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Field-effect and chemical charge-type modulations of carbon nanotubes using functional polymers for thermoelectric energy harvesters

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Abstract. As devices continue to shrink in size and grow in abundance, power supply methods using clean and abundant materials become increasingly important. Single-walled carbon nanotubes (SWCNTs) are promising materials as the thermoelectric (TE) energy-harvesting candidate due to their flexibility, nontoxicity, and relatively large TE power factors. This paper reviews our current studies on the charge-type conversion of SWCNTs for readily pairing several p- and n-type SWCNTs to improve the TE voltage output. First, we describe the polarity tuning of SWCNTs by electric dipoles of ferroelectric polymer. The sign of Seebeck coefficient of SWCNTs could be tuned by the direction of the electric dipoles adjacent to nanotubes in the ferroelectric-gate field-effect transistor-like device configuration. Second, we demonstrate the electron doping into SWCNTs by several versatile polymer-dopant charge transfer. The obtained negative Seebeck coefficients of SWCNTs were correlated to the highest occupied molecular orbital energy levels of the dopant polymers. Our findings enables the direct use of low-temperature waste heats around dwelling environments using eco-friendly materials and techniques.

1. Introduction

Seamlessly sensing every object around us and connecting their information through the Web systems offer us comfortable daily lives with accuracy, efficiency, and economic benefits. On the monitoring, vast of wearable sensing devices embedded in the objects will play a crucial role, connecting our physical world to the networks; the supply of electrical power to these sensors is a recent important problem. For automatic operations of these sensors over an extended period of time without any additional maintenance, energy harvesting technologies have emerged as the promising candidates. Of these, thermoelectric (TE) conversion devices, which generate electrical power from temperature differences, will provide a good solution because heat flows is quite common in dwelling environments.

Single-walled carbon nanotubes are considered the main candidate for this application due to their relatively large Seebeck coefficient, electrical conductivity, flexibility, nontoxicity, and printability onto plastics, papers, and textiles, efficiently harvesting the most ubiquitous energy source available to



us: human body heats. In order for this technology to become truly pervasive, we should develop the way to generate sufficient power from the small temperature differences. Typically, any TE device should be modularized so that it contains many p- and n-type TE legs that are connected electrically in series and thermally in parallel, because this device architecture enables to directly add the TE voltages of each leg that is subject to the same temperature difference. Both the p- and n-type materials are therefore needed for developing the practical TE devices. However, SWCNTs generally show a p-type nature in ambient air conditions, as electrons are withdrawn by oxygen impurities; air-stable n-type conversion of SWCNTs is a current challenging issue for TE application. In this Article, we review our recent studies on the charge-type conversion of SWCNTs using field-effect-induced charge-carrier accumulation by electric dipoles of a ferroelectric polymer [1] and a charge-transfer interaction between nanotubes and versatile polymer dopants.[2]

2. Polarity tuning of SWCNTs by ferroelectric dipole

Conventional techniques of charge-carrier injection into the SWCNTs include (1) the lattice substituent of carbon networks by hetero atoms, (2) the charge-transfer interaction between nanotubes and dopants, and (3) the charge-carrier accumulation into the nanotube in the field-effect transistor (FET) configuration.[3–5] The lattice substituent enables the stable electron injection into nanotubes; however, the introduction of hetero atoms destroys the expanded sp^2 framework of nanotubes and causes the significant decrease in the charge-carrier mobility. Charge carriers could be conveniently injected via charge-transfer interaction between nanotubes and dopants physically adsorbed on the nanotube surfaces. However, the n-type SWCNTs are generally unstable in air due to autoxidation. The development of air-stable n-type SWCNTs via polymer-dopant charge transfer will be described in the next section.

In this section, we demonstrate the polarity (charge-type) tuning of the SWCNTs using (3) the charge-carrier accumulation in the FET configuration.[1] Several authors have reported an ambipolar charge transporting properties of SWCNTs-based FETs; SWCNTs could intrinsically accumulate and transport both holes and electrons.[5] Therefore, using field-effect-induced charge carrier modulation should be an effective way to tuning their polarities. However, this charge-type conversion, in principle, need a gate voltage in order to continuously accumulate the carriers. To this problem, we used a ferroelectric polymer (P(VDF/TrFE)) and applied the ferroelectric-gate FET (FeFET)-like device configuration as shown in figure 1 (a) and (b). This polymer holds a relatively large electric dipole field perpendicular to its carbon main chain. The dipole can be reversed and retained by the electric field; one can expect that the charge-carrier accumulation can be maintained once it is applied to a poling treatment.

