

Water-Processable Polymer–Nanocrystal Hybrids for Thermoelectrics

Kevin C. See,^{†,‡,⊥} Joseph P. Feser,[§] Cynthia E. Chen,[†] Arun Majumdar,^{§,||,⊥} Jeffrey J. Urban,^{*,‡,⊥} and Rachel A. Segalman^{*,†,⊥}

[†]Department of Chemical Engineering, University of California, Berkeley, California 94720, United States, [‡]The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 67 R41 10, Berkeley California 94720, United States, [§]Department of Mechanical Engineering, University of California, Berkeley, California 94720, United States, ^{||}Advanced Research Projects Agency—Energy (ARPA-E), U.S. Department of Energy, 1000 Independence Avenue, S.W., Washington, D.C. 20585, United States, and [⊥]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

ABSTRACT We report the synthesis and thermoelectric characterization of composite nanocrystals composed of a tellurium core functionalized with the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Solution processed nanocrystal films electronically out perform both PEDOT:PSS and unfunctionalized Te nanorods while retaining a polymeric thermal conductivity, resulting in a room temperature $ZT \sim 0.1$. This combination of electronic and thermal transport indicates the potential for tailored transport in nanoscale organic/inorganic heterostructures.

KEYWORDS Thermoelectrics, nanocomposites, conducting polymer, nanocrystals, solution process

Thermoelectrics provide the unique capability to directly convert heat to electricity and provide spot cooling or heating. Performance of these materials depends on a combination of Seebeck coefficient, electrical conductivity, and thermal conductivity, consolidated into the thermoelectric figure of merit, $ZT = S^2\sigma T/k$. Nanostructuring of bulk materials has led to significant improvements in ZT^{1-4} as engineered nanoscale interfaces introduce possibilities for both phonon scattering and the energy-dependent scattering of electrical carriers.⁵⁻⁸ Historically, these nanostructured materials required energy-intensive, high-temperature processing methods. Here, we demonstrate that high-performance thermoelectric materials can be realized in solution-processable polymer–inorganic hybrid materials. This hybrid material combines a high electrical conductivity polymer with an inorganic nanoparticle with high Seebeck coefficient. Additionally, attention was paid to work function alignment in order to open possibilities of energy-dependent scattering. The result is a hybrid organic–inorganic material with a higher power factor than either the nanoparticle thin film or polymer thin film, while maintaining polymer-like thermal transport. The measured $ZT \sim 0.1$ is the largest reported value for an aqueous processed material, and the largest reported in an organic or organic/inorganic hybrid to date.

Recently, there has been considerable focus on the development of solution-processable electronic and photo-

voltaic materials, driven by substantial reductions in processing and manufacturing costs enabled by high throughput, large area production processes such as spray coating and printing.^{9,10} Thermoelectrics, a class of energy conversion devices with high module processing costs, could find significant use in spot cooling of microelectronics and the scavenging of waste heat from large area electronics if processed with similarly inexpensive methods amenable to large-area fabrication.

To satisfy this need, thermoelectric transport in two classes of materials—soluble conjugated molecules¹¹⁻¹³ and colloidal quantum dots^{14,15}—have recently received increased attention. However, there exists no obvious strategy to stably improve the intrinsic power factor ($S^2\sigma$) of either materials class, thereby limiting the intrinsic applicability of either individual material as candidate thermoelectrics. Solution-processed inorganic nanoparticles have been previously suggested for these applications, but they remain limited by low electrical conductivities which result in a very low power factor $\sim 0.5 \mu\text{W}/(\text{m K}^2)$ at 300 K.¹⁴ Similarly, evaporated organic thin film systems exhibit intriguing thermoelectric properties but are limited by low conductivities as well.¹⁶ In contrast, solution processed polymers have sufficiently high electrical conductivities but lack competitively high thermopowers.¹¹ Recently, all-organic composites comprised of carbon nanotubes and conjugated polymers have demonstrated intriguing composite properties, but a maximum ZT of only 0.02. In this case, both component materials possess high electrical conductivities and low thermal conductivities, but neither has a particularly high Seebeck coefficient.¹⁷

*To whom correspondence should be addressed, jurban@lbl.gov and segalman@berkeley.edu.

