High thermoelectric figure of merit in nanocrystalline polyaniline at low temperatures

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Thermoelectric coolers with figure of merit \(ZT\) close to unity at low temperatures are the need of the hour with new advances in high temperature superconductors, superconducting microelectronic circuits, quantum computers, and photonics. Here, we demonstrate that the conducting polymer polyaniline (Pani) doped with camphor sulfonic acid synthesized in semi-crystalline nanostructures, possesses a giant Seebeck effect at low temperatures. The resulting enormously large Seebeck coefficient (up to 0.6 V/K) combined with an intrinsically low electrical conductivity and thermal conductivity give rise to a \(ZT = 0.77\) at 45 K and \(ZT = 2.17\) at 17 K.

A thermoelectric module is composed of \(p\)- and \(n\)-type semiconductor legs connected electrically in series and thermally in parallel via top and bottom electrodes. When a current flows in the device, majority charge carriers of each leg brings with them a small amount of heat, so that a temperature gradient is created between the top and the bottom electrodes. The heat flow \(dQ/dt\) is equal to the magnitude of the current \(I\) times the Peltier coefficient \(\Pi\). The latter is related to the Seebeck coefficient \(S\) via the Kelvin relation, so that the heat flow \(dQ/dt\), measured as Joule per second) is given by \(\Pi = (S/T) I\). Low temperature cooling requires a multistage Peltier cooler. Commercially available \(Bi_2Te_3\)-based modules stacked above each other create a drop in temperature across the cooler from 282 K to 154 K.⁹ To achieve lower temperature and more efficient cooling, the thermoelectric materials at each stage should be ideally different and have an optimum figure of merit \(ZT\) at their working temperature. The figure of merit which gives a measure of the efficiency of a material is defined as \(ZT = (S^2\sigma/k)T\), where \(S\) is the thermo-induced voltage or Seebeck coefficient, \(\sigma\) is the electrical conductivity, \(k\) is the thermal conductivity, and \(T\) is the temperature. There are only a few materials that display \(ZT\) values close to unity below room temperature, say \(p\)-BiSbTe legs with \(ZT = 1\) at 300 K (0.6 at 220 K),² \(p\)-CsBi₄Te₆ with \(ZT = 0.8\) at 220 K (0.4 at 140 K, 0.1 at 60 K),³ and \(n\)-type BiSb alloys with a \(ZT\) peak value of 0.4 at 60 K.⁴ The lack of \(p\)-type thermoelectric materials for low temperature applications has been partially circumvented with superconducting \(YBa_2Cu_3O_7\) legs to avoid losses.⁵ Hence, there is still a lack of efficient thermoelectric material for low temperature applications.

In the search for low temperature thermoelectric materials, our attention has been focused on the giant Seebeck (phonon-drag) effect at low temperatures. The phonon-drag effect specifically implies that the Seebeck coefficient not only has an electronic contribution \(S_e\) but also a phonon contribution \(S_{ph}\). The phonons, with appropriately long mean-free path at low temperatures, drag efficiently the electronic charge carriers towards the end of the material, thus increasing the thermo-voltage \(S_{ph}\) significantly below a threshold temperature \(T_{th}\). Below about one fifth of the Debye temperature \(\theta_D\), there are not enough phonons and \(S_{ph}\) decreases due to the diminishing specific heat \(C\) at low temperatures, leading to the appearance of a phonon-drag peak (PDP). Above \(T_{th}\), there are too many phonons and thus phonon-phonon scattering dominates, the drag effect to the Seebeck voltage is greatly weakened. For instance, metals display a PDP of about a few \(\mu V/K\) (1 \(\mu V/K = 10^{-6} V/K\))⁶ and skutterudites of about 120 \(\mu V/K\).⁷ High \(S_{ph}\) values have been reported for \(HgTe\) (2000 \(\mu V/K\) at 25 K),⁸ and an astounding value of about 46,000 \(\mu V/K\) (but with \(ZT = 0.005\) at 12 K) was found for the strongly correlated semiconductor \(FeSe_2\).⁹ The essential ingredient for observation of a PDP in a material is its (good) crystallinity.⁶ However, \(S_{ph}/k\) ratio and hence figure of merit \(ZT\) at the PDP is negligible since crystalline materials possess large lattice contribution to the thermal conductivity \(k\). This motivates us to investigate the Seebeck coefficient of low thermal conductivity crystals with a glassy matrix, a highly sought-after material for the high potential thermoelectrics, i.e., a semi-crystal.¹¹ We expect a possibly high \(ZT\) value in conducting polymers by crystallization, wherein glassiness, which is ubiquitous along with very small size metallic (crystalline) regions with aligned chains, resulting in a glassy-crystal compositive. In fact, organic conducting polymers known to date possess a \(ZT = 0.1–0.25\) at room temperature because of the intrinsically low thermal conductivity (<0.35 W m⁻¹ K⁻¹) balancing the modest power factor \((\sigma S_e^2 = 30–320 \mu W m^{-1} K^{-2})\).¹²,¹³

