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Nanoparticle-loaded highly flexible fibrous structures exhibiting desirable thermoelectric properties

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ABSTRACT

Thermoelectric, the science of transforming heat to electrical energy or vice versa, provides the possibility to reserve heat losses as an electrical energy, which is called green energy. In recent years, producing a wearing thermoelectric generator that capable using human body temperature receives a great interest. In this research, a nanocomposite of Polyvinylpyrrolidone (PVP)/carbon nanotubes (CNTs)/copper oxide (CuO) nanoparticles were used in order to produce electrical current from heat losses. The nanocomposite structures were prepared using two methods of electrospinning and coating the fabrics with a homogenous solution of PVP, CNTs and CuO nanoparticles. SEM, XRD, TEM and FTIR analysis were used to study the structural and morphological characteristics of the nanocomposite. The results showed that the fabric coated with a mixture of 20:20 (wt%) CNT and CuO nano-particles had a Seebeck coefficient of 39.21 μV/K and the electrical conductivity of 3.5×10^{-2} S/cm which were the best thermoelectric properties. Moreover, the results indicated that nanofibers fabricated via electrospinning which consisted of 20:20 (CuO: CNT) nanoparticles had the Seebeck coefficient up to 29.13 μV/K and the electrical conductivity of 2.114×10^{-4} S/cm.

1. Introduction

In recent years, global energy issues and the limited resources along with increased energy demands are the major challenges facing the 21st century [1]. Hence, the need for alternative energy sources (such as solar energy, hydrogen energy, and biomass energy) to replace the conventional fossil fuels has prompted widespread researches for improving the efficiency of energy conversion technologies [2]. Thermoelectric (TE) functional materials are considered as the most potential candidates to convert heat energy directly into usable electricity from waste heat such as the sun, industrial sectors and automobile exhausts [3]. TE devices are capable of generating electricity when there is a different temperature between the hot and cold junctions of two dissimilar conductive or semiconductive materials [4,5]. TE energy conversion efficiency is mainly determined by the dimensionless figure of merit (ZT), defined as $ZT = \sigma S^2 T/K$, where σ, S, T and K are the electrical conductivity, Seebeck coefficient, absolute temperature and thermal conductivity, respectively. Accordingly, to achieve high performance TE convertor at the working temperature, high electrical conductivity, large Seebeck coefficient, and low thermal conductivity are required [6,7]. TE materials present many unique advantages such as easy fabrication processes without noise, low material cost and long operating lifetime that make them a promising devices for military, aerospace, medical thermostats, micro sensors and other civilian areas [8].

The most efficient TE materials are inorganic semiconductors include Bi–Te series, Pb–Te series and Si–Ge series however the high cost and poor processing performance prevent their applications. In contrast, conducting polymers possess unique features for application as thermoelectric (TE) materials because of their low density, low cost due to rich resources, easy synthesis, and easy processing into a light and flexible form as compared with inorganic semiconductor materials. Among the typical conducting polymers, polyaniline (PANI) and polypyrrole (PPY) have recently attracted wide attention as promising candidates as TE materials [9,10]. However, most of the conducting polymers exhibit poorer electrical transport properties and lower power factors ($S^2\sigma$), as compared with the inorganic thermoelectric materials. Incorporating carbon nanotubes or graphene, along with the conducting polymers have been studied as an enhanced electrical transport and are very promising candidates [11].

CNTs have many exceptional electronic, optoelectronic, and mechanical properties compared to the conventional semiconductors. Fundamental studies on the thermoelectric performance of the CNTs reveal a remarkable enhancement in ZT due to their high electrical conductivity and thermopower properties [11]. Kim et al. [12] found that PEDOT: PSS particles were uniformly coated on the surface of

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CNTs, leading to tube/tube junctions and transport pathways in which electrons could travel through the composite and resulted in an increased electrical conductivity. On the other hand, thermal conductivity was suppressed because of different vibrational spectra between CNT and PEDOT: PSS. The highest ZT achieved was 0.02 when 35 wt% CNT was added to the polymer matrix. Caroll et al. [13] demonstrated individual composite films of multiwall carbon nanotubes (MWNT)/polyvinylidene fluoride (PVDF) that were layered into multiple element modules resembling a felt fabric. Slobodian et al. [14] created polymer composites from multiwall carbon nanotubes or carbon nanofibers and ethylene-octane copolymer. The thermoelectric efficiency of created composites with a nanotube or nanofiber concentration of 30 wt% evaluated by a thermoelectric power at room temperature is 13.3 μV/K and 14.2 μV/K, respectively. Moreover, incorporation of semiconductor/metal oxide together with conductive fillers was confirmed to improve the Seebeck coefficient and consequently the thermoelectric properties of composites [15–17]. Andrei et al. [15] reported that a high Seebeck coefficient up to 127 μV/K was obtained in a polychlorotrifluoroethene (PCTFE) composite filled with Cu_2O/graphite when the particles content exceeded 87.5 wt%. In addition, a very low power factor of 2.75×10^{-5} μW/mK^2 was obtained due to the low electrical conductivity of the composite. Pötschke et al. [18] prepared flexible thermoelectric materials by melt mixing technique. Hybrid filler systems of carbon nanotubes (CNTs) and copper oxide (CuO) were melt mixed into a polypropylene (PP). The significant enchantment in Seebeck coefficient and electrical conductivity at 5 wt% CuO and 0.8 wt% CNTs was explained with the formation of a loose percolated network.

