the vigorously stirred solution. The resulting solution immediately turned from orange to black (in the case of DT) or dark green (in the case of TSH), and stirring was continued for more than 12 h. The organic phase was then separated and subjected to complete evaporation of the solvent using a rotary evaporator. The Au NPs were redissolved in toluene (30 mL) and precipitated with methanol (400 mL). The particles were washed with toluene and methanol several times by centrifugation.

To prepare hybrid films of PEDOT and Au NPs, aqueous solution of poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT–PSS, Aldrich) was mixed with methanol, water, and a dispersion of thiol-protected Au NPs in tetrahydrofuran (THF) at the designed volume ratios, and the mixtures were then drop-cast on glass substrates. The film sample was dried overnight at room temperature and annealed at 80°C for 1 h. The thickness of the hybrid films was determined with a linear gage from 10 μm to 20 μm.

Measurement of Thermoelectric Properties

The temperature dependence of the electrical conductivity and the Seebeck coefficient was determined with a four-point measurement unit for thermoelectric properties on rectangular film samples in an electric oven at temperatures from room temperature to 443 K. Pt and Pt/Pt-Rh 13% wires were bound to a sample with conductive paste as electrodes and thermocouples, respectively. When a constant direct current was applied between the Pt electrodes placed at both edges of the sample across a long length, the potential drop was detected between the Pt wires of the thermocouples placed on the center of the sample surface with a certain separation. The electrical conductivity was determined from the applied current, the potential drop, and the sample dimensions. The Seebeck coefficient was obtained from the slope of the produced thermoelectric voltage as a function of the temperature difference along the length of the sample. The power factor was calculated from the corresponding Seebeck coefficient and electrical conductivity at a certain temperature.

RESULTS AND DISCUSSION

Hybrids of Polyaniline and Au NPs

Hybrid materials of polyaniline and Au NPs were prepared by redox reaction of aniline and gold(III) ions with successive oxidation of the residual aniline with ammonium peroxodisulfate. Casting of the mixtures of the polyaniline–gold NP hybrids, camphorsulfonic acid, and *m*-cresol provided conducting hybrid polyaniline films. The electrical conductivity

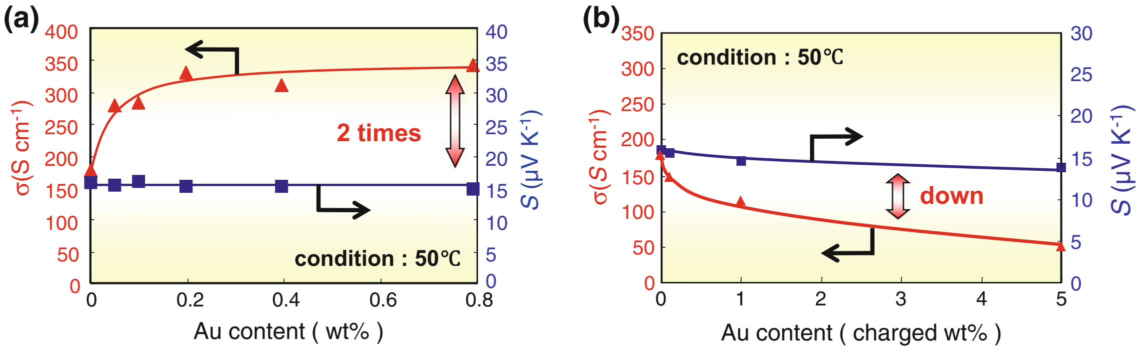

Fig. 1. Seebeck coefficient and electrical conductivity of hybrid film of polyaniline and (a) Au NPs, and (b) PVP-protected Au NPs.

of the hybrid polyaniline film is shown in Fig. 1a. The conductivity increases rapidly on increasing the content of Au NPs, saturating at a constant value which is about twice that of the pristine polyaniline film. This behavior is very different from those of the hybrid films prepared by mixing polyaniline and PVP-protected Au NPs prepared separately, as shown in Fig. 1b.