We investigate the thermoelectric properties of the nanocrystalline conducting polymer, polyaniline (emeraldine form) doped with different concentrations \(x\) of camphor sulfonic acid (Pani-CSA); the samples are labeled as 0.1 M, 0.5 M, 1.0 M, or 2.0 M CSA. The polymerization of aniline is realized in an aqueous solution containing the oxidant (ammonium persulfate) and the dopant CSA (see supplementary material for more details).¹⁴ The amphiphilic character of

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Camphor sulfonic acid\(^1\) and the possibility to form hydrogen-bonds between water and polyaniline\(^2\) lead to a self-assembly of the polymer chains forming nanostructures (see Figs. 1(a)–1(d) and Scheme 1). One of the advantages of conducting polymers, compared to conducting organic charge transfer salt, is the possibility to tune their oxidation level. For the emeraldine form, the oxidation is simply controlled by the concentration of CSA in the polymerization medium.

The nanostructured polymers are characterized by X-ray diffraction (XRD) (Fig. 1(a)) and various electron microscopy techniques. Thermopower or Seebeck coefficient (\(S\)) measurements in the temperature range of 5–300 K were carried out using compressed pellets sandwiched between two copper blocks, with reference to which absolute \(S\) was measured.\(^3\) The temperature difference was kept in the range of 1.7–2.6 K depending on the temperature. Measurements were repeated several times to check the reproducibility. Electrical conductivity was measured (5–300 K) by the standard two-probe method for high resistive samples (Keithley Model 6517A electrometer) in guarded mode by sourcing the voltage and measuring the current.\(^4\) Thermal conductivity measurements were carried out in a closed-cycle refrigerator, using a direct heat-pulse technique\(^5\) in the temperature range of 10–300 K. The sample was cut to a rectangular parallelepiped shape with one end of the sample glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor as a heat source glued to the other end. The temperature difference was detected by using an E-type differential thermocouple with junctions thermally attached to two well-separated positions along the sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation, and the sample space was maintained in a good vacuum (approximately \(10^{-4}\) Torr) during measurements. All experiments were performed during warming with a rate slower than 20 K/h. The uncertainty of our thermal conductivity measurements is less than 10\%, mainly arising from the error on the determination of the geometrical factor of the specimen.

