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Deepa Madan, Xingang Zhao, Robert M. Ireland, et al.



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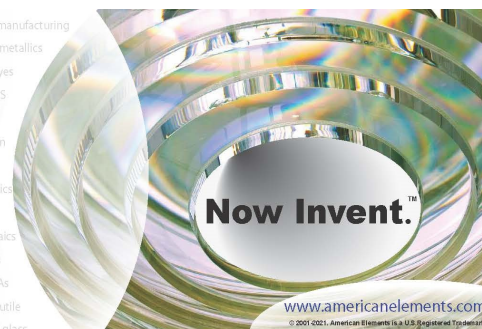
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Conductivity and power factor enhancement of n-type semiconducting polymers using sodium silica gel dopant

Deepa Madan,^{1,2,a} Xingang Zhao,^{1,a} Robert M. Ireland,¹ Derek Xiao,¹ and Howard E. Katz^{1,b}

¹*Department of Materials Science and Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, USA*

²*Department of Mechanical Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250, USA*

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This work demonstrates the use of sodium silica gel (Na-SG) particles as a reducing agent for n-type conjugated polymers to improve the conductivity and thermoelectric properties. Substantial increase in the electrical conductivity (σ , from 10^{-7} to 10^{-3} S/cm in air) was observed in two naphthalenetetracarboxylic diimide solution-processable n-type polymers, one of which was designed and synthesized in our lab. Systematic investigations of electrical conductivity were done by varying the weight percentage of Na-SG in the polymers. Additional evidence for the reduction process was obtained from electron spin resonance spectroscopy and control experiments involving nonreducing silica particles and non-electron-accepting polystyrene. The Seebeck coefficient S of the highest conductivity sample was measured and found to be in agreement with an empirical model. All the electrical conductivity and Seebeck coefficients measurements were performed in ambient atmosphere. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4990139>]

Polymers are promising materials for thermoelectric (TE) devices because they are solution-processable and lighter weight, composed of more readily available chemical constituents, and have lower processing costs than many inorganic alternatives. To make flexible TE generator devices (TEGs), n- and p-type solution-processable polymers are required.

A significant amount of work has been reported for solution processable, air-stable p-type TE polymers with suitable dopants.^{1,2} TE performances of p-type polymers are remarkably improving over the last decade.^{3,4} On the other hand, far fewer reports on n-type solution-processable thermoelectric polymers are disclosed in the literature.^{5–9} First, n-type polymers are often air and moisture sensitive in their doped forms, making them less stable in ambient conditions.¹⁰ Second, many n-type polymers have low solubility, making them difficult to use for flexible electronics applications. Third, their conductivity is less than desired.^{11–13} A suitable n-dopant can accomplish doping by directly transferring an electron to the host material. A suitable strong reducing agent added to the n-type polymer as a dopant has the potential to increase the conductivity of n-type polymers.^{12–15}

Chabinyk *et al.* demonstrated solution doping of an n-type polymer P(NDIOD-T2), using 2-(4-dimethylamino phenyl)benzimidazoline N DMBI and its derivatives as potential dopants.¹² Pei *et al.* developed a series of n-type polymers that can be easily doped and solution-processable and had record high conductivity of 14 S/cm for one of them doped with 2-(4-dimethylamino phenyl)benzimidazoline (N-DMBI).¹⁶ Recently, Bao *et al.* showed that perylene diimide (PDI) and naphthalene diimide (NDI) based copolymers can be reduced by the dimeric dopant (2-Cyc-DMBI)₂

^aD. Madan and X. Zhao contributed equally to this work.

