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Semiconductor to metallic behavior transition in multi-wall carbon nanotubes/polyaniline composites with improved thermoelectric properties

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ABSTRACT

Multi-wall carbon nanotubes/polyaniline (MWCNT/PANI) composites were prepared by the *in situ* polymerization at room temperature and in ice-water bath, respectively. Raman spectra and X-ray diffraction patterns showed that the molecular conformation and the degree of order of PANI were greatly affected by the synthesis temperature. In low temperature condition, quinoid units converted into benzenoid in PANI and meanwhile, the chain segments of MWCNT/PANI arranged in a more orderly arrangement, which resulted in a change of the conducting behavior from semiconductor to metallic and almost twice increase in conductivity. Power factor (PF) of both composites increased with the increase of MWCNTs content, and 66.7% higher PF value was obtained in metallic-like composite with 80 wt% MWCNTs loading.

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1. Introduction

Thermoelectric (TE) materials and devices are attracting increasing attention for their eco-friendly applications in power generation and refrigeration. The performance of TE materials is quantified by the TE figure of merit: $ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. $S^2\sigma$ is the power factor (PF). Organic semiconductor materials offer advantages over inorganic semiconductors in thermoelectric applications, such as low density, low cost due to rich resources, high toughness and elasticity [1,2]. Furthermore, the intrinsically low thermal conductivities of conductive polymers make them stand out as potential candidates for high-performance thermoelectric materials [3,4]. Polyaniline (PANI) has gained special attention among conductive polymers due to its good processability, environmental stability, and tunable electrical properties. However, the relatively low conductivity ($\sim 10^{-7} \sim 320$ S/cm) and Seebeck coefficient of PANI compared to inorganic semiconductor TE materials have prevented it being applied as high-performance TE materials. The properties of PANI can be improved by selecting the method of preparation, the dopants, or by mixing with other materials to form composites [5–8]. Carbon nanotubes (CNTs)

showing excellent intrinsic electrical properties and structural characteristics have been employed as ideal fillers to improve the TE performances of PANI-based TE composites [9–11]. A maximum conductivity of PANI/CNT was reported to reach 769 S/cm due to the formation of an ordered PANI chain structure on the surface of CNTs induced by strong π - π conjugated interactions between carbon nanotubes and polyaniline [9].

Doping is the key to maximizing the TE power factor of organic TE materials because dopants can not only modify the conformation of conducting host molecules and thereby alter their carrier transport properties, but also typically increase the tunneling distance between these molecules and hence greatly reduce the rate of thermally activated hopping [12]. Meanwhile, doping PANI is strongly dependent on preparation conditions and temperature [1,13]. Thus, in this study, MWCNTs/PANI composites were synthesized via *in situ* polymerization at room temperature and in ice-water bath, respectively; to tune the conformation of PANI molecules and morphology of polymer chains. Their effects on the conducting behavior and TE properties of the composites were investigated.

2. Experimental

The MWCNTs (purity > 97 wt% with diameter between 10–20 nm, length more than 5 μ m) were purchased from the Shenzhen Nanotech Port Co. Ltd. Aniline was purified through

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distillation before use. All chemicals were of analytical grade and used as received. The PANI/MWCNTs composites were fabricated via *in situ* polymerization method with the following process. 2.328 g aniline was added in 100 ml of 0.5 M HCl and stirred until the aniline was completely dissolved in the solution. The CNTs were dispersed in the mixed solution by sonication for 30 min. Then the mixture was kept in ice-water bath and stirred. After 30 min, 5.705 g ammonium persulfate was dissolved in HCl solution and then added to the reaction mixture dropwise. Subsequently, the mixture was stirred for 4 h in ice-water bath. The product was filtered, washed repeatedly with distilled water and acetone, and dried at 60 °C. The obtained samples were marked as *i*-PANI/MWCNTs. The same procedure was used to make samples with polymerization reaction occurring at room temperature, marked as *r*-PANI/MWCNTs.

X-ray diffraction (XRD) analysis was carried out on Smartlab (Rigaku). Raman spectroscopy measurement was carried out on a LabRAM HR Evolution (HORIBA) using an Ar–Kr laser in wavelength 632.8 nm. Scanning electron microscopy (SEM, JEOL JSM-6010) was used to observe the morphologies of the composites. Electrical conductivity and Seebeck coefficient were measured on bulk samples made from cold-pressing by a ZEM-3 system (ULVAC-RIKO). Hall measurements were carried out on Physical Properties Measurement System.