This difference could be attributed to the insulating property of PVP. In the case of directly hybridized Au NPs, Au NPs are directly surrounded by polyaniline, resulting in intimate contact of Au NPs with polyaniline molecules. This intimate contact may enhance the electrical conductivity of the polyaniline film, because the conductivity between polyaniline molecules is usually thought to be less than that within a polyaniline molecule. In the case of PVP-protected Au NPs, in contrast, Au NPs are completely surrounded by insulating PVP molecules and cannot be in direct contact with polyaniline molecules. The presence of insulating PVP between the polyaniline molecules probably lowers the electrical conductivity of the polyaniline hybrid film. Thus, the insulating property of PVP results in a drop in the electrical conductivity of polyaniline film as shown in Fig. 1b.

The Seebeck coefficient and thermal conductivity of the hybrid films of polyaniline and Au NPs are nearly the same as those of pristine polyaniline films without NPs. Thus, the thermoelectric power factor ($P = S^2\sigma$, where S is the Seebeck coefficient and σ is the electrical conductivity) of the hybrid film is enhanced by increasing the content of Au NPs until Au content of 0.2 wt.%, above which it remains constant, as shown in Fig. 2.

Hybrids of PEDOT and Au NPs

Since an aqueous dispersion of PEDOT–PSS was commercially available, hybrid films of PEDOT–PSS and Au NPs were prepared by mixing aqueous dispersion of PEDOT–PSS with dispersions of Au NPs in THF and casting the mixed dispersions on glass substrates. Two kinds of thiol, TSH and DT, were used as the capping reagent for Au NPs. Thiol-capped Au NPs were prepared by reduction of $HAuCl_4$ with $NaBH_4$ in the presence of the corresponding thiol.

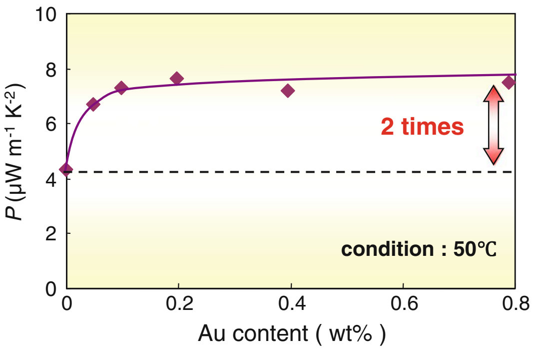

Fig. 2. Power factor of hybrid films of polyaniline and Au NPs.

The Au NPs stabilized with TSH (Au-TSH NPs) were obtained as a black powder. The dispersion stability in toluene and CH_2Cl_2 was so poor that aggregations of Au-TSH NPs occurred spontaneously in a few hours and overnight, respectively, while they were well dispersed in THF. The particle size of the Au NPs obtained at various TSH/Au molar ratios was examined by transmission electron microscopy (TEM). The TEM images and histograms indicating the particle size distribution are collected in Fig. 3. A narrow size distribution is observed for each image. The average diameter is not affected by the TSH/Au ratio. Coagulation of Au-TSH is also observed in the TEM image for every TSH/Au ratio. Thermogravimetric analysis (TGA) of the prepared Au-TSH NPs indicated that the Au/TSH molar ratio was 1:0.18, close to the feed ratio of 1:0.17.

The Au-DT NPs were also synthesized by the same procedure as the Au-TSH NPs, being well dispersed in THF. TEM (Fig. 4) revealed a rather large average particle size of 6.9 ± 1.6 nm.