^bAuthor to whom correspondence should be addressed: hekatz@jhu.edu

and are solution-processable.^{13,14} Although the power factors obtained in above-mentioned cases are encouraging, all the TE properties are measured under an inert atmosphere, whereas in practical applications, the thermal barriers associated with separating the active TE materials from the environment would greatly diminish TE efficiencies. It seems that for n-type solution-processable polymers, N DMBI and its derivatives are the most popular dopants to improve the electrical conductivity.^{12–14,16}

We continue to seek new methods to improve the conductivity of n-type polymers so they can be used in flexible TE devices together with the p-type polymers. Alkali metals are known to have excellent reducing properties for n-type polymers.¹⁷ However, they are neither readily dispersible nor straightforward to handle in the open air.¹⁸ Lefenfeld *et al.* have reported the convenient encapsulation of sodium atoms into nanostructured silica gel.¹⁹ Encapsulation decreases the danger of handling sodium metal in the ambient atmosphere while maintaining its reducing properties.²⁰ While Lefenfeld's goal was to facilitate chemical reduction reactions, we were motivated to use sodium silica gel as a reducing agent to reduce, and thus dope, the n-type TE polymers under study.

Since the first air-stable high-electron-mobility NTCDI derivative was reported by Katz *et al.* in 2000,^{21,22} NTCDI has been a most popular n-type building block.^{23–25} In this work, we used two solution processable, air-stable n-type polymers based on NTCDI main chains. One is the commercially available NTCDI2DT-2T (N1), and the other has a tetrafluorophenylene linker to promote planarity, π -conjugation and lowering of the LUMO, abbreviated as NTCDI-AF4A (N2). NTCDI-AF4A was synthesized in the lab, and details are given in the supplementary information. Figure 1 shows the chemical structures of the host matrix NTCDI2DT-2T (N1) and NTCDI-AF4A (N2) polymers.

We mixed polymers with a varied weight percentage of Na-SG salts and achieved three orders of magnitude improvement in the conductivity of doped polymers compared to pristine polymers measured in air. This establishes the use of Na-SG as a reducing/doping agent for n-type polymers, effective in the ambient atmosphere. As will be seen, both polymers gave similar values of electrical conductivity when mixed with the particles.

Na-SG was purchased from Sigma Aldrich. To confirm the presence of the sodium in the supplied sodium silica gel, we sent it for chemical analysis, and the report confirmed that 33% sodium (Na) was present. Na-SG solid particles were added to NTCDI2DT-2T (N1) and NTCDI-AF4A (N2) polymers in the range of 0% to 75 wt. %. Na-SG was found to be dispersed in the host matrix. Figure 2 shows scanning electron microscopy images of Na-SG particles dispersed in N1 and N2 polymers.

The nominal particle size of Na-SG was in the range of 1 μm to sub micron range. Therefore, the Na-SG doped polymer films were inhomogeneous. To confirm that sodium in sodium silica gel is present in the composites, we performed X-ray photon spectroscopy (XPS) of 75 wt. % Na-SG particles in N1 and N2 composite films. Figure 3 shows XPS of NTCDI2DT-2T with 75 wt. % of Na-SG polymer and NTCDI-AF4A with 75 wt. % of Na-SG. For pure polymer films, significant peaks for C, O, and F are present, indicative of the polymer matrix. Also the polymers show small traces of Si and N. The peak for C 1s is present at 287 eV, O 1s peak is observed at 529–532 eV, and F is present at 700–710 eV. N1 doped with 75 wt. % doped Na-SG particles shows a very sharp