This study demonstrates a possibility to design the highly flexible fibrous structures with high thermoelectric performance through combining the MWCNTs, CuO nanoparticles and PVP polymers via electrospinning method. In this work, we demonstrate single layer fibrous composite in which the MWCNTs were embedded in the conducting polymer chains and oriented along the fiber axis. Previously polyaniline (PANI) has been widely studied as a promising conducting polymer for TE materials [11,19]. Herein, we applied PVP which is cheaper and more easily processed than polyaniline. Moreover, PVP has the biocompatibility properties [20,21]. The electrical field during the electrospinning makes it possible for MWCNTs to align parallel into a long fiber. It is conjectured that the strong л-л conjugated interactions between carbon nanotubes and PVP molecules in the composite would induce the formation of an ordered chain structure [22] and therefore improve both the electrical conductivity and Seebeck coefficient. In the present work, two kinds of materials, on one hand MWCNTs as an inorganic semiconductors with high electrical conductivity, and on the other CuO as an inorganic materials with high Seebeck coefficient, were combined to improve the thermoelectric efficiency of a fibrous composite. Finally, our fibrous composite reach high electrical conductivity and seebeck coefficient, good processability, mechanical flexibility, low-cost synthesis, and light weight.

2. Experiments

2.1. Materials

PVP (Mw: 1,300,000) and ethanol (95%) were provided by Sigma Aldrich (USA). Multi-wall CNTs with a particle size of 20–30 nm and Cu-oxide nanoparticles with a particle size of 40 nm were prepared from Nanosany company, Mashhad, Iran. Several solutions with the same weight percentage of MWCNT and copper oxide nanoparticle and also different mixtures of them were prepared (shown in Table 1). All the chemicals used in the experiment were used without further purification. It should be noted that the weight percentage of nanoparticles is determined based on the weight percentage of the polymer (8 wt%).

To prepare TE solution, first 8 wt% solution of ethanol and PVP polymer stirred for about 1 h in order to solve completely the given polymer. Then, CNTs were added to the solution and kept under ultrasonic stirrer for 30 min to disperse entirely nanotubes in the given solution. In the next stage, CuO nanoparticles were added and stirred for 30 min with an ultrasonic stirrer. After that, we continued stirring with a magnetic stirrer for about 12 h, and before electrospinning or fabric coating to ensure homogeneity of particle distribution, the solution was stirred again for about 10 min using ultrasonic stirrer. Table 1 presents the prepared TE solutions.

Table 1
Prepared TE solutions.

NO.	CuO (wt%)	CNT (wt%)	PVP (wt%)
1	0	0	8
2	1	0	8
3	5	0	8
4	10	0	8
5	20	0	8
6	0	1	8
7	1	1	8
8	5	1	8
9	10	1	8
10	20	1	8
11	0	5	8
12	1	5	8
13	5	5	8
14	10	5	8
15	20	5	8
16	0	10	8
17	1	10	8
18	5	10	8
19	10	10	8
20	20	10	8
21	0	20	8
22	1	20	8
23	5	20	8
24	10	20	8
25	20	20	8

2.2. Electrospinning the composite nanofibrous web

Electrospinning was carried out at a temperature of 24 °C and relative humidity of 23%. The speed of syringe pump (model TOP-5300) was 1 ml·h^{-1}, the distance between the needle with an inner diameter of 0.6 mm and the distance between needle and drum was 14 cm, the applied voltage was 11–16 kV and the drum rotational speed was adjusted at 100 rpm.

2.3. Preparation of MWCNT/CuO nanoparticle coated fabric

As a comparison, coated fabric was also fabricated by the solution mixture of PVP, MWCNTs and CuO nanopowder. For fabric sample, we used viscos-polyester woven fabric with characteristics of 40 warp per cm, 30 wefts per cm and the weight of 0.0092 g·cm^{-2}. The immersion technique was used to coat the fabric with TE solution and then located under the hood for 2 h in order to complete evaporation of ethanol.

2.4. Characterization of the composite nanofiber and coated fabric

The structure information of the samples was analyzed by x-ray diffraction (XRD). The XRD patterns with diffraction intensity versus 2θ were recorded using a Philips XRD (Philips, X9 pert, and CuKa). The transmission electron microscopy (TEM) studies were carried out with a Philips CM30 to investigate the internal morphology of composite nanofiber. The surface morphology of fibrous structures was studied by Philips 30XL scanning electron microscopy (SEM). The diameter of the nanofibers is measured by using the Digimizer software and analyzed with the SPSS software. The compositions of the products were characterized by Fourier transform infrared (FTIR) spectroscopy in a