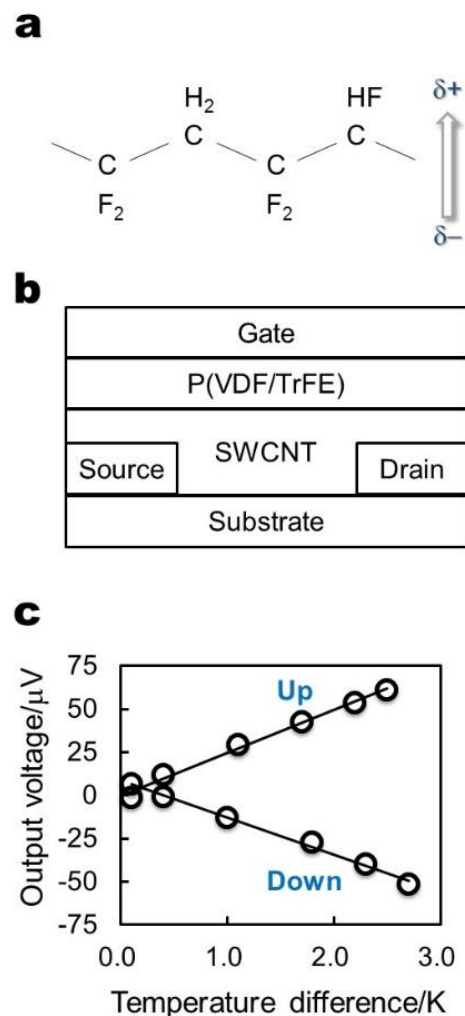


Figure 1. (a) Chemical structure of P(VDF/TrFE). (b) Device configuration. (c) Seebeck measurements under dipole.

The device fabrication procedure is described in our current paper. The charge-carrier type was evaluated by the TE charge-carrier determination after the poling treatments. Figure 1 (c) graphically shows the Seebeck coefficients of SWCNT thin films under ferroelectric dipoles. The sign of the coefficient could be tuned by the direction of the dipoles; positive and negative coefficients were observed in the “up” and “down” states, respectively. It was evident that the majority charge carrier changed according to the direction of the dipoles, as positive and negative coefficients directly reflect the hole and electron majority charge-carrier types, respectively. The Seebeck coefficients under the dipoles ($\pm 25 \mu\text{V K}^{-1}$) decreased by half compared to that of a control SWCNT thin film ($+50 \mu\text{V K}^{-1}$). On the other hand, the electrical conductivities showed two-fold increases from 0.5 to 1.0 S cm^{-1} after the poling. These changes of Seebeck coefficient and electrical conductivity are straightforward according to the conventional theory in which these parameters are complementary regarding the carrier density. The carrier accumulation induced by the poling improved the carrier density of SWCNTs, thus increasing the conductivity but decreasing the Seebeck coefficients.

In general, TE power factor is defined as $P = S^2\sigma$ (S : Seebeck coefficient, σ : electrical conductivity). The power factors of SWCNT thin films under dipoles were about $0.05 \mu\text{W K}^{-2} \text{ m}^{-1}$ in both the directions of dipoles. This value is about a half of that of control film ($0.13 \mu\text{W K}^{-2} \text{ m}^{-1}$). However, it should be noted that the polarity-controlled SWCNTs can be connected as TE modules. To demonstrate this, we fabricated the TE module consisting the p- and n-type SWCNTs. The TE output voltage of $50 \mu\text{V K}^{-1}$ was obtained from one module; the TE voltages of the polarity controlled SWCNTs could be combined to improve the overall TE voltage.

3. N-type conversion of SWCNTs by doping of vinyl polymers

Next, we demonstrate the charge-transfer-induced electron injection into the SWCNTs via versatile polymer doping. [2] As mentioned above, charge transfer interaction can conveniently inject electrons into nanotubes. In early case, amine compounds such as poly(ethyleneimine) (PEI) were demonstrated as successful molecular dopants behaving as Lewis bases, where a lone pair (lp) of electrons on nitrogen was partially injected into conduction band of nanotubes via charge transfer interaction. However, it is known that the electron transport behaviour and negative Seebeck coefficient of these amine-doped SWCNTs gradually reverts into p-type upon exposure to air. It is when a new class of molecular dopants with versatility, stability, biocompatibility, and low-cost must be explored.

