Poly (3,4-ethylene dioxythiophene) / copper sulfide hybrid thermoelectric materials with large Seebeck coefficient around room temperature

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Nanocomposites were prepared from poly (3,4-ethylene dioxythiophene): poly (styrene sulfonic acid) (PEDOT:PSSA) / copper sulfide synthesized in this study. Seebeck coefficient and electrical conductivity of PEDOT:PSSA were measured as 1125 µV/K and 1.08 S/cm, respectively. Electrical conductivities of the nanocomposites do not decrease considerably whereas their Seebeck coefficients were found 4 or 6 times larger than pristine polymer. Their power factors were found 15 or 19 times higher than pristine polymer. The largest Seebeck coefficient was measured as 7000 µV/K and the highest power factor was found as 2646 µW/mK^2. These are the highest values reported up to date for polymer based thermoelectric materials.

1. Introduction

Thermoelectric (TE) devices can directly produce electricity by harvesting thermal energy from solar heat, radioactive decay, body heat, thermal springs and industrial waste heat, etc. for practical applications. The TE process is one of the most promising alternatives among the green renewable energy technologies without pollutants and noise [1-3]. TE technology has other advantages such as simple structure, small size, easy maintenance, high thoroughness and feasibility. The efficiency of a TE material is determined by the dimensionless thermoelectric figure of merit (Z_T) defined as; $Z_T = S^2 \sigma T / \kappa$ where S is the Seebeck coefficient, σ and κ are the electrical and thermal conductivities of the material, respectively, at the temperature T (K). The higher Z_T means the higher efficiency. It is self-evident that higher S and σ in combination with lower κ lead to higher efficiency. However, the biggest difficulty to enhance Z_T is that these three parameters of a material cannot be changed independently, i.e., κ increases but S decreases with increasing σ. A value of $Z_T > 1$ is required to make an efficient commercial TE device. Today's TE materials are inorganic semiconductors with high S value and adequate σ value. However, their high value of κ affects adversely their Z_T. In addition, their toxicity, brittleness and scarcity in nature play a crucial and binding role in their utilization. Therefore, the state-of-the-art TE materials which are alloys such as bismuth-telluride and lead-telluride cannot be used widely for large-scale applications. The production of cheap and environmentally friendly materials is very attractive, nowadays.

On the other side, the conductive polymers which are promising candidates as a TE materials have benefits such as abundance, non-toxicity, flexibility, low cost of processing, low thermal conductivity and suitability for printing or roll-up processing, which are expected to make up the shortages of inorganic TE materials [4]. However, there are no highly efficient polymeric TE materials so far and the most advanced research is moving toward the development of new materials with high Z_T. Since the magnitude of thermal conductivity of the polymers are close to each other and do not change significantly with inorganic additives, the efficiency of the polymeric TE materials can be compared with their power factor (P) which is defined as P = $S^2 \sigma$ instead of Z_T. Although less stability of conductive polymers restricts its use at high temperatures, they can operate properly up to 150 °C. The maximum Z_T of 0.42 [5], which is attained at room temperature have leaded to an expectation to fabricate polymeric TE materials since 0.42 is close to 1 which is attained in the case of the best conventional inorganic material (Bi_2Te_3) so far at room temperature. Among the conductive polymers, poly (3,4-ethylene dioxythiophene) (PEDOT) : poly(styrene sulfonate) (PEDOT:PSS) is the most promising and the most studied candidate for polymeric TE materials [4]. Its dispersions in aqueous poly (styrene sulfonate) (PSS) is commercially available and easily applicable in various applications. This dispersion (PEDOT:PSS) is water-dispersible, air stable, restorable, highly transparent, and convenient to a solution-based coating. In addition, its conductivity can be remarkably enhanced (by 2-3 orders of magnitude) by reduction or additional solvent treatments, such as hexafluorobutanol, sorbitol, ethylene glycol (EG), dimethyl sulfoxide, sulfuric acid or nitric acid [6-11].

