Journal of ELECTRONIC MATERIALS, Vol. 45, No. 6, 2016
DOI: 10.1007/s11664-015-4326-z

Thermoelectric Properties of Hybrid Thin Films of PEDOT-PSS and Silver Nanowires

AKIHITO YOSHIDA[1,2] and NAOKI TOSHIMA[1]

1.—Department of Applied Chemistry, Tokyo University of Science Yamaguchi, SanyoOnoda-shi, Yamaguchi 756-0884, Japan. 2.—e-mail: akihito-yoshida@aist.go.jp

We report the thermoelectric (TE) properties of organic–inorganic hybrid thin films composed of conductive polymer, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS), and inorganic silver nanowire (AgNW). Two kinds of AgNW with different wire length, 3 μm and 27 μm, were used in this study. The AgNW/PEDOT-PSS hybrid films showed an increase in electrical conductivity (σ) with increase in AgNW concentration. The maximum value of σ obtained in this system was ca. 10,000 S cm^{-1}. The films containing long AgNWs (L-AgNWs) showed higher σ relative to short AgNWs (S-AgNWs) at given concentration, which results from the fact that longer nanowires can easily form a percolated structure. The formation of a percolated structure was confirmed by scanning electron microscopy (SEM) observation. On the other hand, the Seebeck coefficient (S) of the hybrid films showed the opposite dependence on AgNW concentration. This decrease in S with increasing AgNW concentration is probably because of increase in carrier number due to the AgNWs. These results suggest that the presented organic–inorganic hybrid system is one example where the electrical conductivity and TE properties can be tuned by use of a nanocomposite.

Key words: Organic thermoelectric materials, silver nanowires, conductive polymers, PEDOT-PSS, hybrid films

INTRODUCTION

There has been increasing interest in polymer electronics in recent years. Characteristics of organic polymer materials such as flexibility, light weight, and printability are attractive advantages over inorganic materials. Continuous efforts have been devoted to their development for polymer-based applications, including light-emitting diodes (LEDs),[1,2] transistors,[3,4] touch sensors,[5,6] and photovoltaic cells.[7,8] The key materials supporting such applications are conducting polymers. Among these materials, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) is one of the most widely used because of its stability and high level of electrical conductivity.[9]

Our group has been studying development of polymer-based thermoelectric (TE) materials.[10–13] In the area of thermoelectrics, highly conducting PEDOT-PSS films are also becoming popular and are often used as p-type TE material.[14–17] We believe that use of organic–inorganic composite materials is one of the effective routes to improve TE properties and consider PEDOT-PSS to be a suitable matrix; For example, we previously reported on the TE properties of composite thin films of PEDOT-PSS containing several types of metal nanoparticle (NP) as inorganic component. The effects of addition of gold (Au) NPs with different protecting ligands or different particle shape (spherical or rod) into PEDOT-PSS film were examined, revealing that some additives can contribute to improvement of TE properties, probably due to increase in carrier mobility or control of carrier concentration.[11,12]

In this study, we focused on another composite system consisting of PEDOT-PSS and silver nanowires (AgNWs). We previously showed that rod-

---

(Received November 13, 2015; accepted December 24, 2015;

shaped gold nanorods (AuNRs) greatly influence the electrical conductivity (σ) and/or Seebeck coefficient (S), compared with spherical AuNPs. This can probably be attributed to formation of percolated structure, thus suggesting that one-dimensional metallic nanomaterials with much higher aspect ratio will lead to still greater alteration of these properties. We selected AgNWs as such a one-dimensional nanomaterial because of their ease of synthesis and high electrical conductivity. Two kinds of AgNWs, long Ag nanowires (L-AgNWs) and short Ag nanowires (S-AgNWs), were prepared to examine the effect of length distribution. The TE properties of composite films containing these AgNWs were examined systematically, and the dependence of these properties on the concentration and distribution of the particles in the film is discussed.

EXPERIMENTAL PROCEDURES

Chemicals

Silver nitrate ($AgNO_3$), potassium nitrate (KNO_3), copper(II) chloride ($CuCl_2$), poly(*N*-vinyl-2-pyrrolidone) (PVP, K30), and ethylene glycol (EG) were purchased from Wako Pure Chemicals and used as received. All water used was deionized.