3. Results and discussions

Raman spectra of *i*-PANI/MWCNTs and *r*-PANI/MWCNTs composites are shown in Fig.1(a). The characteristic Raman peaks of

PANI changed greatly with different reaction temperatures. The strong peak at 1462 cm^{-1} of *r*-PANI/MWCNTs assigned to the C=N stretching of the quinoid diamine units remarkably weakened in *i*-PANI/MWCNTs. The peak assigned to C–H bending of benzenoid rings located at 1168 cm^{-1} in *i*-PANI/MWCNTs slightly shifts to 1160 cm^{-1} in *r*-PANI/MWCNTs, which is the same C–H bending mode in the quinoid segments. A small shift of C–C stretching vibration mode of benzenoid rings at 1596 cm^{-1} to C=C stretching vibration in the quinoid segments at 1586 cm^{-1} was also observed. These changes of Raman modes unambiguously confirm the transformation of quinoid units to benzenoid rings in PANI as preparation temperature decreases to 0 °C. The mode at 1334 cm^{-1} is regarded as the characteristic vibration from radical cation C–N⁺ [9], whose intensity is stronger in *i*-PANI/MWCNTs than in *r*-PANI/MWCNTs, indicating higher doping level of *i*-PANI/MWCNTs. Furthermore, the doping level could also be promoted by increasing MWCNTs contents in both *i*-PANI/MWCNTs and *t*-PANI/MWCNTs. Meanwhile, the modes at 1391 and 1643 cm^{-1} are related to delocalized polarons in the extended polymeric conformation, which appeared only in *i*-PANI/MWCNTs demonstrating that molecular conformation of PANI became more expanded and the number and effective degree of delocalization of the polarons are enhanced in low-temperature fabricated *i*-PANI/MWCNTs [9]. Therefore, the PANI molecular conformations are concluded and schematically illustrated in Fig.1(c) as preparation temperature changes.

XRD patterns of PANI/MWCNTs composites are shown in Fig.1 (b). For PANI, three characteristic diffraction peaks locate at $2\theta = 15^\circ, 20^\circ$ and 25° , assigned to the periodicity of the repeat unit of the PANI chains, the periodicities perpendicular and parallel to

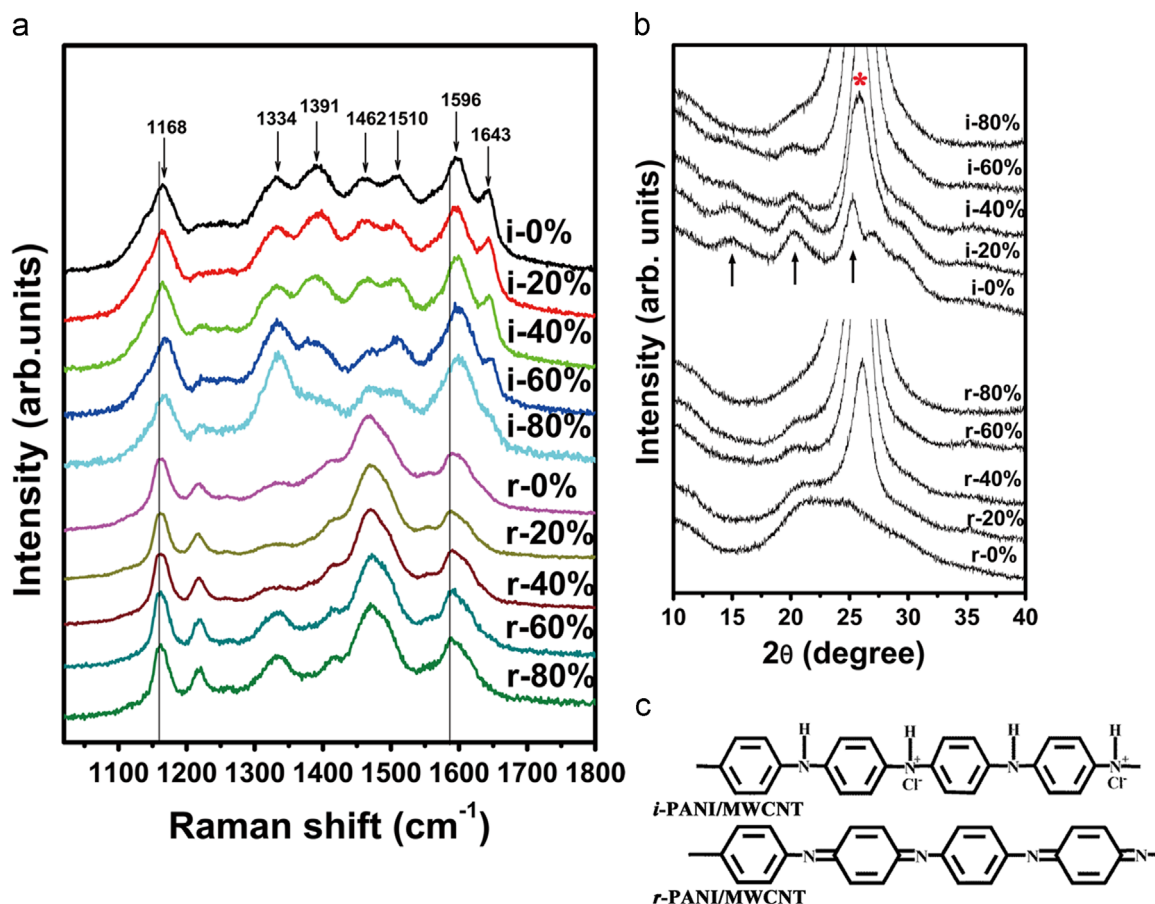


Fig. 1. (a) Raman spectra and (b) XRD patterns of PANI/MWCNTs composites with different weight fraction of MWCNTs. (* stands for the peak of CNTs) (c) Schematic illustration of PANI molecular conformations at different preparation temperature.

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