The researchers turned to study on the nanocomposites of conducting polymers after it was found that the interdependence on S and σ could be broken down

by the incorporation of inorganic or organic nanoparticles into them [12]. It was demonstrated both theoretically and experimentally that nanostructured TE materials can effectively increase Z_T values because of quantum confinement and increased scattering of phonons at interfaces. In order to combine the easy processability of polymers and good TE performance of nanosized inorganic semiconductors, nanocomposites of a conducting polymer and inorganic TE nanoparticles have become a hot research topic. Then, researchers have paid attention to incorporate different types of inorganic semiconductor materials into the conductive polymers [11-20]. Exploring a high performance, readily synthesized, air stable and eco-friendly inorganic semiconductor material is bound to make the design concept of "inorganic/organic hybrids" more and more promising.

In recent years, it was revealed that copper sulfides exhibit p-type conductivity with a narrow band gap therefore they can be promising TE materials [21]. They deserve to be investigated in detail because they are abundant and cheap and environmentally friendly materials. Their improved P values are reasonably high at room temperature and also, earlier studies on thermal properties of copper sulfide have shown that their thermal conductivities are low as compared to the metals [22]. Among the copper sulfides, $Cu_{1.8}S$ possesses a band gap of 1.5 eV, and a high electrical conductivity but a low Seebeck coefficient.

In this study, we at first synthesized $Cu_{1.8}S$ nanoparticles as dispersion in ethylene glycol by using copper (I) chloride and thiourea [23]. Then we added $Cu_{1.8}S$ into the aqueous PEDOT dispersion which is synthesized by chemical oxidation of 3,4-ethylene dioxythiophene with hydrogen peroxide/copper (II) nitrate: oxidant/catalyst system in the presence of poly (styrene sulfonic acid) (PSSA). It was found that the synthesized PEDOT:PSSA/$Cu_{1.8}S$ composites displayed an enhanced TE performance compared to that of pristine PEDOT:PSSA. To the best of our knowledge, this is the first study reporting the TE properties of PEDOT:PSSA/ $Cu_{1.8}S$ nanocomposites. At the same time, these composites are the first inorganic / organic hybrid materials with the larger Seebeck coefficient and the higher power factor reported to date in the literature.

2. Experimental

2.1. Materials

3,4-Ethylene dioxythiophene (EDOT), Poly (4-styrene sulfonic acid) (PSSA), hydrogen peroxide (H_2O_2), zinc chloride ($ZnCl_2$),Copper(I) chloride (CuCl), thiourea (CH_4N_2S), Ethylene glycol ($C_2H_6O_2$) and copper nitrate hydrate ($Cu(NO_3)_2.H_2O$) were purchased as analytical reagent grade from Sigma-Aldrich Company Ltd. and used without further purification.

2.2. Synthesis of PEDOT:PSSA and $Cu_{1.8}S$

A known amount of EDOT was added into a known amount of PSSA (30 %) solution in a small amount deionized water and the mixture was stirred vigorously for 1 hour at room temperature. Then, a known amount of H_2O_2 was added drop by drop into the mixture as oxidation agent. Finally, a small piece of crystal Cu $(NO_3)_2.8H_2O$ was put into the above mixture. The mole ratios of the reagents were kept constant throughout the study as PSSA/H_2O_2/EDOT = 0.3/4/1. After the reaction mixture was stirred vigorously for 24 hours at room temperature, PEDOT:PSSA was obtained as a dark blue solution.

2.500 M thiourea solution in EG including glucose was added dropwise into the 0.333 M copper (I) chloride solution in EG, which is kept at reaction vessel at 80 ^{o}C under nitrogen gas. After the addition of thiourea is completed, the mixture is heated to 140 ^{o}C by continuing to stir. The $Cu_{1.8}S$ particles were obtained as a black solution after 5 hours of reaction at 140 ° C under nitrogen gas. The solutions were prepared only in dried EG and no water was used throughout the synthesis process.

