



# Enhanced thermoelectric performance by self-assembled layered morphology of polypyrrole nanowire/single-walled carbon nanotube composites



Lirong Liang<sup>a, b, c</sup>, Guangming Chen<sup>b, \*</sup>, Cun-Yue Guo<sup>a, \*\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

<sup>b</sup> Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>c</sup> Sino-Danish Center for Education and Research/Sino-Danish College, University of Chinese Academy of Sciences, Beijing 100190, China

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## ABSTRACT

Organic conducting polymer thermoelectric (TE) composites have witnessed a rapid progress in the recent several years. Here, we report a new morphology design strategy to enhance the TE performance by a unique layered morphology containing nanosheets of single-walled carbon nanotubes (SWCNTs) sandwiched by polypyrrole (PPy) nanowires. The free-standing PPy/SWCNT composite films were fabricated via convenient physical mixing followed by vacuum filtration, where PPy nanowires were synthesized by chemical oxidative polymerization. A typical layered morphology, composed of parallel SWCNT nanosheets sandwiched by PPy nanowires with a diameter of 55–75 nm, was directly observed by scanning electron microscopic images. The composites reveal greatly enhanced TE performance with the maximum power factor of  $21.7 \pm 0.8 \mu\text{W m}^{-1} \text{K}^{-2}$ , which is the largest value among PPy and its composites reported so far. Furthermore, both SWCNT content and surfactant type have obvious effects on the TE performance. The present study opens a new avenue to greatly enhance the TE performance by construction of layered morphology containing inorganic nanosheets sandwiched by polymer nanostructures.

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## 1. Introduction

Based on the mobility of solid internal carriers, thermoelectric (TE) material can achieve direct conversion between heat and electricity. TE devices have many unique advantages, such as no moving parts, no noise, easy maintenance, high reliability and long operating lifetime. Therefore, TE materials are very promising for diverse applications in thermoelectric generator (TEG) using waste or low-quality heat, refrigeration and sensors, etc. [1–3]. Inorganic TE materials, such as  $\text{Bi}_2\text{Te}_3$ ,  $\text{PbTe}$  and  $\text{Sb}_2\text{Te}_3$ , are most extensively-studied, however, their scarcity and high cost, the toxicity and poor processability seriously limit the applications [4–11]. Compared with these inorganic materials, organic TE materials have achieved a rapid progress in the recent several years, mainly due to various advantages of low thermal conductivity ( $\kappa$ ), low cost, light-weight,

solution processability, good flexibility and adjustable molecular structure [12–16]. Conducting polymers, including poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polypyrrole (PPy), and polycarbazole (PC), have attracted much of current interest in TE researches. Because of their low intrinsic  $\kappa$  ( $< 1 \text{ W m}^{-1} \text{K}^{-1}$ ), the TE performance of organic conducting polymers and their composites has always been evaluated by power factor ( $S^2\sigma$ ) rather than Figure of merit ( $ZT = (S^2\sigma T)/\kappa$ ), where  $S$ ,  $\sigma$ , and  $T$  are the Seebeck coefficient, electrical conductivity and absolute temperature, respectively.

Morphology tuning and evolution have been demonstrated to be an effective way to conveniently achieve significantly-enhanced TE performance for conducting polymers and their composites [17–38]. Amongst, surface coating of conducting polymers on inorganic nanoparticles, nanostructure fabrication of conducting polymers, and 3D network construction composed of polymer nanostructure adsorbed on nanoparticles are three main techniques developed so far. For example, we reported for the first time the *in situ* polymerization synthesis of PEDOT/graphene TE composite with a sandwiched structure of PEDOT wrapping on the

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [chengm@iccas.ac.cn](mailto:chengm@iccas.ac.cn) (G. Chen), [cyguo@ucas.ac.cn](mailto:cyguo@ucas.ac.cn) (C.-Y. Guo).

surfaces of graphene nanosheets [17]. By the surface coating method, a series of composites with enhanced TE property, such as PEDOT/graphene [17,18], PEDOT/carbon nanotube (CNT) [19], PANI/graphene [20,21], PANI/CNT [22,23], PPy/graphene [24,25] and PPy/CNT [26–28], have been successfully fabricated. Recently, we reported the tuning of TE performance by nanostructure evolution of PEDOT [36]. Interestingly, both the electricity and the Seebeck coefficient follow the same sequence of bulk PEDOT without nanostructure < globular nanoparticle < nanorod < nanotube < nanofibre. Furthermore, the carrier mobility and concentration, the ordered alignment of macromolecular chains and the level of oxidation were found to contribute to the controlled dependence of TE performance of PEDOT nanostructure evolution [36]. In addition, by interfacial adsorption-soft template polymerization method, we constructed a unique 3D network morphology composed of PPy nanowires adsorbed on the surfaces of graphene nanosheets, which displayed greatly enhanced power factor compared with the neat PPy nanowires [38]. Although significant progresses have been achieved, it is still a main challenge to realize greatly enhancement of TE property by construction of novel morphology for polymers and their composites.