Synthesis of AgNWs

AgNWs were synthesized by the polyol method.[18–20] First, 50 mL 0.28 M KNO_3 EG solution was heated at 151.5°C for 1 h with stirring. Next, 400 μL 4 mM $CuCl_2$ EG solution and 15 mL 0.147 M PVP EG solution were injected into the KNO_3 solution and stirred for 15 min. Finally, 15 mL 0.094 M $AgNO_3$ EG solution was slowly dropped (~1 mL/min) into the solution, followed by maintenance at 151.5°C for an additional 90 min, leading to production of opaque white suspension of AgNWs. After the solution had cooled to room temperature, the as-prepared AgNWs were washed and purified by repeated centrifugation–precipitation–redispersion processes. Purified AgNWs were finally redispersed with water for subsequent use. AgNWs with shorter length were obtained by a conventional sonication process with a sonicating bath. Long ultrasonic treatment can lead to fragmentation of the wires.[21] The as-synthesized AgNWs and those with short length are referred to hereinafter as L-AgNWs and S-AgNWs, respectively.

Fabrication of Hybrid Thin Films

Hybrid films were obtained by a simple, drop-casting method. Casting dispersions were prepared by mixing two aqueous dispersions, i.e., commercially available PEDOT-PSS solution (Clevios PH1000, Heraeus) and synthesized AgNW colloidal dispersion. The mass content of silver NWs in the hybrid films was adjusted by changing the mixing conditions (concentration of silver dispersion or volume ratio). These mixed dispersions were cast onto quartz substrates (4 mm × 16 mm) and dried in air at 80°C for 1 h. Finally, the dried films were posttreated with EG. EG (40 μL) was cast onto the hybrid films preheated at 130°C and kept at that temperature for 30 min. The thickness of the hybrid films was measured using a linear gage and ranged from 1.5 μm to 3 μm.

Measurements

Transmission electron microscopy (TEM) observations were performed using a JEM-1230 (JEOL) at accelerating voltage of 80 kV. The film surfaces were observed using an S-4800 (Hitachi Hi-tech) scanning electron microscope. The TE properties were measured at several temperatures using a ZEM-3 (ULVAC). σ was measured by the four-terminal method, and S was measured by the static direct-current (DC) method. The measurement accuracy for both parameters is less than ±7%.

RESULTS AND DISCUSSION

The synthesized L-AgNWs and S-AgNWs were observed by SEM (Fig. 1a and b). The average length of the L-AgNWs and S-AgNWs was 27.4 ± 14.8 μm and 3.4 ± 2.2 μm, respectively (Fig. 1c and d). The average width of the AgNWs was estimated to be about 100 nm by TEM observation (Fig. 1e).

Figure 2 shows the x-ray diffraction (XRD) pattern of the AgNWs. The position of the diffraction peak for the AgNWs matches well with that of bulk silver with face-centered cubic (fcc) structure (reference), and almost no signal from impurities such as Ag_2O is observed in this figure, suggesting that high-quality AgNWs were synthesized.

The temperature dependence of the electrical conductivity (σ) and Seebeck coefficient (S) for the L-AgNW/PEDOT-PSS hybrid film (20 wt.%) and pure PEDOT-PSS film without AgNWs is shown in Fig. 3. For both film samples, σ shows a gradual decrease while S increases with increasing temperature. All the other hybrid films showed similar behavior (not shown), suggesting similar carrier conduction (probably metallic) in these films.

Figure 4 shows how the thermoelectric parameters are affected by the content of AgNWs. For both hybrid films containing L-AgNWs and S-AgNWs, σ increases with increase in the content (Fig. 4a). In particular, the highly concentrated films showed σ reaching more than 10,000 S cm^{-1}, which is about 10 times higher than that of pure PEDOT-PSS film. Such high σ can be ascribed to aggregation (percolation) of AgNWs in the film. As the concentration of AgNWs increases, a lot of connections are formed between them, consequently generating a number of paths (networks) for carrier transfer that lead to enhancement of metallic conductivity. Note that the observed σ values are lower than that of individual