2.3. Preparation of the films

The glass substrates were cleaned in the concentrated sulfuric acid solution then successively transferred to water, pure water and acetone. Later they were ultrasonically cleaned in isopropyl alcohol, finally with deionized water. The films of PEDOT-PSSA or the certain proportions of PEDOT-PSSA solutions and $Cu_{1.8}S$ particles in EG were prepared by drop coating of 1 mL solution on the cleaned glass substrate. Thin films on the glass substrates were also dried at 120 ^{o}C for 15 min after drying at ambient conditions.

2.4. Instruments

UV-vis spectra of solutions were taken using A109351 05066 model Shimazdu UV mini-1240 UV-vis. spectrophotometer.The morphology and structure of sample were characterized using a field–emission scanning electron microscope (FE-SEM; PhilipsXL30FEG, FEL Co., Hillsboro, OR, USA) with an accelerating voltage of 5 kV and high resolution transmission electron microscope (HRTEM; JEOL JEM-2100 F, JEOL Ltd., Akishima, Tokyo, Japan). X-ray diffraction (XRD) was carried out on a diffractometer (D/max-2200/PC, Rigaku Corp., Tokyo, Japan) equipped with a high-intensity Cu Kα radiation (λ=105418 A). The values of electrical conductivity and Seebeck coefficient of the film samples were obtained by FPP470 Model point probe and by 001 model Seebeck Coefficient measuring devices, respectively, produced by Entek-Turkey.

3. Results and discussion

The copper sulfide nanoparticles have been successfully synthesized in this work. Their phase structure was identified as digenite phase ($Cu_{1.8}S$) according to the PDF#47-1748 card and Zhao's report [22, 24] by the powder XRD spectrum given in the Fig. 1. In 2014, He et al. showed that the TE performances of Cu_xS (x = 1.97, 1.98, and 2) are very high Z_Ts of 1.4–1.7 at 1000 K [21]. Among these copper sulfides, digenite ($Cu_{1.8}S$) is known as a steady phase and their high ZTs are mainly attributed to the ultralow lattice thermal conductivities (0.3-0.5 W/mK) caused by the liquid-like copper ions [25] similar with β-Cu_2Se phase with the character of "phonon-liquid electron-crystal" [26]. When temperature of the digenite rises over 364 K, the position of the Cu atom in the crystal structure changes from ordered states to confused states. The $Cu_{1.8}S$ could be used as a p-type semiconductor originated from the high mobility of copper ions in the lattice. $Cu_{1.8}S$ has not attracted enough attention since it has a low Seebeck coefficient (about 10 µV/K) [22] although it possess a band gap of 1.5 eV and a high electrical conductivity.
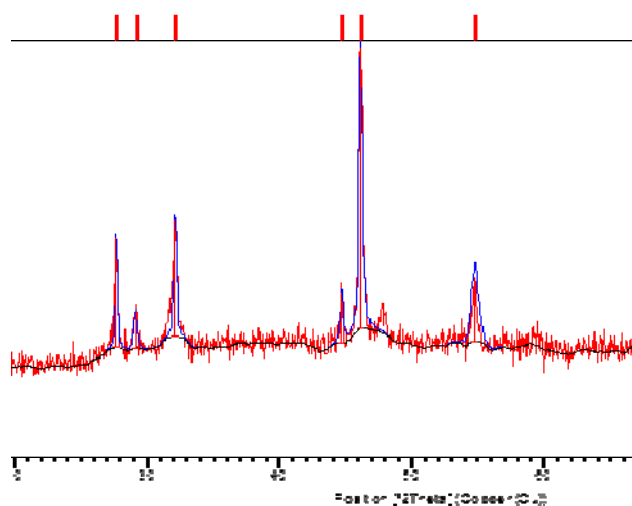
The PEDOT:PSSA was synthesized as a dark blue solution by means of oxidation of EDOT with a mild oxidant, hydrogen peroxide, and a small amount catalyst, $Cu(NO_3)_2$. This pristine aqueous PEDOT:PSSA dispersion was used as synthesized without doping or annealing.