Figure 5 displays the temperature dependence of the electrical conductivity of films of pristine PEDOT, PEDOT treated with solvents, and PEDOT/Au-TSH hybrids treated with solvents. The electrical conductivity of all samples decreased slightly with increasing temperature. At 50°C the PEDOT

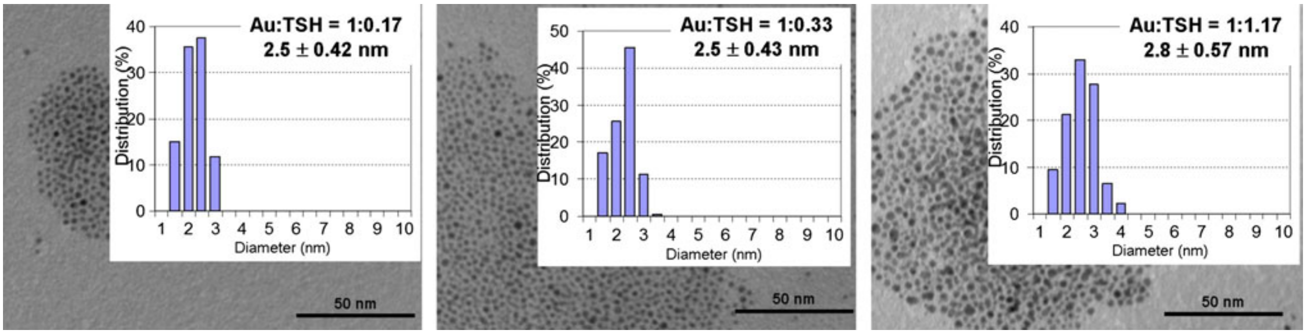

Fig. 3. TEM images and particle size distribution histograms of Au-TSH NPs at Au/TSH molar ratios of 1:0.17, 1:0.33, and 1:1.17.

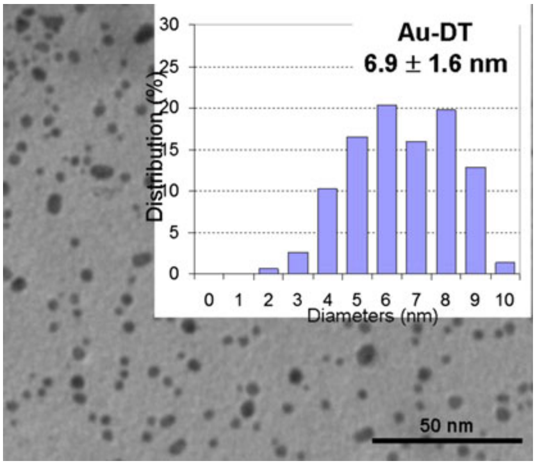

Fig. 4. TEM image and particle size distribution histogram of Au-DT NPs at Au/DT molar ratio of 1:1.

treated with solvents exhibits an electrical conductivity of 104 S cm^{-1}, whereas that of pristine PEDOT is 122 S cm^{-1}. The addition of solvents into an aqueous dispersion of PEDOT slightly lowered the electrical conductivity of the resulting films, which could be related to the change in morphology of the dispersed particles of PEDOT and in the linkage of PEDOT into the elongated domains.[22] The electrical conductivities of hybrid films with various amounts of Au-TSH NPs are summarized in Table I. The hybrid films exhibit electrical conductivity similar to that of PEDOT treated with solvents and lower than that of the pristine PEDOT. Thus, addition of Au-TSH NPs to the PEDOT does not improve the electrical conductivity.

The Seebeck coefficient of PEDOT and its hybrid films were also nearly the same at 50°C, increasing with temperature (Fig. 5). Thus, the power factor P and the figure of merit [$ZT = (S^2\sigma/\kappa)T$, where κ is the thermal conductivity and T is absolute temperature] of the hybrid films are inferior to those of pristine PEDOT and nearly the same as those of PEDOT treated with solvents (Fig. 5). In other words, the constancy of the Seebeck coefficient and the decrease in the electrical conductivity result in a decrease of the power factor for the hybrid films of PEDOT with Au-TSH NPs.