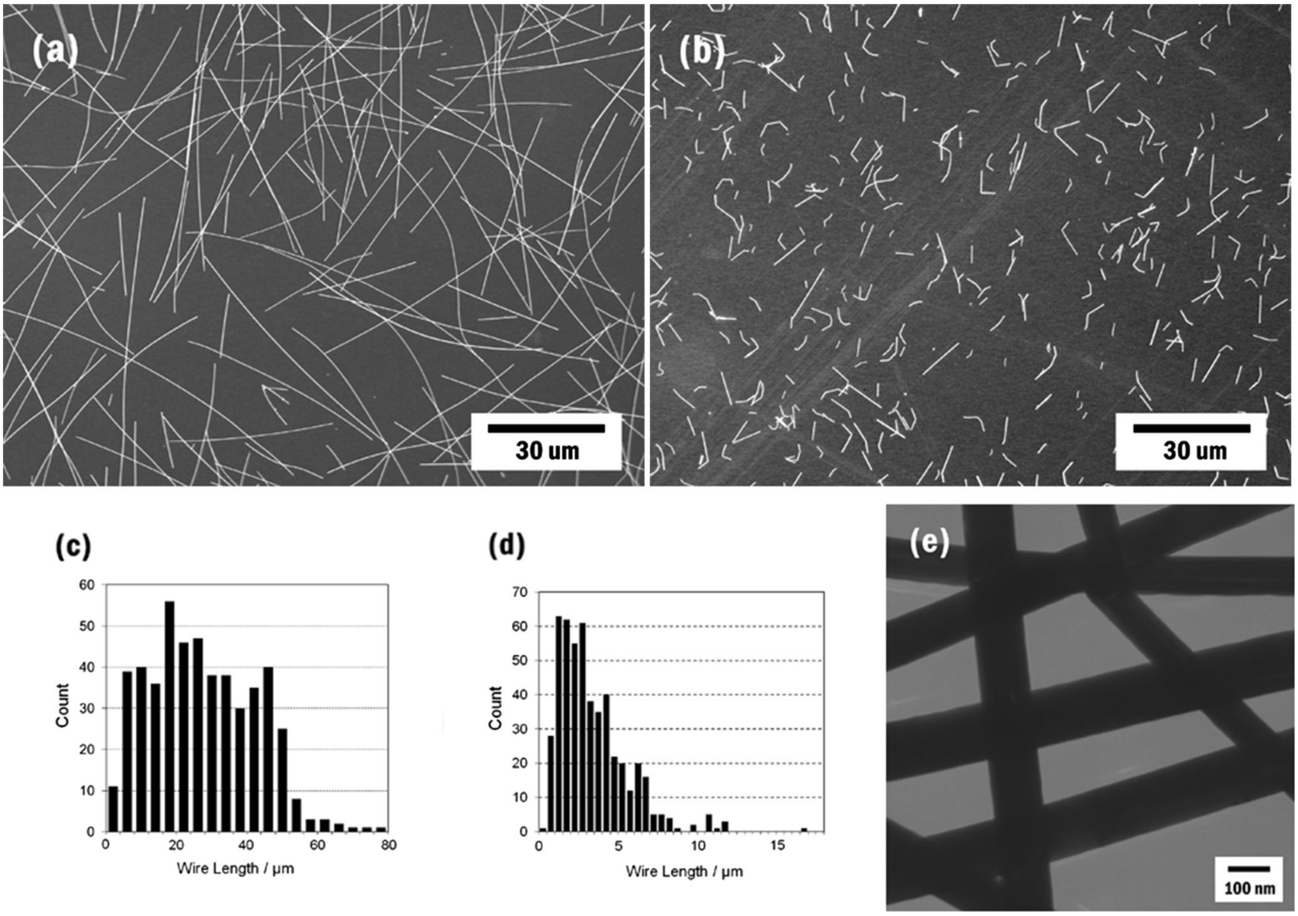

Fig. 1. SEM images and length distribution of L-AgNWs (a, c) and S-AgNWs (b, d). (e) TEM image of AgNWs.