PPy is a main conducting polymer. Unfortunately, compared with PEDOT and PANI, the studies of PPy and its composites for TE applications are very limited. As for pure PPy, granular or nanotubes have been studied of PPy TE materials [29,34,35]. In the case of PPy based TE composites, a few investigations on surface coating of PPy on reduced graphene oxide [24], graphene nanosheets [25], single-walled CNT (SWCNT) [26] or multi-walled CNT (MWCNT) [28] have been carried out. In this study, we report a new morphology design strategy to enhance TE performance by construction of a layered structure of PPy nanowire/SWCNT composites. The free-standing films for the composites were obtained by a convenient procedure of solution mixing and subsequent common vacuum filtration, where the PPy nanowires were fabricated *via* a chemical oxidative polymerization method.

## 2. Material and methods

### 2.1. Raw material

Pyrrole (CP, purity  $\geq 98.0\%$ ), sodium dodecyl benzene sulfonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) were purchased from Sigma Aldrich. Single-walled carbon nanotube (SWCNT) (diameter:  $< 3$  nm, purity:  $> 85.0$  wt%) were provided by Shenzhen Nanotech Port Co. Ltd, China. All of the other reagents, including ammonium peroxodisulfate (APS, AR), anhydrous ethanol (AR) and de-ionized water, were used as received in the preparation procedure without any further purification or treatment.

### 2.2. Preparation process of PPy nanowires

The polypyrrole (PPy) nanowires were fabricated by a simple chemical oxidative polymerization method with CTAB and APS as surfactant and oxidant, respectively. The preparation procedure is described as follows. First, 0.36 g of CTAB was dissolved in 100 mL of de-ionized water to obtain a homogeneous solution. Then, pyrrole monomers (55  $\mu$ L) were added into the above CTAB solution (20 mL) and stirred for 10 min. Soon afterwards, the above dispersion was stirred for 20 min at 0–5 °C. Subsequently, 4.4 mL of the precooled APS solution (0.21 mol L<sup>-1</sup>) was slowly dropped into the above mixture. After that, the polymerization reaction was allowed to proceed for 8 h at 0–5 °C with constant mechanical stirring. Finally, the resulting black precipitate was filtered and rinsed with ethanol and deionized water for several times until the

filtrate became colourless. The product was obtained after dried under vacuum at 60 °C for 24 h.

### 2.3. Preparation process of PPy-nanowires/CNT nanocomposites

The PPy nanowire/SWCNT nanocomposites were fabricated by directly solution mixing SWCNTs and the above obtained PPy nanowire powder. In a typical procedure, exactly weighted CTAB (3.6 g L<sup>-1</sup>) or SDBS (8 g L<sup>-1</sup>) were first dissolved in 100 mL of distilled water to obtain the aqueous solution of CTAB or SDBS. After that, the PPy nanowires (0.03 g) were dispersed into the 25 mL CTAB (3.6 g L<sup>-1</sup>) or SDBS (8 g L<sup>-1</sup>) aqueous solution with vigorous stirring for 15 min, and then ultrasonicated for another 30 min. Subsequently, a desired amount of SWCNT was dispersed in 30 mL of the SDBS (8 g L<sup>-1</sup>) aqueous solution under vigorous stirring for 15 min and ultrasonication for 40 min. Then, the PPy dispersion (in CTAB or SDBS) and SWCNTs dispersion (in SDBS) were mixed directly with simultaneously vigorous stirring (5 min) and ultra-sonication for 30 min. Finally, the suspensions were filtered with distilled water and ethanol for several times to remove the excess surfactant. The resultant product (C/S-PPy/SWCNT or S/S-PPy/SWCNT composite) was dried in a vacuum oven at 45 °C for 24 h. Herein, the mass ratios of SWCNT:PPy nanowire varied from 0.1:1 to 0.6:1.

### 2.4. Characterization

The morphology of the PPy nanowire and its composites with SWCNT was directly observed using HITACHI S-4800 scanning electron microscopy (SEM) and JEM-2010 transmission electron microscopy (TEM). The surface composition changes of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). The PPy nanowire/SWCNT composite films were cut into rectangular shape for electrical conductivity measurement, while the pure PPy nanowire pellets for measurements were obtained by cold pressing the powder samples at 15 MPa. The electrical conductivities were measured by Keithley 2000 Multimeter (Keithley Instruments Inc, USA) using a standard four point configuration method. The Seebeck coefficients were measured by a commercial Thin-Film Thermoelectric Parameter Test System (Nanicro-F3, JiaYiTong Company), where a quasi-steady-state mode was employed.

## 3. Results and discussion

### 3.1. Preparation of PPy-nanowire/SWCNT nanocomposite film

Fig. 1 shows the schematic illustration of the preparation process. First, PPy nanowires were prepared *via* a chemical oxidative polymerization approach using CTAB and APS as surfactant and oxidant, respectively, with reference to previous publications [38–40]. Then, a certain amount of the PPy nanowires was dispersed in CTAB or sodium dodecyl benzene sulfonate (SDBS) solution. Additionally, SWCNTs were dramatically exfoliated and homogeneously dispersed in water aided by SDBS due to  $\pi$ - $\pi$  attractions between SWCNTs and benzene rings of SDBS as well as hydrophobic interaction. Subsequently, the two dispersions of PPy in CTAB or SDBS and SWCNT in SDBS were mixed together under sonication treatment. Here the abbreviation of C/S stands for the dispersing agents of CTAB and SDBS to disperse PPy nanowires and SWCNTs, respectively, while the S/S represents the employment of SDBS to disperse both PPy nanowires and SWCNTs. After the mixtures were filtrated under vacuum, washed and dried, both composite films under the two different dispersion systems were achieved. Thus, by the convenient solution mixing and subsequent

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