DT (a typical alkyl thiol) was used as a protecting ligand of Au NPs instead of TSH, being applied to the hybrid films with PEDOT. Figure 6 displays the temperature dependence of the electrical conductivity of films of pristine PEDOT, PEDOT treated with solvents, and PEDOT/Au-DT hybrids. The electrical conductivity of all the samples decreases slightly with increasing temperature. The electrical conductivity of hybrid films of PEDOT with various amounts of Au-DT is summarized in Table II. All the hybrid films exhibit significantly higher electrical conductivity than those of PEDOT treated with solvents and the pristine PEDOT. The hybrid film with Au-DT/polymer weight ratio of 10^{-5} shows the maximum electrical conductivity of 240 S cm^{-1} at 50°C, which is 2.4 times higher than that of PEDOT treated with solvents. In other words, the addition of Au-DT NPs improved the electrical conductivity of the PEDOT films. The increase of the electrical conductivity in the PEDOT/Au-DT hybrid films should be attributed to Au-DT NPs. The presence of Au-DT NPs may enhance the carrier mobility, which could result in an improvement in the electrical conductivity of the hybrid films.

This idea could be supported by the following observation: The dispersion of Au-TSH NPs looks better than the Au-DT NPs based on TEM images (Fig. 7), indicating strong π–π interaction between the TSH molecules and PEDOT chains because both contain thiophene rings. This strong π–π interaction between the thiophene rings of PEDOT chains and TSH molecules in the Au-TSH/PEDOT hybrids may inhibit direct contact of PEDOT chains with Au NPs. In other words, it will be difficult for carriers to hop from one PEDOT molecule to another through the Au NPs. Thus, no improvement in electrical conductivity was observed with the addition of Au-TSH NPs to PEDOT.

Although some Au-DT NPs are not well dispersed and formed agglomerates, other Au-DT NPs are well dispersed in PEDOT and can enhance carrier hopping among PEDOT chains. In this case, some agglomeration observed in the TEM image suggests weak interaction between PEDOT chains and DT

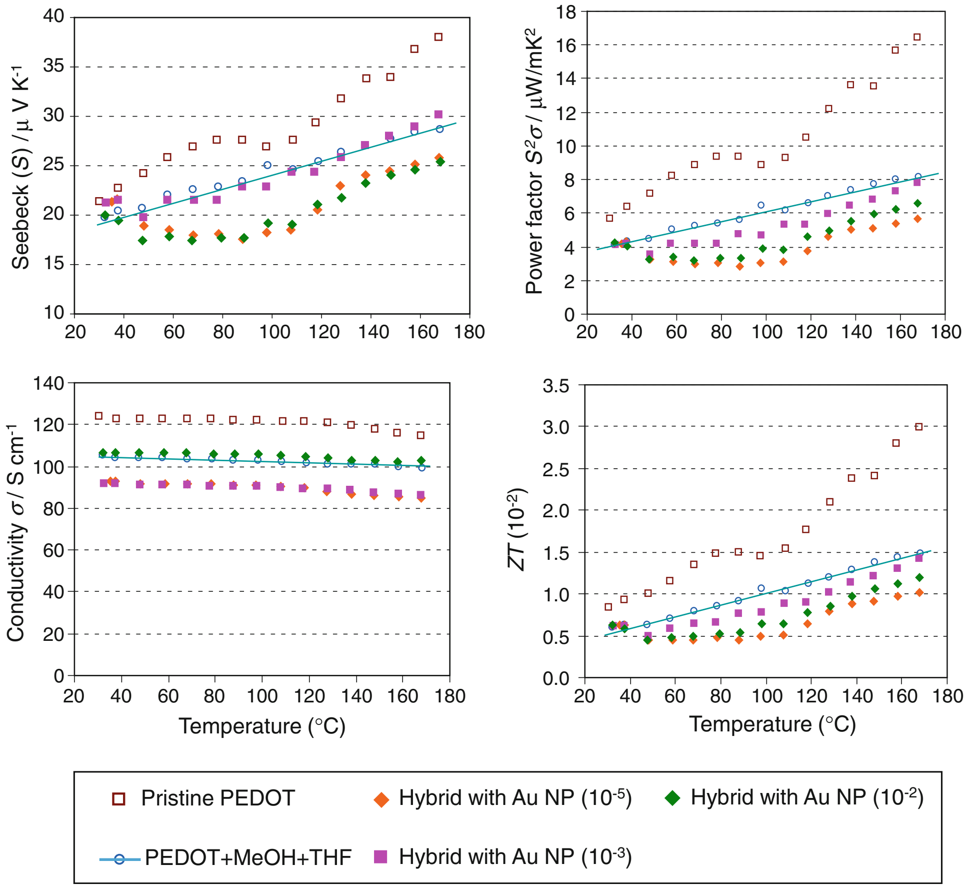

Fig. 5. Electrical conductivity, Seebeck coefficient, power factor, and *ZT* of PEDOT-PSS/Au-TSH hybrid films with various Au-TSH NP contents (weight ratio of Au NPs to PEDOT shown in parenthesis).

