Synthetic Metals 195 (2014) 132–136

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Preparation and thermoelectric properties of multi-walled carbon nanotubes/polypyrrole composites

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ARTICLE INFO

Article history:
Received 18 February 2014
Received in revised form 17 May 2014
Accepted 2 June 2014
Available online 20 June 2014

Keywords:
Carbon nanotubes
Polypyrrole
Composite
Thermoelectric properties

ABSTRACT

Multi-walled carbon nanotubes (MWCNT)/polypyrrole (PPy) composite powders with MWCNT content ranging from 0 to 20 wt% were prepared by an in-situ polymerization method using p-toluenesulfonic acid (TSA) as a dopant and iron chloride ($FeCl_3$) as an oxidant. The powders were examined by X-ray diffraction, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The composite powders consist of PPy nanoparticles and quasi-one-dimensional MWCNT/PPy core/shell nanostructures. The electrical conductivity and Seebeck coefficient of the cold pressed powders were measured from 295 to 375 K. The electrical conductivity of the samples increases with the MWCNT content when the MWCNT is lower than 15% and then decreases when higher than 15%, whereas the Seebeck coefficient of the samples first gradually increases with the MWCNT content and then increases quickly when the MWCNT content is higher than 15%. As a result, the power factor of the samples increases with the MWCNT content and the maximum value is 2.079 $\mu W\,m^{-1}\,K^{-2}$ when the MWCNT content is 20%. It is about 26 times as high as that of pure PPy.
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1. Introduction

Thermoelectric (TE) materials have recently attracted worldwide attentions because they can be applied in solid-state refrigeration and power generation. The TE performance of a material is evaluated by its dimensionless figure of merit $ZT = \alpha^2\sigma/\kappa$, where α, σ, T, and κ, are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. To obtain high ZT, TE material should have a high α, a high σ but a low κ; however, it is very difficult to modulate the three parameters to get a high ZT value because they are dependent on each other.

Until now, the studies on TE materials have been mainly focused on inorganic semiconductors. However, the high costs and poor processability of inorganic TE materials limit their wide applications. Conducting polymers are flexible, easy fabrication and usually have much lower thermal conductivity than inorganic TE materials [1], which is beneficial to the enhancement of their ZT values. TE performances of conjugated polymers have recently attracted increasing attentions and many progresses have been made [2–9]. For example, the ZT value are 0.25 for a tosylate doped poly(3,4-ethylenedioxythiophene) (PEDOT) [8] and 0.42 for a poly(styrenesulphonate) (PSS) doped PEDOT at room temperature, respectively. Even though conjugated polymers have lower ZT values than those of traditional inorganic TE materials such as Bi-Te based alloys [10] or PbTe based alloys [11,12], they are promising for mass-produced and large-area applications, and their ZT values can certainly be further improved by various methods.

Although an isolated carbon nanotube (CNT) has a high thermal conductivity (~3000 $Wm^{-1}\,K^{-1}$) at room temperature but a packed bed of three-dimensional (3D) random networks of CNTs has a very low thermal conductivity (only about 0.13–0.19 $Wm^{-1}\,K^{-1}$) [13], so 3D random networked CNT/polymer composites are expected to have high electrical conductivities and low thermal conductivities as desired. Yu et al. [14] reported that the electrical conductivity of a polymer-based composite can be dramatically increased by incorporating CNTs in a network fashion, while the thermal conductivity and Seebeck coefficient are insensitive to the CNTs content, which makes it possible to tune the properties to get a high ZT value. Recently, many works on polymer

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http://dx.doi.org/10.1016/j.synthmet.2014.06.003
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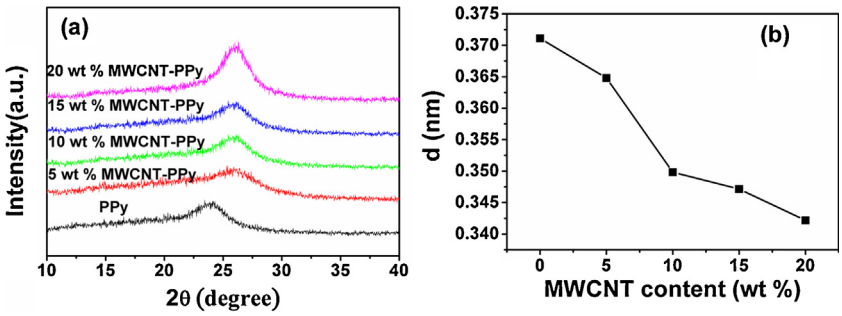

Fig. 1. (a) XRD patterns and (b) the in-plane inter-chain distance between pyrrole rings for the samples with different contents of MWCNT.

based composites such as CNT/PEDOT: PSS composites [15], single-walled CNT (SWCNT)/polyaniline (PANI) composites [16], CNT network/PANI composites [17,18], multi-walled carbon nanotube (MWCNT)/poly(3-hexylthiophene) (P3HT) [19] and PANI-coated MWCNT [20–22] have been reported.