Received for review: 08/13/2010

Published on Web: 00/00/0000



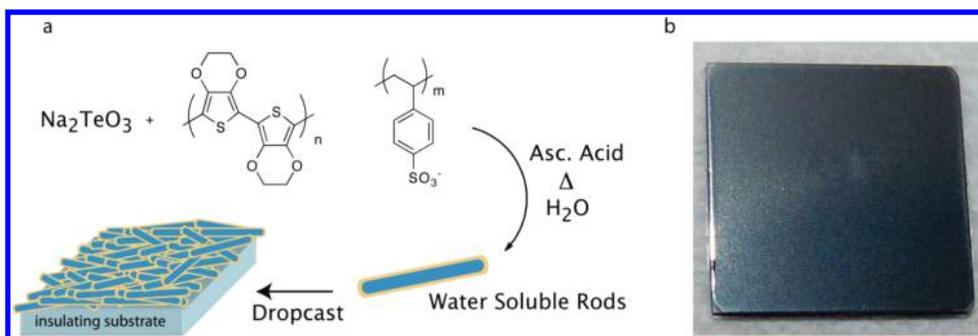


FIGURE 1. (a) Synthesis of PEDOT:PSS passivated Te nanorods, followed by formation of smooth nanocomposite films during solution casting. (b) Picture of a typical drop-cast composite film on a 1 cm² quartz substrate, illustrating excellent film uniformity.

Large gains in thermoelectric figure of merit (ZT) have been realized in inorganic systems by nanostructuring, primarily to reduce thermal conductivity via phonon scattering^{1–4} and, in a few cases, also realizing power factor enhancements derived from energy-dependent scattering.^{6,18,19} However, synthesizing such materials requires high-temperature processing and often exquisite control and precision in the materials architecture.^{1–4} A similar strategy is, in concept, easier to implement in solution-processed materials where nanostructured interfaces are made routinely during the synthetic procedure.²⁰

For example, to capitalize on the potential benefits of carrier filtering, both components (polymer and inorganic) are p-type with similar work functions (~ 150 meV offset).^{21,22} Tellurium (Te) possesses a high thermopower²³ and is easily synthesized in nanocrystalline form in water solutions in the presence of a structure directing surfactant.²⁴ Here, a conductive polymer coating on the rods is introduced with the intention of increasing the electrical conductivity while diminishing the thermal conductivity of the system. Specifically, the Te nanorods are synthesized in situ with a water-soluble conducting polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), yielding a continuous, two-component material. The resulting nanorod film is a continuous electrical network of nanoscale organic/inorganic interfaces.

PEDOT:PSS is a highly conducting polymer capable of conductivities >100 S/cm and, moreover, plays an additional role by serving as a structure directing agent to the Te nanocrystals during growth while imparting water solubility. As a result, the nanocrystalline rod is formed completely covered in a conformal coat of PEDOT:PSS, as shown schematically in Figure 1 and confirmed by both high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) (Figure 2B and Figures S2–4 in the Supporting Information). Furthermore, X-ray diffraction on individual rods demonstrates that they are composed of crystalline tellurium (Figure S1 in the Supporting Information). The polymer also serves to passivate the surface of the nanocrystalline rod and prevent oxidation during processing and use. The resulting particles are highly processable, with aqueous solutions forming stable, high-quality, smooth films with a mirror-like surface (Figure 1b) upon drop-casting or spin-coating. After casting,

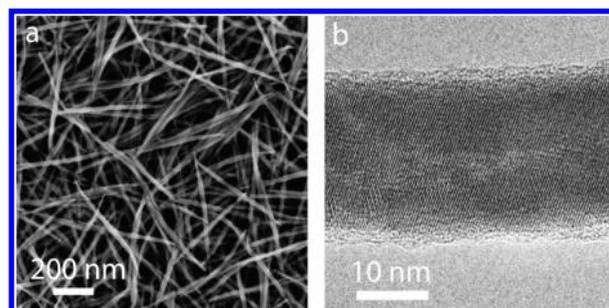


FIGURE 2. (a) SEM image of a drop-cast composite nanorod film. (b) TEM image showing the crystalline Te nanorod passivated with PEDOT:PSS.

mild annealing to drive off residual water results in films with excellent thermoelectric properties, without the need for any high-temperature processing.