Table I. Thermoelectric properties of pristine PEDOT and hybrid films with various weight ratios of Au-TSH NPs at 50°C

Film	σ (S/cm)	S (μV/K)	PF (μW/mK^2)	ZT (10^{-2})
Pure PEDOT	123	24	7.15	1.00
PEDOT + solvents	104	21	4.48	0.62
PEDOT + Au-TSH 10^{-7} w/w	96	21	4.23	0.59
PEDOT + Au-TSH 10^{-6} w/w	91	22	4.46	0.62
PEDOT + Au-TSH 10^{-5} w/w	92	19	3.27	0.45
PEDOT + Au-TSH 10^{-3} w/w	91	20	3.53	0.49
PEDOT + Au-TSH 10^{-2} w/w	107	18	3.27	0.45

ligand molecules. Thus, carriers can hop directly from PEDOT chains to Au NPs without passing through ligand molecules. In other words, the conductivity enhancement on adding Au-DT NPs into the PEDOT-PSS matrix may be due to the higher mobility of carriers between Au NPs and PEDOT chains. To confirm this idea, we tried to carry out scanning electron microscopy (SEM) of the hybrid films of PEDOT-PSS with Au-TSH and Au-DT NPs at a high enough concentration of NPs (Au/PEDOT-PSS = 10^{-2}). The results are shown in Fig. 8. However, only agglomerated NPs were detected in both cases, and no clear difference in the morphology of PEDOT-PSS was observed. It is expected that a large part of the Au NPs are agglomerated and only a small part is dispersed in the PEDOT matrix in the hybrid film with higher weight ratio of Au NPs, while, in the film filled with the lowest amount of Au NPs (weight ratio 10^{-5}), most Au NPs may be well dispersed. This is a possible explanation for the fact that the hybrid film with the smallest amount of Au NPs has the highest electrical conductivity.

As shown in Fig. 6, the Seebeck coefficients of PEDOT and its hybrid films increase with increasing temperature. The Seebeck coefficient of the hybrid films shows a value similar to that of the