The aggregation of elongated nanostructures of 0.1 M CSA is displayed in Fig. 1(b) and a single nanotube is shown in Fig. 1(c). The high resolution transmission electron microscope (HRTEM) image (Fig. 1(d)) clearly shows the formation of aligned Pani chains along the rod axis with an interchain spacing of about 3.5 Å. The observed sharp X-ray diffraction patterns (Fig. 1(a)) are better than those in earlier reports,\(^6\) indicative of good crystallinity of our polymer samples. Still, there are feeble noisy backgrounds suggesting that the samples are glassy-crystals or semi-crystals. The characteristic peaks at \(2\theta = 20^\circ\) and 25° in XRD patterns exhibit significant crystalline nature of samples. The peak at \(2\theta = 20^\circ\) corresponds to (100) reflections (parallel periodicity) and the peak at \(2\theta = 25^\circ\) is associated with the (110) reflections (perpendicular periodicity).\(^7\) Pani synthesized directly in the form of emeraldine salt has the ES-I structure\(^8\) where the layers (b,c) of tightly packed polymeric chains are separated along ‘a’ (2\(\pi/a^*\)). The peak at \(2\theta \approx 10^\circ\) is associated with (001) intra-chain reflections indicating that polymer chain direction ‘c’ is tilted with respect to the reciprocal lattice vector ‘c*’. The chains are tilted within the layer in order to avoid face to face repulsion between the adjacent aromatic rings compactly packed along ‘b.’ The degree of crystallinity in the nanotubes increases with concentration \(x\), which might be attributed to the increased cohesive energy via electrostatic interactions between the CSA anions and the charged polymer chains. The multiple XRD peaks in the range of \(2\theta = 4.4^\circ–40^\circ\) indicate the molecular order at

**FIG. 1.** Structural and morphological characterization of the Pani-CSA nanostructures. (a) X-ray diffraction of four Pani-CSA samples and (b)–(d) representative HRTEM images of 0.1 M CSA polyaniline at increasing magnifications.

**SCHEME 1.** Schematic of the arrangement of polyaniline chains in a nanotube.
various scales, from 0.2 nm to 2.0 nm, as illustrated in Scheme 1. At the atomic scale, the maximum intensity peak at 25° represents a distance of 3.5 Å (using Bragg’s law) separating adjacent polyaniline chains. This promotes the electronic coupling between the p-electrons of adjacent chains, which is a prerequisite for efficient charge transport and interchain electronic band formation.21 The nanotubes are agglomerated into smooth cylindrical wires of average diameter ranging from ~150 nm to 2 μm having submicron to several micrometers in length (see Fig. S1 in supplementary material).14

The electrical conductivity of the compacted Pani-CSA nanopowder pellets at 300 K decreases with decreasing protonation level: 0.25 S/cm (2.0 M), 0.11 S/cm (1.0 M), 2.3 × 10⁻² S/cm (0.5 M), and 5.4 × 10⁻⁴ S/cm (0.1 M). The temperature evolution of the normalized electrical conductivity of the studied samples is shown in Fig. 2(a). At low oxidation levels, the conductivity decreases from 300 K to about 60 K and 150 K for 0.1 M and 0.5 M CSA, respectively, a semiconducting behavior presumably due to the thermally activated polaron-hopping transport24 (detailed analysis is described in the supplementary material14). This corroborates with a strong response in the near-infrared region typical of the polaronic network formed in the highly oxidized Pani-CSA films observed in the optical reflectance spectrum25,26 (Fig. S2 in supplementary material14). It is found that the electrical conductivity increases slightly below these respective temperatures, a phenomenon attributed to a metal-insulator transition (MIT).27 At high oxidation levels, the conductivity is metallic-like, from 300 K to about 74 K for 2.0 M CSA and to 140 K for 1.0 M CSA. This behavior, also found in semi-crystalline polyaniline films, is reminiscent of metallic transport.21 Below 74 K and 140 K, they become semiconducting and exhibit a reverse MIT. Such an atypical MIT conductivity is found to be due to 3D VRH in the semiconducting regime combined with 3D localization-interaction in metallic regime (see supplementary material14). The 3D VRH transport observed here has been reported in single nanowire,27 a further evidence of good crystallinity of our polymer samples. Moreover, in contrast to the previous reports,28,29 a sudden drop in conductivity below 140 K for 1.0 M CSA (74 K for 2.0 M CSA) is clearly seen (Fig. 2(a)). Such a behavior is most likely attributed to the enhanced polaron-phonon scattering, a feature typically observed in the presence of a phonon-drag effect in inorganic crystals.30