The resulting film is smooth, yet nanoporous, with uniformly distributed rods bridged by conducting polymer, as shown in surface and cross-sectional scanning electron microscopy (Figure 2a and Figure S5 in the Supporting Information). Nanoporosity in these samples appears high, but quantification in this hybrid materials system is difficult and is the subject of ongoing work. Elemental analysis (Table S1 in the Supporting Information), energy-dispersive X-ray analysis (Figure S6 in the Supporting Information), and HRTEM all affirm that the film has $\sim 85\%$ weight Te, though it should be noted that carrier filtering and other mechanisms of enhancing the thermoelectric figure of merit are largely interfacial in nature and related to surface area, rather than weight fraction, of the components.

Although the films are nanoporous, they possess smooth, high-quality surfaces enabling facile shadow-mask evaporation of electrodes and dielectrics to allow for electrical and thermal characterization. Here, electrical conductivity is measured via a classical four-point probe Van der Pauw measurement. Thermopower measurements are performed using a similar device configuration, by applying a temperature gradient across the sample; the thermopower is calculated from the slope of the open circuit voltage measured as a function of temperature bias. It is important to note that thermovoltage is an intensive material property not dependent on the amount of material present in the device. (Note:

TABLE 1. Room Temperature Thermoelectric Properties of Te/Pedot:PSS Nanocomposite and Control Films

system	σ (S/cm)	S (μ V/K)	$S^2\sigma_{\max}$ (μ W/(m K ²))	κ (W/(m K))	ZT_{\max}
hybrid	19.3(\pm 2.3)	163(\pm 4)	70.9	0.22–0.30 ^a	0.10
PEDOT:PSS	1.32(\pm 0.12)	18.9(\pm 0.2)	0.05	0.24–0.29	6×10^{-5}
Te NWs	0.08(\pm 0.03)	408(\pm 69)	2.7	2 ^b	4×10^{-4}

^a Films prepared in identical manner to those used for electrical measurements. ^b Bulk value.²⁶ Reported errors are standard deviations; details on statistics are included in the Supporting Information. Thermal conductivity is reported as a range of values for multiple heater lines on different samples (see text for additional discussion).

All samples for electronic measurements were fabricated on insulating substrates to ensure that measured properties were representative of the material only).

The composite film demonstrates both high electrical conductivity (similar to both the polymeric component and bulk Te at >10 S/cm, and 2 orders of magnitude higher than Te nanowires (Te NWs, Table 1) synthesized without conducting polymer) and high thermopower (comparable to bulk Te, but approximately an order of magnitude higher than the bulk polymer alone). Figure 3a shows representative four-probe I - V curves of a composite film in both the forward and reverse directions. These measurements reveal Ohmic behavior and a definitive lack of hysteresis. A plot showing the measurement of the open circuit voltage V_{oc} as a function of the temperature gradient across the film is shown in Figure 3b and shows the expected linear relationship, allowing extraction of the Seebeck coefficient via: $S = -dV_{oc}/dT$.

The values for Seebeck coefficient and electrical conductivity of this composite are compared to the individual components in Table 1 with error bars reflecting standard deviations. The sign of the Seebeck coefficient is positive and significantly larger than that of the pure polymer, indicating that holes are the majority carrier and that transport does not occur strictly through the PEDOT:PSS. Interestingly, all hybrid films display higher electrical conductivity than both PEDOT:PSS and unfunctionalized Te nanorods, indicating

that the PEDOT:PSS protects the Te nanorods from oxidation²⁵ and improves interparticle contact. In fact, the average conductivity of the hybrid films equals or exceeds that reported for thermally evaporated films of Te (~ 13 S/cm),²⁶ remarkable considering the granular nature of the hybrid films and the concomitant high value of thermopower.

Thermal conductivity was characterized using the 3-omega method, which provides reliable data on the through-plane thermal conductivity of thin-film samples.²⁷ The value of thermal conductivity for the hybrid ranges from 0.22 to 0.30 W/(m K). This value is approximately the same as that measured for the polymer itself (Table 1).²⁸ This reduced value of thermal conductivity can be attributed to three factors: (1) the porosity of the films as evident from electron microscopy and inferred from the 13% reduction in the value of thermal conductivity for the hybrid measured in vacuum versus air²⁹ (Figures S5 and S7 in the Supporting Information), (2) the drastic difference in characteristic available vibrational states in the two components,^{30,31} and (3) the fact that the diameter of the nanorods is approaching the intrinsic mean-free-path of heat carrying phonons.³²

Here, we have only presented the through-plane values of thermal conductivity.³³ While some anisotropy in thermal transport may be expected, the hybrid's combination of enhanced power factor while retaining the thermal conductivity of the polymer is remarkable. This combination of an excellent power factor $S^2\sigma$ ($\sim 70 \mu$ W/(m K²)) and low thermal conductivity (~ 0.2 W/(m K)) yields ZT values ~ 0.1 at room temperature, noteworthy considering the fact that the system is processed directly from water.