Herein, we describe our recent findings on the simple, cheap, non-toxic, chemically stable molecular dopants for nanotubes. It is reasonable to consider that the atom, which participates in the highest occupied molecular orbital (HOMO) and has high electron density, mainly contributes to the charge transfer interaction. In the PEI case, the nitrogen corresponds to such a kind of atom because (1) the lp on the nitrogen is not involved in the covalent bonding and thus should participate in the HOMO, and (2) the nitrogen has a relatively high electron density due to its large electronegativity. On the basis of these consideration, we selected poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc) as the eco-friendly, cheap, and potential electron donors. The oxygen atoms of these polymers have an abundant lps and are negatively charged, thus providing a possibility to effectively donate electrons to nanotubes. To compare the electron donating ability, we also used poly(vinyl chloride) (PVC) and poly(vinyl pyrrolidone) (PVP) which have the identical carbon main chain and the different functional side groups.

The experimental details are described in our current paper. After depositing SWCNT thin films on the substrates, the polymers were doped by spin coating or drop casting directly onto the SWCNT thin films.

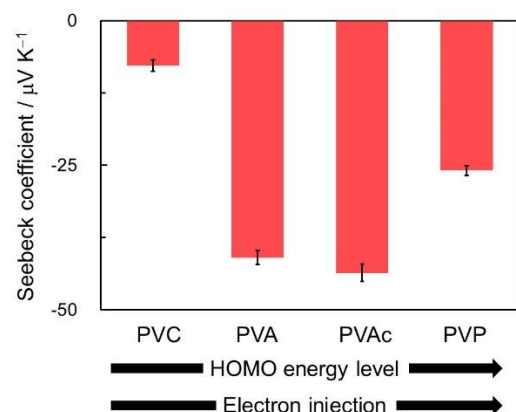


Figure 2. Seebeck coefficients of polymer-doped SWCNTs at 300 K.

Figure 2 shows the Seebeck coefficients and power factors of the control and the doped SWCNTs. The positive coefficient of control SWCNTs indicate the p-type nature due to the hole injection from the oxygen impurities. The doping of the polymers changed this coefficient into negative. Of these, the largest negative values were obtained by doping of PVA and PVAc, matching with that of control SWCNTs. These differences in the values are suitably explained by the HOMO energy levels of the dopant polymers (PVC: -7.9 , PVA: -7.1 , PVAc: -7.0 , PVP: -6.3 eV, calculated by density functional theory method at B3LYP/6-31G* levels on the monomer units). The higher HOMO energy level provides the more electron injection. The electron donation of PVC is relatively weak, and the electrons were mainly devoted to cancel out the original holes introduced from oxygen impurities, changing the Seebeck coefficient close to zero. The doping of PVA and PVAc injected adequate amount of electrons, thus recovering the coefficients to the matching levels to the control. The greater amount of electrons were injected from PVP so that the coefficient took smaller value than those of PVA- and PVAc-doped SWCNTs owing to the complicated behaviour of Seebeck coefficient and charge carrier density. The PVA-doped SWCNTs showed the largest TE power factor among the tested materials.

The stabilities of the negative coefficients of the SWCNTs in ambient air condition were evaluated. The PVC-doped SWCNTs showed poor stability to readily revert into p-type after 1 day. Although PVP has been considered a relatively stable electron donor; however, the doped SWCNTs indicated significant decrease in the negative coefficient. On the other hand, the PVA- and PVAc-doped SWCNTs showed excellent stabilities in air exceeding at least 3 weeks. We roughly attribute these differences in the stability to oxygen impurity blockage abilities of the dopant polymers; the low oxygen transmission coefficient of the polymer disturbed the adsorption of additional oxygen impurities and the hole injections by autooxidation. The higher polarity tends to provide the smaller oxygen transmission coefficient in general; this property is unique aspect to the polymers with oxygen atoms.

4. Conclusions and future perspectives

We reviewed our current studies on the charge-type conversion of SWCNTs. The ferroelectric dipoles of P(VDF/TrFE) effectively tuned the polarity of SWCNTs. Hybrid energy devices harvesting temperature differences, temperature changes, and vibrations may be developed in the future, as ferroelectric materials intrinsically hold pyroelectric and piezoelectric properties. The doping of versatile vinyl polymers successfully turned the charge type species of SWCNTs from hole into electron. The obtained negative Seebeck coefficients strongly related to the HOMO energy levels of the polymers. The largest coefficients and the considerable stabilities were obtained using oxygen abundant polymers such as PVA and PVAc. We expect that our findings will contribute to the more effective molecular dopants.

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