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Revealing the anisotropy in thermoelectric transport performances in CNT/PANI composites

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ABSTRACT

Although the carbon nanotube (CNT) based organic composites thermoelectric materials arouses considerable attentions, up to now the anisotropy in their thermoelectric performances has been overlooked. Herein, strong anisotropy in the temperature-dependent thermal and electrical transport properties have been demonstrated for organic composites thermoelectric materials, made by cold pressing the CNT powders coated by *in situ* polymerized polyaniline (PANI). The Seebeck coefficient, electrical and thermal conductivity are larger along the direction perpendicular to the cold pressing axis compared to the direction parallel to pressing axis. The anisotropy observed in the thermal conductivity and electrical conductivity maximizes at a CNT content of 30–40% (expressed in mass%), while the one observed for the Seebeck coefficient is small. The highest thermoelectric performances of the thermoelectric composites are achieved at a CNT mass ratio of ~40% for both multi-walled CNT (MCNT)/PANI and single-walled CNT (SCNT)/PANI at a direction perpendicular to the cold pressing axis. These results highlight the importance of optimizing the CNT contents during the *in situ* polymerization with PANI to achieve a homogeneous nanostructure and reducing the agglomerate of the uncoated CNTs, in order to obtain high thermoelectric properties.

1. Introduction

Thermoelectric materials, which can realize direct conversion between heat and electric, have been considered as a promising way to solve the increasing energy crisis [1–5]. The performance of thermoelectric materials is evaluated by the dimensionless figure of merit, defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, $S^2\sigma$ is the power factor (PF) and T is the absolute temperature. Among numerous reported thermoelectric materials, conducting polymers are attracting increasing attentions because of their low cost, light weight and easy processibility as compared to conventional inorganic thermoelectric materials [1,6–13]. However, increasing the electrical conductivity of conducting polymers by doping commonly leads to a extremely low Seebeck coefficient [14–16]. As a result, the thermoelectric power factor of conducting polymers are still several orders of magnitude smaller than state-of-the-art inorganic compounds [17–22].

In recent years, coating the nanocarbon materials (such as CNTs and graphene) with conductive polymers has been proved to be an effective approach to simultaneously improve the electrical conductivity and Seebeck coefficient of conducting polymers [16,23–30]. For example, Yao et al. synthesized SCNT/PANI nanocomposites and found the strong π–π interaction between SCNT and PANI can induce ordered PANI molecular chain structures, thereby resulting in enhanced carrier mobility as well as power factor [27]. Likewise, Chen et al. reported greatly improved thermoelectric properties of *in situ* polymerized graphene/ poly(3,4-ethylenedioxythiophene) (PEDOT) nanocomposites for the first time [25]. Most recently, extremely high thermoelectric power factor (2700 $\mu W\,m^{-1}\,K^{-2}$) rivaling commercial bismuth telluride was achieved in layer-by-layer processed PANI/CNT/graphene nanocomposite films [31,32]. Unfortunately, the thermal conductivities are unknown since it is still very challenging to measure the in-plane thermal conductivity in such thin film [11]. Similarly, most works on nanocarbon/polymer thermoelectric composites just presented the power factor or used the cross-plane thermal conductivity to estimate the ZT value [23,24,29,33–42].