In summary, a water-soluble composite was synthesized with novel thermoelectric transport properties not captured by any of the individual components, resulting in the highest reported ZT of any aqueous processed material. This exciting development may expand the possible applications of thermoelectric devices due to reduced processing costs. Future efforts targeted at compositional optimization and variation of quantum confined inorganic cores may lead to even higher ZTs. In combination with the facile synthesis and

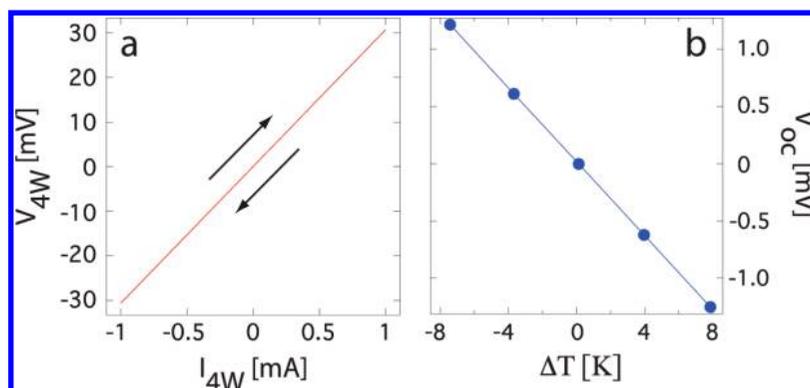


FIGURE 3. (a) Four-probe current/voltage characteristics of a typical nanorod film in the forward and reverse directions showing the negligible hysteresis in the hybrid thin films. (b) Open circuit voltage versus applied temperature gradient for a typical composite film. The Seebeck coefficient is derived from the slope of the linear fit as noted in the text.

solution-processing from a benign solvent such as water, this presents an exciting new platform for both thermoelectrics and studying charge transport in nanoscale heterostructures.

Acknowledgment. We gratefully acknowledge support through the Department of Energy BES-LBL Thermoelectrics Program. This work was partially performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, which is supported by the Office of Science, Office of Basic Energy Sciences, Scientific User Facilities Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231s. We also gratefully acknowledge Dr. Shaul Aloni for assistance in obtaining the High-Resolution TEM images and associated EELS mapping.