The hybrid materials of PEDOT:PSSA/$Cu_{1.8}S$ were prepared by mixing the certain amounts of their dispersions and coated as thin films on the glass substrates by drop casting technique. The TE properties of the PEDOT:PSSA and the hybrid nanocomposites were determined by measuring the electrical conductivity and Seebeck coefficients of their thin films at room temperature, and then their power factor (=$S^2\sigma$) were calculated. The results were given in the Table 1 together with the estimated Z_T values which are calculated for 300 K by assuming as κ=0.4 W/mK. Table 2 summarizes the studies of the PEDOT:PSS and its nanocomposites with high thermoelectric properties which are reported up to now in the literature.

It can be seen from the thermoelectric properties of the pristine PEDOT:PSSA in Table 1, its electrical conductivity is significantly low (1.08 S/cm) but Seebeck coefficient is positive and significantly high (1125 µV/K) compared to those of PEDOT:PSS reported in the literature, given in the Table 2.

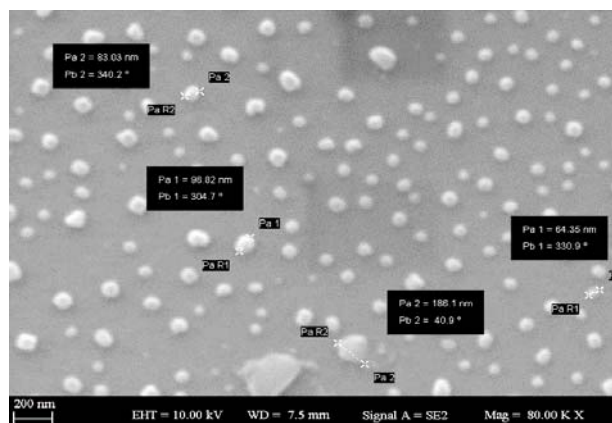*Fig. 1. XRD pattern of the Cu1.8S nanoparticles powders*

Fig. 2. SEM image of a $Cu_{1.8}S$ nanoparticles dispersed in ethylene glycol

As seen in Fig. 2, the morphology of the synthesized digenite nanoparticles can be described as a mixture of nanosized cubic and spherulitic particles although they are not monodisperse. It can be assumed that the nanoparticles do not contain oxidized copper compounds because they are synthesized in an anhydrous and nitrogen atmosphere. The synthesized $Cu_{1.8}S$ nanoparticles were used as dispersions in ethylene glycol without purification in preparation of their nanocomposites with PEDOT:PSSA.

Consequently, the power factor of pristine PEDOT:PSSA was found considerably higher (137 µW/mK) than those of untreated PEDOT:PSS reported up to date. The PEDOT:PSS samples which have high TE properties were included into the Table 2 and most of them were underwent some treatment to improve their TE properties.

Table 1. Seebeck coefficient (S,) electrical conductivity (σ) measured at room temperature, and power factor (P) calculated by means of $P = \sigma S^2$, and figure-of merit (Z_T) estimated at 300 K by assuming as $\kappa = 0.4$ of PEDOT:PSSA and its nanocomposites with $Cu_{1.8}S$ synthesized in this study

PEDOT:PSSA/$Cu_{1.8}S$ w/w	S (µV/K)	σ (S/cm)	P (µW/mK²)	Estimated Z_T at 300 K
0.60/0.40	1000	0.93	93	~ 0.07
0.75/0.25	5000	0.80	2000	~ 1.50
0.80/0.20	7000	0.54	2646	~ 1.98
0.90/0.10	3900	0.81	1232	~ 0.92
1.00/0	1125	1.08	137	~ 0.10