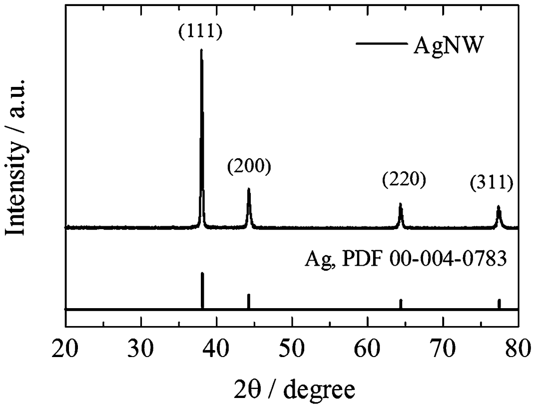

Fig. 2. XRD pattern of AgNWs with XRD reference lines for bulk silver (PDF 00-004-0783).

NW ($\sim 10^5$ S cm^{-1}),[22] which means that the carrier conduction in these films is not fully dominated by only the embedded AgNWs but the PEDOT-PSS matrix is still responsible for carrier conduction. The above explanation for the σ enhancement is supported by the results of SEM observations shown in Fig. 5. For hybrid film with 20 wt.% S-AgNW, the AgNWs are sparsely dispersed (Fig. 5a). In this case, percolation is not realized, and so the effect of the AgNWs on the σ value is small. In the case of 50 wt.% S-AgNW hybrid film, densely dispersed AgNWs are observed and many of them form percolated structure, resulting in the increase in the σ value. The L-AgNW hybrid films also showed a similar tendency. However, in this series, percolation structure can be formed at lower content (20 wt.%) owing to the greater length (Fig. 5c). Longer one-dimensional materials are generally preferable for forming long-range conductive networks at lower content, thus leading to a low threshold.[23]

In contrast to σ, the S values decreased with increase in AgNW concentration (Fig. 4b). The L-AgNW/PEDOT-PSS films showed a rapid decrease of S. We previously reported a similar tendency in PEDOT-PSS films including one-dimensional gold nanorods (AuNRs).[12] This is a negative effect on the thermoelectric property due to the use of metal in the hybrid material. Because the power factor P strongly depends on the S value (as S^2), both types of hybrid films show a depression in P as a result of the hybridization (Fig. 4c).

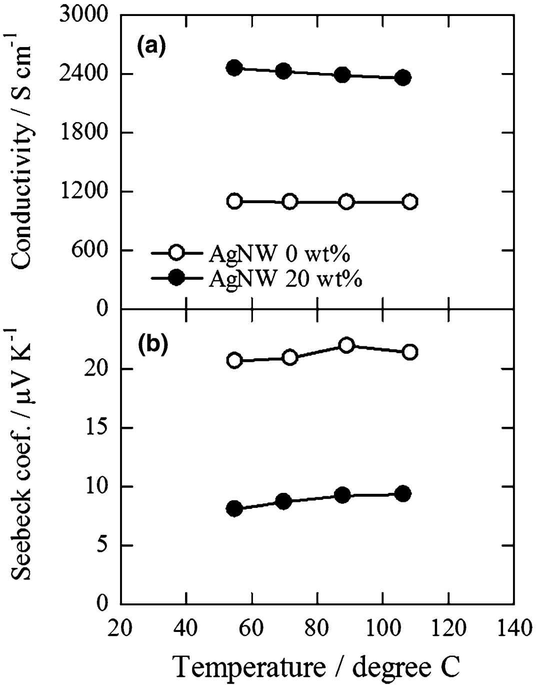

Fig. 3. Temperature dependence of (a) conductivity and (b) Seebeck coefficient for L-AgNW/PEDOT-PSS (20 wt.%) film (filled circles) and PEDOT-PSS film (open circles).