Supporting Information Available. Experimental procedures, elemental analysis, additional images, and transport data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- (1) Poudel, B.; Hao, Q.; Ma, Y.; Lan, Y. C.; Minnich, A.; Yu, B.; Yan, X.; Wang, D. Z.; Muto, A.; Vashaee, D.; Chen, X. Y.; Liu, J. M.; Dresselhaus, M. S.; Chen, G.; Ren, Z. *Science* **2008**, *320*, 634.
- (2) Hochbaum, A. I.; Chen, R. K.; Delgado, R. D.; Liang, W. J.; Garnett, E. C.; Najarian, M.; Majumdar, A.; Yang, P. D. *Nature* **2008**, *451*, 163.
- (3) Venkatasubramanian, R.; Siivola, E.; Colpitts, T.; O'Quinn, B. *Nature* **2001**, *413*, 597.
- (4) Kanatzidis, M. G. *Chem. Mater.* **2010**, *22*, 648.
- (5) Kim, W.; Zide, J.; Gossard, A.; Klenov, D.; Stemmer, S.; Shakouri, A.; Majumdar, A. *Phys. Rev. Lett.* **2006**, *96*, 4.
- (6) Ahn, K.; Han, M. K.; He, J. Q.; Androulakis, J.; Ballikaya, S.; Uher, C.; Dravid, V. P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2010**, *132*, 5227.
- (7) Vashaee, D.; Shakouri, A. *Phys. Rev. Lett.* **2004**, *92*, 106103.
- (8) Humphrey, T. E.; Dwyer, M. F. O.; Linke, H. J. *Phys. D: Appl. Phys.* **2005**, 2051.
- (9) Yan, H.; Chen, Z. H.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679.
- (10) Cho, J. H.; Lee, J.; Xia, Y.; Kim, B.; He, Y.; Renn, M. J.; Lodge, T. P.; Daniel Frisbie, C. *Nat. Mater.* **2008**, *7*, 900.
- (11) Shakouri, A.; Li, S. Thermoelectric power factor for electrically conductive polymers. In *International Conference on Thermoelectrics, 18th*, 1999, p 402.
- (12) Reddy, P.; Jang, S. Y.; Segalman, R. A.; Majumdar, A. *Science* **2007**, *315*, 1568.
- (13) Aich, R. B.; Blouin, N.; Bouchard, A.; Leclerc, M. *Chem. Mater.* **2009**, *21*, 751.
- (14) Wang, R. Y.; Feser, J. P.; Lee, J.-S.; Talapin, D. V.; Segalman, R.; Majumdar, A. *Nano Lett.* **2008**, *8*, 2283.
- (15) Kovalenko, M. V.; Spokoyny, B.; Lee, J.-S.; Scheele, M.; Weber, A.; Perera, S.; Landry, D.; Talapin, D. V. *J. Am. Chem. Soc.* **2010**, *132*, 6686.
- (16) Kentaro, H.; Mao, S.; Chihaya, A.; Saburo, T.; Koji, M. *Appl. Phys. Lett.* **2010**, *96*, 253304.
- (17) Kim, D.; Kim, Y.; Choi, K.; Grunlan, J. C.; Yu, C. *ACS Nano* **2009**, *4*, 513.
- (18) Heremans, J. P.; Jovovic, V.; Toberer, E. S.; Saramat, A.; Kurosaki, K.; Charoenphakdee, A.; Yamanaka, S.; Snyder, G. J. *Science* **2008**, *321*, 554.
- (19) Zebarjadi, M.; Esfarjani, K.; Shakouri, A.; Bahk, J.-H.; Bian, Z.; Zeng, G.; Bowers, J.; Lu, H.; Zide, J.; Gossard, A. *Appl. Phys. Lett.* **2009**, *94*, 202105.
- (20) Yin, Y.; Alivisatos, A. P. *Nature* **2005**, *437*, 664.
- (21) Michaelson, H. B. *J. Appl. Phys.* **1977**, *48*, 4729.
- (22) Hwang, J.; Amy, F.; Kahn, A. *Org. Electron.* **2006**, *7*, 387.
- (23) Horne, R. A. *J. Appl. Phys.* **1959**, *30*, 393.
- (24) Xi, G.; Liu, Y.; Wang, X.; Liu, X.; Peng, Y.; Qian, Y. *Cryst. Growth Des.* **2006**, *6*, 2567.
- (25) Andersen, M.; Carlè, J. E.; Cruys-Bagger, N.; Lilledal, M. R.; Hammond, M. A.; Winther-Jensen, B. r.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 539.
- (26) P. Gonçalves, A.; Lopes, E. B.; Alves, E.; Barradas, N. P.; Franco, N.; Rouleau, O.; Godart, C., New Approaches to Thermoelectric Materials. In *Properties and Applications of Thermoelectric Materials*; Springer: Dordrecht, 2009; p 51.
- (27) Cahill, D. G. *Rev. Sci. Instrum.* **1990**, *61*, 802.
- (28) Scholdt, M.; Do, H.; Lang, J.; Gall, A.; Colsmann, A.; Lemmer, U.; Koenig, J.; Winkler, M.; Boettner, H. J. *Electron. Mater.* **2010**.
- (29) Fricke, J.; Lu, X.; Wang, P.; Buttner, D.; Heinemann, U. *Int. J. Heat Mass Transfer* **1992**, *35*, 2305.
- (30) Swartz, E. T.; Pohl, R. O. *Rev. Mod. Phys.* **1989**, *61*, 605.
- (31) Wang, R. Y.; Segalman, R. A.; Majumdar, A. *Appl. Phys. Lett.* **2006**, *89*, 173113.
- (32) Dames, C.; Chen, G. In *Thermoelectrics Handbook: Macro to Nano*; Rowe, D. M., Ed.; Taylor and Francis Group: Boca Raton, FL, 2006; p 12.
- (33) Considerable effort was made to assess the degree of anisotropy in the measured thermal conductivity of the composite; however these results were inconclusive due to intrinsic uncertainties inherent to this measurement. Comprehensive discussion and error analysis of anisotropic contributions to the thermal conductivity are included in the Supporting Information.