The temperature evolution of the Seebeck coefficient of Pani-CSA is displayed in Fig. 2(b). At 300 K, the value of S for the metallic samples (Sₚ = 2.5 μV/K) is smaller than that of the semiconducting samples (Sₚ = 14 μV/K for 0.5 M and 21 μV/K for 0.1 M). The metallic (semiconducting) samples show a smooth (rapid) decrease in S with temperature, a typical behavior of charge carrier diffusion (hopping), and then S eventually reaches slightly negative values (see supplementary material14). In Pani, the electrical conduction is achieved through protonation (in present case through CSA doping) implying that the charge carriers are holes. This is further confirmed by the positive value of S, indicating that Pani-CSA system is a p-type semiconductor. Below a threshold temperature Tₚₘ, the Seebeck coefficient displays an extraordinary increase by almost five orders of magnitude to reach values up to 0.6 V/K (Fig. 2(b)) at its peak. Such a giant Seebeck effect has never been reported in any other materials including conducting polymers31 and Pani-CSA films.32 The maximum Seebeck coefficient Smax systematically decreases with increase in x, whilst the samples become
more metallic, i.e., \( S_{\max} \) is 0.58 V/K at 40 K, 0.17 V/K at 25 K, 0.09 V/K at 10 K, and 0.07 V/K at 14 K for 0.1 M, 0.5 M, 1.0 M, and 2.0 M CSA, respectively. Clearly, the oxidation level controls \( T_{th} \) over a wide range (72–245 K). The threshold temperatures \( T_{th} = 72 \), 85 K, and 120 K for 2.0 M, 1.0 M, and 0.5 M CSA samples are lower than their MIT temperatures (74 K, 140 K, and 150 K in Fig. 2(a)). For 0.1 M CSA however, \( T_{th} \sim 245 \) K is four times the MIT temperature (60 K).

Since phonon-electron interactions are of importance for the thermoelectric properties, the phonon transport is investigated by measuring the temperature evolution of the thermal conductivity for different CSA concentrations (Fig. 2(e)). More details of the thermal conductivity measurement are found in the supplementary material. At 300 K, \( \kappa \) is larger (0.5–0.7 W m\(^{-1}\) K\(^{-1}\)) than that of thin Pani-CSA film (0.15 W m\(^{-1}\) K\(^{-1}\)) but comparable to those of inorganic thermoelectrics (0.6–1.5 W m\(^{-1}\) K\(^{-1}\)) and Pani-CSA thick film (0.6 W m\(^{-1}\) K\(^{-1}\)). These low thermal conductivities are typical of amorphous materials. The smallest possible thermal conductivity in a solid as predicted by Slack in 1977 is when the mean-free path of the phonons is equal to the smallest distance in the solid. In our case, it is not the interatomic distance in the polymer chain but rather the interchain distance (weak interchain interaction) that limits the phonon mean-free path and ensures the low thermal conductivity. It is found that the thermal conductivity of all studied samples decreases rather linearly from room temperature to 100 K, as expected for a conducting polymer or a glass (amorphous). Below 70 K, \( \kappa \) increases rapidly and develops a peak at \(~25\) K with a value of about 0.5–0.8 W m\(^{-1}\) K\(^{-1}\), below which it falls abruptly as \( T \) decreases. The peak, observed commonly in semi-crystalline and crystalline organic materials, not in previously known conducting polymers, is interpreted as that of a semi-crystal, i.e., glassy material in a crystal form, and it is a potential candidate for good thermoelectrics (see supplementary material). The overall feature is attributed to the attenuation of the phonon-phonon scattering, promoting large phonon mean-free path at low temperature, but limited by the grain boundaries of the nanotubes. In brief, the thermal conductivity depicts features of both crystalline and amorphous phases of the conducting polymer system. As a matter of fact, we have also obtained a similar behavior of thermal conductivity for Pani-HCl nanofibers. The low-temperature peak is most likely due to the competition between phonon-boundary scattering and Umklapp phonon-phonon scattering, while the quasi-linear behavior of \( \kappa \) above 100 K is attributed to thermally activated hopping of localized optical-phonons interacting anharmonically with extended acoustic-phonons.