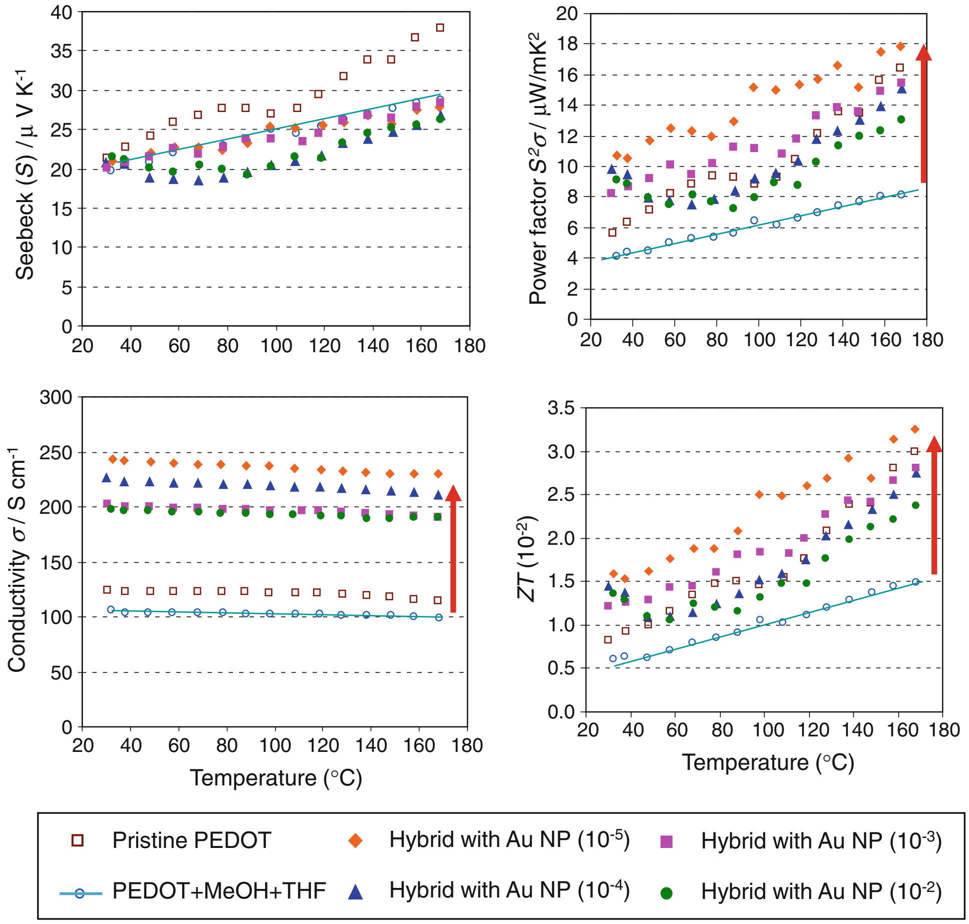

Fig. 6. Electrical conductivity, Seebeck coefficient, power factor, and *ZT* of PEDOT-PSS/Au-DT hybrid films with various Au-DT NP contents (weight ratio of Au NPs to PEDOT shown in parenthesis).

Table II. Thermoelectric properties of pristine PEDOT and hybrid films with various weight ratios of Au-DT NPs at 50°C

Film	σ (S/cm)	S (µV/K)	PF (µW/mK^2)	ZT (10^{-2})
Pristine PEDOT	123	24	7.15	1.00
PEDOT + solvents	104	21	4.48	0.62
PEDOT + Au-DT 10^{-5} w/w	241	22	11.68	1.63
PEDOT + Au-DT 10^{-4} w/w	223	19	7.92	1.10
PEDOT + Au-DT 10^{-3} w/w	200	21	9.23	1.28
PEDOT + Au-DT 10^{-2} w/w	196	20	7.95	1.10

pristine PEDOT film in spite of an increase in the electrical conductivity. For the hybrid films, both the constancy in the Seebeck coefficient and the increase in electrical conductivity result in an increase of the thermoelectric power factor. These results lead to an increase in the *ZT* value for all hybrid films. In particular, the hybrid film with Au-DT/PEDOT-PSS weight ratio of 10^{-5} showed a *ZT* value increased by up to 2.7 times compared with the PEDOT films treated with solvents. Since Au NPs in hybrid films at high weight ratio easily form agglomerates, those at low weight ratio may provide well-dispersed hybrid films. Thus, it is speculated that well-dispersed Au NPs can enhance the electrical conductivity and increase the *ZT* value.

CONCLUSIONS

The effect of Au NPs on the thermoelectric performance of conducting polymers, i.e., polyaniline and PEDOT, was investigated. In the case of hybrid films of polyaniline with Au NPs, hybridization with PVP-protected Au NPs decreased the electrical conductivity of the polyaniline films because of the