In the case of nanocomposites, Seebeck coefficient firstly increases with the increase of $Cu_{1.8}S$ and then decreases with a further increase. The optimum composition was determined as 20 % $Cu_{1.8}S$ for the highest Seebeck coefficient. However, the electrical conductivity did not change considerably with the amount of $Cu_{1.8}S$ in the composition. It is seen that the sample with highest Seebeck coefficient has the lowest electrical conductivity. Compared with the Seebeck coefficients of the nanocomposites given in Table 2, it is seen that Seebeck coefficients of nanocomposites containing 20% and 25% $Cu_{1.8}S$ in the present study are much higher than those of the nanocomposites in Table 2, which are reported up to now. The reason for these high Seebeck coefficients may be that the PEDOT is mildly oxidized with hydrogen peroxide, resulting in a lower charge carrier concentration. This may also be due to the high mobility of copper ions in the crystal structure of $Cu_{1.8}S$. In addition, the ethylene glycol in the $Cu_{1.8}S$ nanoparticle dispersion may also behave as a secondary dopant by extending the PEDOT chains. It is also possible that all of these reasons work concurrently. The estimated figure of merits (Z_T) of the PEDOT:PSSA and its nanocomposites were also given in Table 1, which are calculated by assuming their thermal conductivity as 0.4 µW/mK since PEDOT:PSSA has not exceed this value for the composites reported in the literature. It is seen that the nanocomposite with 20 % $Cu_{1.8}S$ can have a highest Z_T (= ~2) reported up to date for polymeric composites. It means that this nanocomposite can be used as a p-type TE material to fabricate efficient polymeric TE devices. It should be also emphasized that the TE properties of these nanocomposites can be improved by means of further treatments since these nanocomposites are untreated.

Table 2. Seebeck coefficient (S) electrical conductivity (σ) thermal conductivity (κ) power factor (P) figure-of merit (Z_T)of PEDOT:Tos, PEDOT:PSS and its nanocomposites prepared with various inorganic thermoelectric materials

Sample	S (µV/K)	σ (S/cm)	κ (W/mK)	P (µW/mK²)	Z_T	Ref.
PEDOT ClO_4^- doped hydrazin treated	35	230	0.35	41	-	7
PEDOT PF_6^- doped hydrazin treated	34	312	0.22	60	-	7
PEDOT BTFMSI doped hydrazin treated	42	708	0.19	147	0.22 (RT)	7
PEDOT:Tos TDAE trated	-	-	0.37	324	0.25 (RT)	8
PEDOT:PSS DMSO mixed, EG post treated	73	880	0.32($\kappa_\perp$) 0.31($\kappa_{//}$)	469	0.42 (RT)	9
PEDOT:PSS (PH750) DMSO 5%	13.5	570	0.34	10.4	0.0092 (RT)	10
PEDOT:PSS (PH1000) DMSO 5%	22.2	945	-	46.57	-	10
PEDOT:PSS (FET) DMSO 5%	30.3	320		29.39	-	11
PEDOT:PSS(PH1000)/p-Bi_2Te_3 10%HCl rinsing of Bi_2Te_3	149	59	-	131	-	11
PEDOT:PSS (PH1000)/n-Bi_2Te_3 10%HCl rinsing of Bi_2Te_3	-125	58	-	91		11
PEDOT:PSS (PH1000)/p-Bi_2Te_3 30% HCl rinsing of Bi_2Te_3	110	65	-	70	-	11
PEDOT:PSS (PH1000)/n-Bi_2Te_3 30% HCl rinsing of Bi_2Te_3	-80	60	-	40		11

Sample	S (µV/K)	σ (S/cm)	κ (W/mK)	P (µW/mK²)	Z_T	Ref.
PEDOT:PSS/Sb_2Te_3 composite	175	130-110	0.15 (300-523K)	-	1.18 (523 K)	14
PEDOT:PSS/Te nanocomposite	163.4±4	19.3±2.3	0.22-0.30	70.9	0.1 (RT)	15
PEDOT:PSS/Te 80% .vol H_2SO_4 treated	114.97	214.86	0.22 estimation	284	0.39 estimation	16
PEDOT:PSS/Te composite 70% wt	26	650	0.197-0.218	51.4	0.076 (292 K)	17
PEDOT:PSS/SnSe nanosheets 20%	110	330	0.38	380	0.32 estimation	18
PEDOT:PSS/$Cu_{1.75}$Te	220	-	-	84	-	19
PP-PEDOT (SCP method&Appl. Pot. 0.5 V)	79.8	1355	0.37	862.9	-	20
PP-PEDOT (SCP method&Appl. Pot. 0.1 V)	-	-	0.37	1270	1.02 (RT)	20