The giant maximum Seebeck coefficient (0.07–0.58 V/K) along with peculiar thermal and electrical conductivities is indicative of an interesting new phenomenon, pertinent to these nanocrystalline materials. Although, a full understanding of the phenomenon will require more experiments and theoretical modeling, we propose that it is a phonon-drag effect, although other hypotheses are not yet fully excluded. Since the effect is seen both when majority part of the material is 3D crystal combined with a small fraction in amorphous form, the origin of this extraordinary effect could be understood as a consequence of the strong polaron-phonon coupling, and possible Umklapp processes due to warped Fermi surface. This may lead to cooperatively dragging of phonons with the polarons, in contrast to the phonon-electron scattering in metals wherein the PDP is usually very small. As stated earlier, in polyaniline systems conductivity is induced by protonation process suggesting that the polarons are trapped positive charge carriers or holes. Therefore, phonon drag process here could be realized as phonon-hole scattering. The strength of this coupling might originate from the match of two key dimensions: First, the size of polaronic domains depends on the CSA concentration but possibly varying from a single polaron (1.5 nm) up to large networks reaching the dimension of the nanotubes due to the high crystallinity (Figs. 1(c) and 1(d)). Second, the mean-free path of phonons transported in these nanostructures is the average of inner and outer diameters ranging from 47 nm to 100 nm. These dimensions provide the order of magnitude of the phonon mean-free path for \( T < T_{th} \) assuming the grain boundary scattering is operative efficiently in the heat transport for these polymers. Hence, polaronic domains and phonon mean-free paths are of the same order of magnitude.

In order to assess their potential thermoelectric properties, the power factor \( \Sigma^2 \) and figure of merit \( ZT \) versus \( T \) are plotted (Figs. 3(a) and 3(b)). Obviously, the giant maximum Seebeck coefficient overwhelms the electrical and thermal conductivities such that both \( \Sigma^2 \) and \( ZT \) plots display rather similar trends as the Seebeck coefficient. The \( \Sigma^2 \) attains \( 1.1 \times 10^{-2} \) W m\(^{-1}\) K\(^{-2}\) at 40 K for 0.1 M CSA, \( 7 \times 10^{-4} \) W m\(^{-1}\) K\(^{-2}\) at 31 K for 0.5 M CSA, \( 1.7 \times 10^{-2} \) W m\(^{-1}\) K\(^{-2}\) at 17 K for 1.0 M CSA, and \( 6.3 \times 10^{-2} \) W m\(^{-1}\) K\(^{-2}\) at 17 K for 2.0 M CSA. The maximum \( ZT \) values vary from 0.012 at 90 K, 0.15 at 70 K up to 0.77 at 45 K for 0.1 M CSA. For the higher oxidation level, \( ZT \) vs. \( T \) displays a sharp peak with high values of \( ZT = 0.5 \) at 16 K for 1.0 M CSA and \( ZT = 2.17 \) at 17 K for 2.0 M CSA; the high value of \( ZT = 2.17 \) indicates good thermoelectric efficiency of the material at such a low temperature which has not been observed in any other material till date. These overall extraordinary thermoelectric properties are ascribed to the nanostructures, wherein 3D electrical transport prevails, yet with glassy background and varying length scales of macro to nanostructures and molecular chains. Such a combination makes the present polymer...
system a suitable complex material with distinct regions providing different functions, which appears to defy the usual band theory but essentially meets all the ingredients for the best thermoelectrics including one dominant carrier (hole). Therefore, the observed large Seebeck coefficient does not have the same temperature profile as the lattice thermal conductivity peak. The high figure of merit of the low conducting samples at still relatively high temperature does not however give its large value above 77 K (see supplementary material). Since the most efficient Pani-CSA sample at high temperature is of low electrical conductivity, Peltier coolers that operate at low temperature are expected to be more efficient in thin-film device architecture to limit the internal resistance.

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