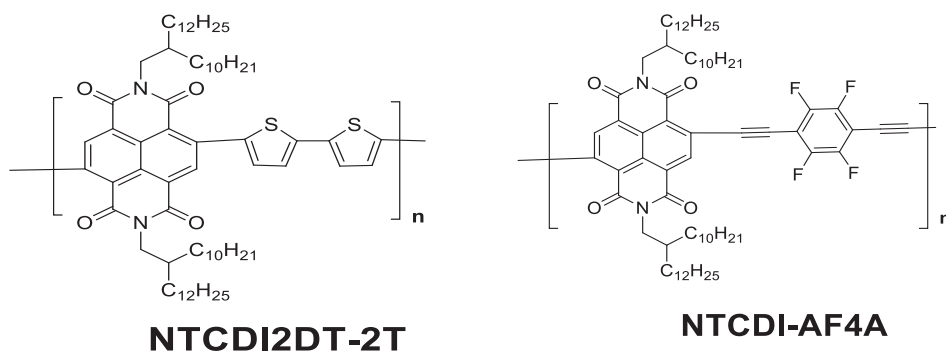
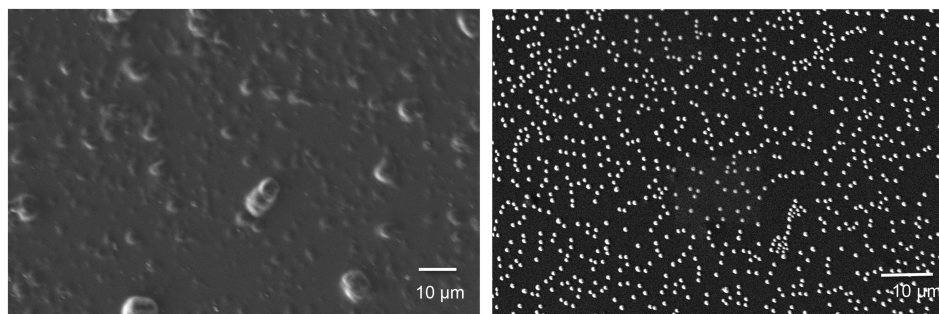
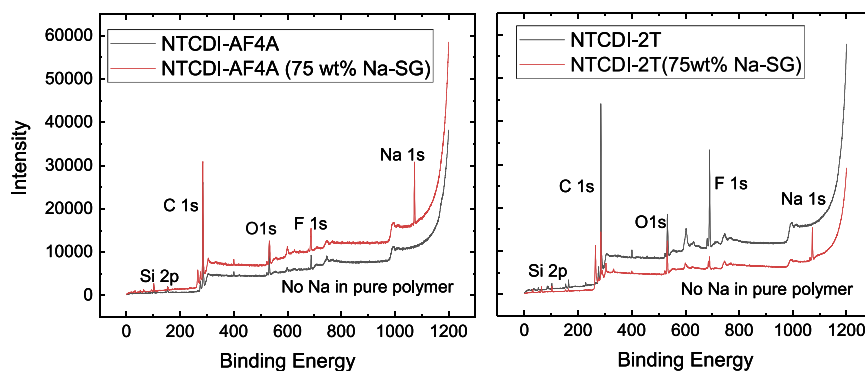


FIG. 1. Chemical structures of NTCDI2DT-2T (N1) and NTCDI-AF4A (N2) polymers.

FIG. 2. SEM image of N1 and N2 polymers (scale bar 10 μm) with Na-SG particles.FIG. 3. XPS image of N1 (top, scale bar 10 μm) and N2 polymers (bottom, scale bar 10 μm) with Na-SG particles.

peak at a binding energy of 1075 eV that corresponds to the Na 1s peak. A similar Na peak was observed at 1070 eV in NTCDI-AF4A with 75 wt. % of Na-SG. The Na 1s peak is observed in 75 wt. % doped N1 and N2 samples, respectively, at 1070-1080 eV. We have also noticed that silica peak from sodium silica gel is much smaller than Na peak in intensity because the sensitivity factor for Si is much smaller than Na.²⁶

Figure 4 shows the conductivity of N1 and N2 polymer composite films measured at room temperature in ambient atmosphere, as a function of weight percentage of Na-SG particles. As shown in Fig. 4, the electrical conductivity of pure polymers N1 and N2 is in the range of 10^{-7} S/cm. With the addition of Na-SG particles, conductivities of N1 and N2 polymer composite films increased by up to four orders of magnitude. Specifically, 75 wt. % Na-SG particles in polymer composite films N1 and N2