RT: room temperature

In order to see the electronic transitions in the visible region, the UV-Vis. absorption spectra of the aqueous dispersions of the pristine PEDOT:PSSA and its nanocomposites were given in the Fig. 3. The spectrum at the bottom (black line) belongs to pristine PEDOT:PSSA and the others are ranked upward according to the increasing amount of $Cu_{1.8}$S.
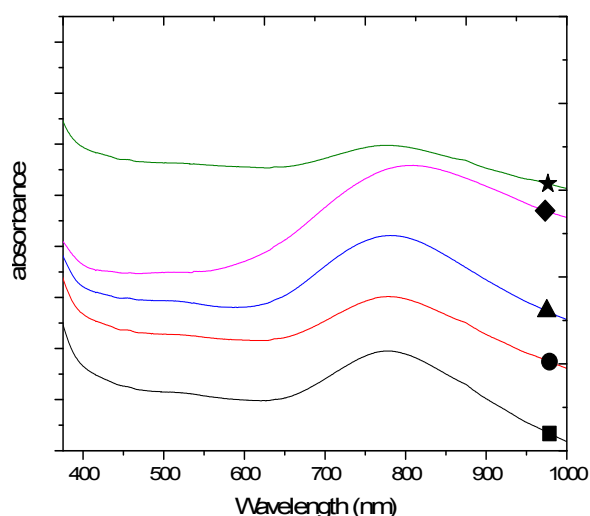

Fig. 3. UV absorption spectra of the PEDOT:PSSA and its nanocomposites. The curves are shifted artificially. The bottom line (square) belongs to pristine PEDOT:PSSA and upward lines belong to the PEDOT:PSSA/$Cu_{1.8}$S nanocomposites in the following ratios: 0.9/0.1 (circle) , 0.80/0.20 (triangle), 0.75/0.25 (diamond), 0.6/0.40 (star), respectively

A broad absorption band between 600 nm and 900 nm originates from the π - π* transition of the polarons or bipolarons in the samples. The absence of tailing at the pristine PEDOT:PSSA and nanocomposites with low amount of $Cu_{1.8}$S indicates that the charge carriers cannot move freely. The polaron band becomes a free carrier tail by increasing amount of $Cu_{1.8}$S dispersion including

ethylene glycol. This indicates that charge carriers can move freely in the chains extended by ethylene glycol. This behavior is in agreement with the electrical conductivity data given in the Table 1.

4. Conclusions

This study suggests that:

PEDOT:PSSA synthesized in this study has the highest positive Seebeck coefficient reported so far in the literature for the pristine PEDOT.

$Cu_{1.8}$S nanoparticles can be readily synthesized by the reaction of copper (I) chloride and thiourea in ethylene glycol as described in this work.

In the PEDOT:PSSA/ $Cu_{1.8}$S nanocomposites, electrical conductivity slightly decreases whereas Seebeck coefficient considerably increases with the increasing amount of $Cu_{1.8}$S. However, the further increase of copper sulfide reduces the Seebeck coefficient of the nanocomposites.

The nanocomposite containing 20% $Cu_{1.8}$S and % 80 PEDOT:PSSA has the largest Seebeck coefficient (i.e., 7000 µV/K) and highest power factor (i.e. 2646 µW/mK²) reported so far for conducting polymer composites in the literature.

Since PEDOT and $Cu_{1.8}$S are abundant and nontoxic materials, PEDOT:PSSA containing $Cu_{1.8}$S nanoparticle in the range from 10 % to 25 % are suitable TE materials to fabricate cheap, environment friendly and efficient TE devices.

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