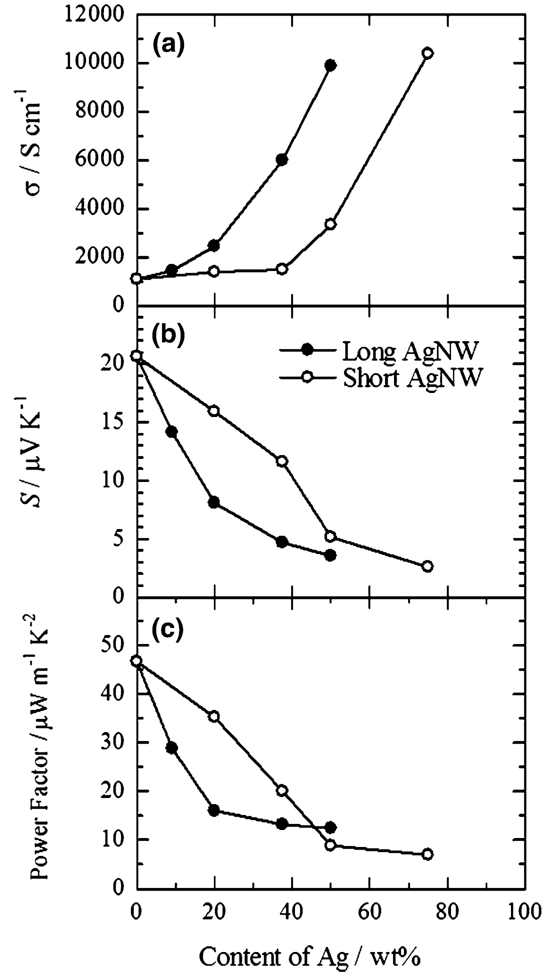

Fig. 4. (a) Conductivity, (b) Seebeck coefficient, and (c) power factor of composite films as functions of AgNW content.

We anticipated the occurrence of hybrid effects on adding AgNWs into the conducting polymers, enhancing σ while simultaneously increasing or maintaining the value of S at some concentrations. Such favorable effects have indeed been realized in some cases. One example is the case of PEDOT-PSS films containing carbon nanotubes (CNTs). With increasing concentration of CNTs, the σ of the hybrid films increases while the S value shows only a small reduction, leading to high power factor values ($\sim$100 μW m^{-1} K^{-2}).[24] Another example is the similar hybrid system of AgNW and PEDOT-PSS. With increase in the concentration of AgNW in the bulky thick hybrid films, σ increased but the S value remained constant and was found to be independent of the content of AgNWs, resulting in enhancement of the power factor (3 μW m^{-1} K^{-2}).[25] This enhancement can be explained based on the energy filtering effect[24,26,27] which hinders transport of low-energy carriers (electrons) across the organic–inorganic interfaces while simultaneously maintaining the carrier concentration. Unlike the above successful cases, it was difficult to find an apparent effect of hybridization in our AgNW/PEDOT-PSS system, even at relatively low AgNW concentration where carrier filtering is expected to be effective. The rapid reduction of the Seebeck coefficient probably reflects increase in the carrier number due to addition of electronically conductive AgNWs, and this fact suggests that the interfaces between (electron-conductive) AgNWs and p-type PEDOT-PSS do not work well to reduce the decrease in Seebeck coefficient. However, we believe that there is room for improvement of the TE properties in our system. Although the above example using bulky thick AgNW/PEDOT-PSS films showed a hybrid effect, the TE performance obtained remained at a low level, which may be because of the low electrical conductivity of the polymer used. Careful design of hybrid material, especially the interfaces between AgNWs and matrix polymer, would be needed for improvement. One example is to construct AgNW–polymer–AgNW conductive paths in the films. Direct contact between AgNWs is probably dominant in this study, which should lead to a strong decrease in S. We believe that completely covering the individual AgNWs with conducting polymer may be an effective way to avoid this. This may be achieved by surface functionalization of the AgNWs and will also contribute to reduce the thermal conductivity. Use of other conducting polymers, especially n-type