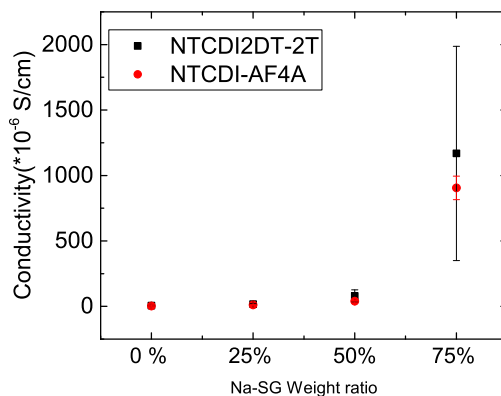


FIG. 4. Electrical conductivity of undoped and Na-SG doped N1 and N2 polymers at varying weight percentage.

resulted in four order magnitude increases in electrical conductivity as compared to pristine films. This increase was similar for films measured in inert atmosphere and for films measured without delay in air. NTCDI2DT-2T with 75 wt. % Na-SG particles has electrical conductivity in the range of 10^{-3} S/cm. The increase in electrical conductivity is consistent with sodium in Na-SG particles reducing the polymers N1 and N2. Reduction of polymers would introduce mobile charge carriers (electrons) into the LUMO of the semiconductors to increase their carrier density and electrical conductivity.¹⁹ After a few minutes in air, the conductivity decreased to near its undoped value and the silica particles became opaque white. In the case of the more electron-demanding NTCDI-AF4A, the radical anion was stable enough to be observable in solution following its generation by the one-electron reduction of the polymer by Na-SG. As shown in Fig. 5, NTCDI-AF4A doped with 75 wt. % Na-SG showed a prominent single-electron peak.

If it is assumed that the density of the silica particles is slightly less than 1 (accounting for porosity or free volume in the particles), then Na-SG particles and polymer will be approximately 80% and 20% by volume, respectively, in the 75 wt. % samples. Thus, the conductivity, taking into account the polymer fraction only, is probably another order of magnitude higher than what we report here. Insulating Na-SG particles would block the path of many of the charge carriers in a polymer. We expect that decreasing the particle size of Na-SG to submicron sizes, the charge carriers could more easily move past the particles, allowing the realization of higher conductivity.

Several control experiments were performed to confirm the fact that Na in Na-SG interacting with the conjugated polymer was associated with the increased electrical conductivity. Pure silica gel was mixed with NTCDI2DT-2T and the solution was dropcast on a pre-patterned gold electrode film on glass. The conductivity of this film was 10^{-7} S/cm, similar to that of a pristine polymer. Conversely, addition of Na-SG to the non-electron-accepting polystyrene did not result in a conductivity increase either. Taken together, these experiments support the idea that an electron acceptor interacting with the Na in Na-SG is required for Na-SG to have an effect on composite conductivity; the particles alone do not form a conductive network and do not affect the conductivity of a nonreducible polymer.

The doping efficiency of Na-SG is low mainly because only a small fraction of Na particles, the ones that are nearest the surface of silica gel particles, participate in the reduction process. The sodium atoms deeper in the bulk of the particles would require excessive charge separation work to be active dopants. The use of smaller particles than are available commercially would ameliorate this issue.

A continuous current of 43 μ A running for one hour across a 2×10^{-5} cm³ sample showed no decrease over that time period and effectively moved a number of charges (10^{18}) equal to the total number of nonhydrogen atoms in the sample, ruling out ionic current as the major origin of the conductance. Finally, we compared Na-SG to a potentially reducing alkoxide salt, potassium tert-butoxide. While the tert-butoxide salt caused a modest increase in conductivity at relatively low

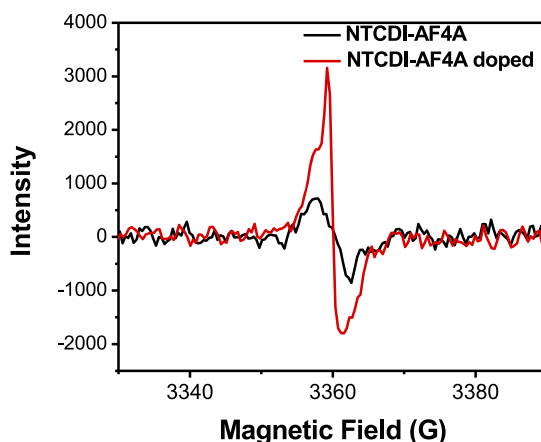


FIG. 5. ESR spectra of NTCDI and 75 wt. % Na-SG doped NTCDI-AF4A in solution.

concentrations of one molar equivalent (10 wt. %), increasing its concentration to 50 wt. % did not result in conductivity increases that were observed for similarly concentrated Na-SG.