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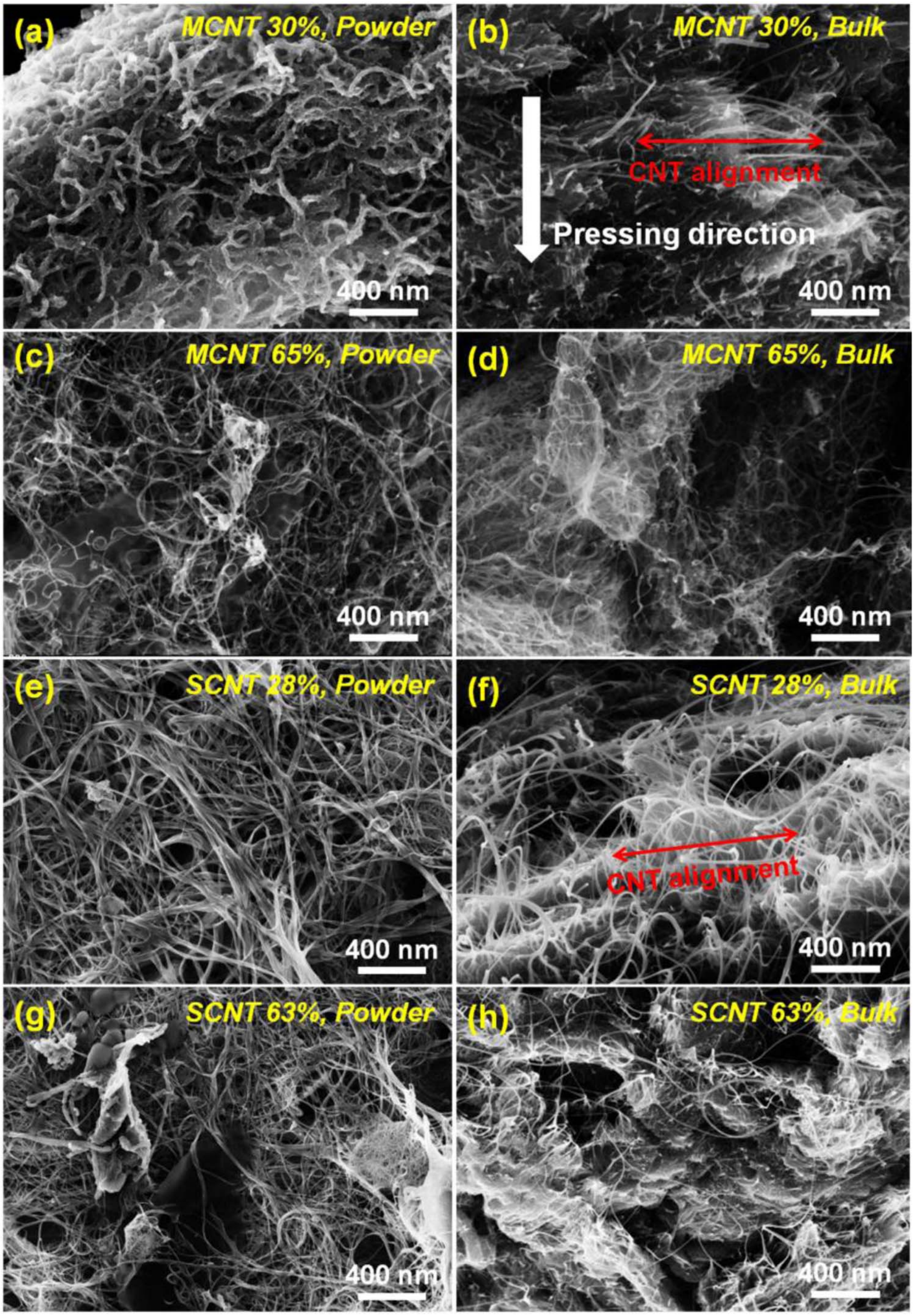

Fig. 1. Morphologies of the MCNT/PANI and SCNT/PANI composites at various CNT contents before and after the cold pressing process.

Nevertheless, it is undeniable that the transport performances of the CNT or graphene exhibit strong anisotropy, since both thermal conductivity and electrical conductivity are larger in the direction parallel to the CNT axis or graphene plane as compared to the ones perpendicular to the CNT axis or graphene plane. This is expected to influence the thermoelectric transport properties of the nanocarbon/polymer nanocomposites when the nanocarbons in the composites exhibit some specific orientation or texturation such as alignment. In addition, polymer molecular chains generally growth along the surface of CNT or graphene to form ordered structures, which will further increase the anisotropy of nanocarbon/polymer nanocomposites. Consequently, it is very important to uncover the anisotropic thermoelectric transport performances in these composites. However, the anisotropic thermoelectric properties of CNT/polymer or graphene/polymer composites are seldomly investigated before [43,44] and none on the anisotropic temperature-dependent thermoelectric properties. Therefore, it is worthwhile to explore the anisotropy at the elevated temperature, which should help expand the scope of nanocarbon/polymer thermoelectric composites.

In this work, we take CNT/PANI system as example and investigate the anisotropy in both MCNT/PANI and SCNT/PANI composites thermoelectric materials, which were made by an *in situ* polymerization of PANI around CNTs followed by cold pressing into bulk material. The content of the CNT during the polymerization process was adjusted to achieve various mass ratio between the CNT and PANI. The temperature-dependent thermoelectric performances, including the electrical