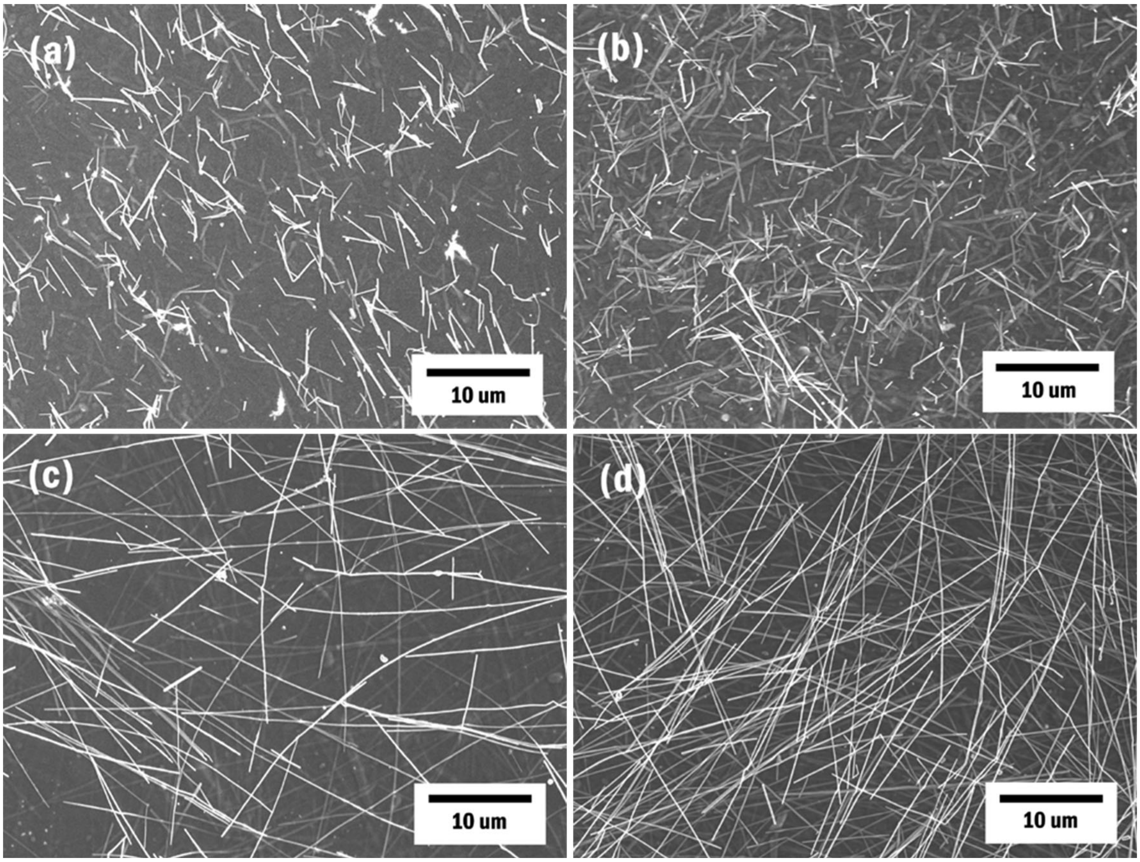

Fig. 5. SEM images of hybrid films containing (a) 20 wt.% S-AgNW, (b) 50 wt.% S-AgNWs, (c) 20 wt.% L-AgNWs, and (d) 50 wt.% L-AgNWs.

materials, would lead to an interesting and better combination.

CONCLUSIONS

We fabricated PEDOT-PSS thin films containing AgNWs as organic–inorganic hybrid TE materials. Two kinds of AgNW with different wire length (L-AgNW and S-AgNW) were used. The electrical conductivity and Seebeck coefficient were examined for several hybrid films with different AgNW concentration. The electrical conductivity of the hybrid films increased with increase in AgNW concentration, resulting from formation of percolated structure of AgNWs. Since the longer AgNWs can easily achieve percolation at relatively low concentration, the increment in the conductivity is larger for L-AgNWs than for S-AgNWs. On the other hand, the Seebeck coefficient of the hybrid films showed a decrease with increasing AgNW concentration, leading to undesirable reduction of TE performance. This behavior suggests that the interaction at the interfaces between the AgNWs and PEDOT-PSS is insufficient, so the carrier mobility and concentration were not well controlled. Adequate design and modulation of the system to optimize carrier transport and concentration will be needed to improve the TE properties. Nevertheless, we want to emphasize that, although the present AgNW/PEDOT-PSS system could not offer good TE performance, control of the electrical conductivity was achieved by tuning the AgNW concentration, which might be useful for design of conducting parts of organic electronic devices.