We also measured the Seebeck coefficient (α) for 75 wt. % Na-SG doped NTCDI-AF4A and NTCDI-2T films in ambient atmosphere. The Seebeck coefficient of the polymer composites had negative sign, confirming that NTCDI-2T and NTCDI-AF4A are n-type polymers. In the literature, many researchers have already shown NTCDI-2T polymers to be n-type, so our results are consistent with those of others.¹² The Seebeck coefficient of the doped NTCDI-AF4A films in ambient air has an average value of $-980 \mu\text{V/K}$. The corresponding electrical conductivity (σ) for these samples was $8 \times 10^{-4} \text{ S/cm}$. Therefore, the average thermoelectric power factor ($\alpha^2\sigma$) was $0.078 \mu\text{W}/(\text{m K}^2)$ for 75 wt. % doped Na-SG. The Seebeck co-efficient of NTCDI-2T doped with 75 wt. % Na-SG films has an average value of $-950 \mu\text{V/K}$. The corresponding electrical conductivity (σ) for this sample was $2 \times 10^{-3} \text{ S/cm}$. Therefore, the average thermoelectric power factor ($\alpha^2\sigma$) was $0.18 \mu\text{W}/(\text{m K}^2)$ for 75 wt. % doped Na-SG. This value of power factor is very similar to that obtained by Chabinyac *et al.* while doping P(NDIOD-T2) with DMBI. In our case, we have processed films in an inert atmosphere, but the electrical conductivity and Seebeck coefficient were measured in the ambient atmosphere.

An interesting calibration of our results can be performed with reference to an empirical “universal plot” of polymer Seebeck coefficients vs. electrical conductivities, which revealed a proportionality between the Seebeck coefficient and conductivity to the $-1/4$ power.²⁷ Our best results of n-type samples (75 wt. % Na-SG doped polymer films) had the highest electrical conductivities about 10^{-3} S/cm and the Seebeck coefficient of about $600 \mu\text{V/K}$. These values of electrical conductivity and the Seebeck coefficient coincide well with the plot. However, it is worth mentioning here that the universal plot of the Seebeck coefficient vs electrical conductivity was for p-type polymers only.

In summary, we report sodium silica gel being used as a reducing agent for n-type polymers. With 75 wt. % Na-SG particles, the maximum conductivity achieved for NTCDI-2DT is $4 \times 10^{-3} \text{ S/cm}$. This conductivity value is very similar to the conductivity reported by Chabinyac *et al.* and Bao *et al.* for n polymer doped with N-DMBI (10 mol. %) in thin film form with measurements done in an inert atmosphere.^{12–14} Our films were several microns, advantageous for thermoelectrics compared to thinner films, and all of our measurements were performed in air. Although 75 wt. % of Na-SG was used to reduce the polymer, only a small fraction of the Na atoms were active as a reducing agent. This inference is based on the observation that Na-SG particles did not dissolve in the polymer solution, but instead were dispersed in the polymer matrix. We also noticed that 75 wt. % Na-SG doped polymer films eventually reacted with air and humidity. Na-SG particles in films turned white when samples were left in the open atmosphere. The use of passivation layer on the top of these films to prevent the interaction with air and moisture can be explored in future research. The electronic properties of the new n-type polymer which we have synthesized are comparable to those of the commercially available P(NDIOD-T2), with more electron-stabilizing main-chain functionality. We also established that Na-SG is a strong reducing agent with analogous electron donating activity to N-DMBI.

See [supplementary material](http://aip.scitation.org/journal/apm/) for the experimental procedures, measurement details, and synthesis of N2 polymers. This material is available free of charge via the Internet at <http://aip.scitation.org/journal/apm/>

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