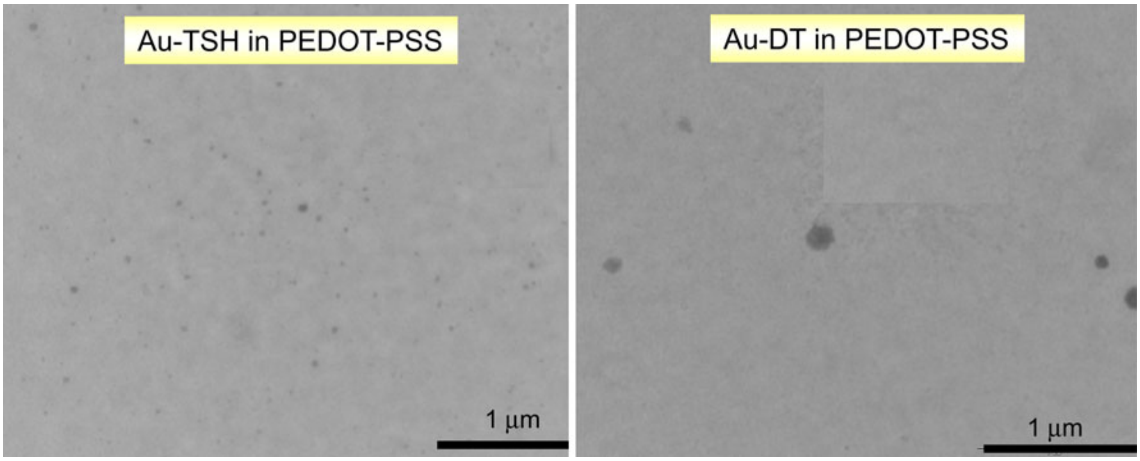

Fig. 7. TEM images of Au-TSH and Au-DT NPs in PEDOT matrices.

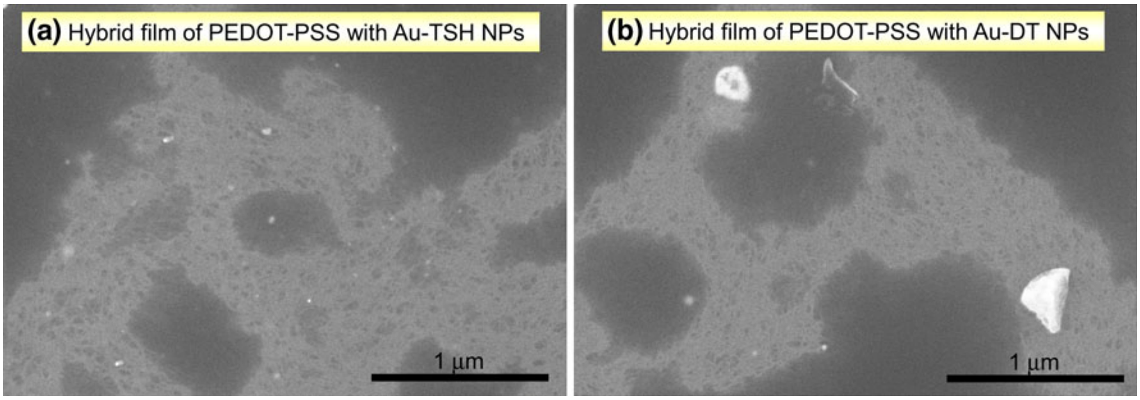

Fig. 8. SEM images of hybrid films of PEDOT-PSS with (a) Au-TSH and (b) Au-DT NPs at Au/PEDOT-PSS weight ratio of 10^{-2}.

insulating property of the PVP. In contrast, direct hybridization of polyaniline with Au NPs greatly increased the electrical conductivity, which might be attributed to enhancement of hopping between polyaniline molecules by direct contact of polyaniline with Au NPs.

In the case of PEDOT hybrid films, the effect of Au NPs on the thermoelectric performance of the PEDOT films depended on the kind of protecting ligand of the Au NPs: addition of Au-TSH NPs to PEDOT did not increase the electrical conductivity of the hybrid films, while Au-DT NPs did provide an increase in the conductivity of the hybrid films. This difference may be attributed to the dispersion property of the Au NPs in the PEDOT films. Well-dispersed parts of the Au-DT NPs in PEDOT can be in direct contact with PEDOT molecules, which may enhance carrier hoping and result in an increase in the electrical conductivity.

Hybridization of conducting polymers with Au NPs can improve the thermoelectric performance of conducting polymer films if the proper method is chosen to ensure good dispersion of the NPs in the hybrid system. This might provide a general concept to improve the thermoelectric performance of organic thermoelectric materials.

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