Polypyrrole (PPy) is one of the most important conducting polymers but its TE properties have not much been reported so far [23–25] and no research on PPY-inorganic TE nanocomposites has been reported [1] In the present work, we prepared PPy and MWCNT/PPy composite powders. The composite powders were prepared by an in-situ polymerization method using MWCNTs as hard templates. The TE properties of the PPy and MWCNT/PPy composite powders after cold pressing were investigated.

2. Experimental

Pyrrole (Py), p-toluenesulfonic acid (TSA), $FeCl_3$ and organic solvents used were obtained from Sinopharm Chemcial Reagent Co., Ltd. MWCNTs (diameter: 10–20 nm, length: 5–15 μm, purity ≥95%) were purchased from Shenzhen Nanotech Port Co., Ltd. All of these materials were used without further purification.

In a typical case, 4.16 g TSA was slowly dissolved in 100 mL distilled water. A designed amount of MWCNT was then dispersed in the TSA solution and ultrasonicated (240 W) for 3 h. 0.5 g of Py monomer was slowly added into the above solution and continuously magnetically stirred for 30 min. 1.8 g $FeCl_3$ was added into 20 mL distilled water with stirring, and then filtered through a 0.45 μm membrane to remove any traces of undissolved aggregates. The oxidant solution was added into the mixed solution of Py and MWCNT dropwise with stirring and further stirred for 3 h, and finally stored at ~5 °C for 10 h. The precipitates at the bottom of the reaction container were filtered through a 0.45 μm PVDF membrane, washed with distilled water and ethanol in sequence for several times. Finally, the black powder was collected and then dried under vacuum for 24 h at 60 °C prior to further analyses.

3. Characterization

X-ray diffraction (XRD) was applied to investigate the crystal structure of the samples with Cu-Kα radiation using a Bruker D8 Advanced XRD equipment. Microstructure of the samples was observed using field emission scanning electron microscopy (FESEM, XL30FEG) and transmission electron microscopy (TEM, Hitachi H-800). The samples for TEM characterization were prepared by dispersing a small amount of the powders in absolute ethanol and ultrasonicated for 10 min before being dropped on a copper grid coated with carbon. Thermogravimetric (TG) analysis was conducted using a NETZSCH STA449 C instrument under nitrogen atmosphere at a heating rate of 10 °C/min. The powder samples were cold pressed into pellets (10 mm in diameter and about 1 mm in thickness) at 10 MPa for the following TE property measurements. The Hall effect of the samples was measured using an HMS-3000 (Ecopia) system at room temperature using a magnetic field of 0.55 T. The bulk electrical conductivity of each pellet was measured using a steady-state four-probe technique with a square wave current (~10 mA in amplitude). The Seebeck coefficient was determined by the slope of the linear relationship between the thermal electromotive force and temperature difference (~10 K) between the two points of each pellet on the same side.

4. Results and discussion

XRD patterns of the samples are shown in Fig. 1(a). For the XRD pattern of the sample without adding MWCNT, only a broad peak at $2\theta = 23.96°$ appears, which is a characteristic peak of amorphous PPy [26], indicating that pure PPy was successfully synthesized. The peak corresponds to $d = 3.71$ Å, which is thought to arise from PPy chains close to the interplanar vander Walls distance for aromatic groups [27,28]. And this value is also in good agreement with the result (3.7 Å) for PPy nanorods and PPy film [29], in which the authors think that it corresponds to the PPy interchain distance. The XRD pattern for the samples with MWCNT is similar to that of the pure PPy except the diffraction peak shifted to a higher angle (accordingly, the d spacing decreases, Fig. 1(b)), and the more the MWCNT contains, the more the peak shifts, which is in agreement with that reported in MWCNT/P3HT [19] and double-walled CNT/P3HT [30] composite materials. The upward shifting of the peak in the MWCNT/PPy composites shows that adding MWCNTs into PPy influences the microstructure of the composites by the means of interfacial interaction between the MWCNTs and PPy matrix.

The thermal stability is the key parameter for polymer materials, which determines the application temperature range of the polymers. Therefore, TG analysis of the composites was carried out under nitrogen atmosphere at a heating rate of 10 °C/min and the result is presented in Fig. 2. The MWCNTs are more stable than

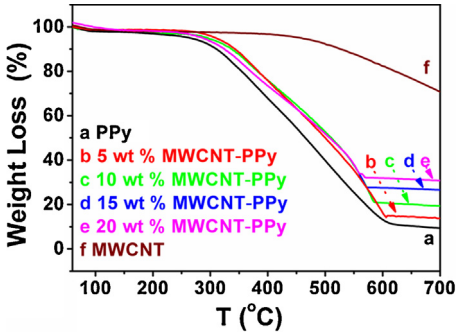

Fig. 2. TGA curves of the MWCNT and the as-synthesized PPy and MWCNT/PPy composites with different contents of MWCNT.

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