ACKNOWLEDGEMENTS

This work was financially supported by the Regional Innovation Strategy Support Program (Global Type), “Yamaguchi Green Materials Cluster,” from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

REFERENCES

1. M.C. Gather, A. Köhnen, A. Falcou, H. Becker, and K. Meerholz, *Adv. Funct. Mater.* 17, 191 (2007).
2. T. Chiba, Y.J. Pu, H. Sasabe, J. Kido, and Y. Yang, *J. Mater. Chem.* 22, 22769 (2012).
3. T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, *Proc. Natl. Acad. Sci. USA* 101, 9966 (2004).
4. S. Allard, M. Forster, B. Souharce, H. Thiem, and U. Scherf, *Angew. Chem. Int. Ed.* 47, 4070 (2008).
5. J. Lee, P. Lee, H. Lee, D. Lee, S.S. Lee, and S.H. Ko, *Nanoscale* 4, 6408 (2012).
6. S.K. Lim, E.M. Park, J.S. Kim, S.H. Na, H.J. Park, Y.S. Oh, and S.J. Suh, *Jpn. J. Appl. Phys.* 51, 096501 (2012).
7. S. Günes, H. Neugebauer, and N.S. Sariciftci, *Chem. Rev.* 107, 1324 (2007).
8. Y. Matsuo, *Chem. Lett.* 41, 754 (2012).

9. S. Kirchmeyer and K. Reuter, *J. Mater. Chem.* 15, 2077 (2005).
10. N. Toshima, N. Jiravanichanun, and H. Marutani, *J. Electron. Mater.* 41, 1735 (2012).
11. N. Toshima and N. Jiravanichanun, *J. Electron. Mater.* 42, 1882 (2013).
12. A. Yoshida and N. Toshima, *J. Electron. Mater.* 43, 1492 (2014).
13. N. Toshima, K. Oshima, H. Anno, T. Nishinaka, S. Ichikawa, A. Iwata, and Y. Shiraishi, *Adv. Mater.* 27, 2246 (2015).
14. R.R. Yue and J.K. Xu, *Synth. Met.* 162, 912 (2012).
15. O. Bubnova, M. Berggren, and X. Crispin, *J. Am. Chem. Soc.* 134, 16456 (2012).
16. D. Kim, Y. Kim, K. Choi, J.C. Grunlan, and C.H. Yu, *ACS Nano* 4, 513 (2010).
17. Q. Wei, M. Mukaida, K. Kirihara, Y. Naitoh, and T. Ishida, *Materials* 8, 732 (2015).
18. K.E. Korte, S.E. Skrabalak, and Y. Xia, *J. Mater. Chem.* 18, 437 (2012).
19. J.-H. Lee, P. Lee, D. Lee, S.-S. Lee, and S.-H. Ko, *Cryst. Growth Des.* 12, 5598 (2012).
20. C.L. Kuo and K.C. Hwang, *Langmuir* 28, 3722 (2012).
21. Y. Sun, B. Mayers, T. Herricks, and Y. Xia, *Nano Lett.* 3, 955 (2003).
22. D. Kojda, R. Mitdank, M. Handwerg, A. Mogilatenko, M. Albrecht, Z. Wang, J. Ruhhammer, M. Kroener, P. Woias, and S.F. Ficher, *Phys. Rev. B* 91, 024302 (2015).
23. S.I. White, R.M. Mutiso, P.M. Vora, D. Jahnke, S. Hsu, J.M. Kikkawa, J. Li, J.E. Fischer, and K.I. Winey, *Adv. Funct. Mater.* 20, 2709 (2010).
24. G.P. Moriarty, S. De, P.J. King, U. Khan, M. Via, J.A. King, J.N. Coleman, and J.C. Grunlan, *J. Polym. Sci. Part B* 51, 119 (2013).
25. Y. Liu, Z. Song, Q. Zhang, Z. Zhou, Y. Tang, L. Wang, J. Zhu, W. Luo, and W. Jiang, *RSC Adv.* 5, 45106 (2015).
26. Y. Zhang and G.D. Stucky, *Chem. Mater.* 26, 837 (2013).
27. H. Yang, J.-H. Bahk, T. Day, A.M.S. Mohammed, G.J. Snyder, A. Shakouri, and Y. Wu, *Nano Lett.* 15, 1349 (2015).