Renewable and Sustainable Energy Reviews 53 (2016) 653–671

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Recent advances in CNT/graphene based thermoelectric polymer nanocomposite: A proficient move towards waste energy harvesting

Abhijit Dey [a,*], Om Prakash Bajpai [b], Arun K. Sikder [a], Santanu Chattopadhyay [b,**], Md Abdul Shafeeuulla Khan [a,***]

[a] EMR Division, DRDO-HEMRL, Pune 411021, Maharastra, India
[b] Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

ARTICLE INFO

Article history:
Received 11 April 2015
Received in revised form
5 June 2015
Accepted 2 September 2015

Keywords:
Polymer
Carbon nanotube
Graphene
Thermoelectric
Seebeck coefficient

ABSTRACT

Carbon nano tube (CNT)/graphene filled organic composites have great potential for making cheaper thermoelectric materials towards their gear up for applications in energy harvesting due to their low cost, low density, facile routes of preparations, versatile processability and low thermal conductivity. These properties make them superior compared to previously reported hybrid alloys. Now a day's CNT and graphene are most frequently used nanofillers due to their unique shape and characteristics such as superconductivity, light weight, high stiffness and axial strength. Moreover, to achieve superior dispersion and properties of composites, various functionalizations on the graphene and CNT have been accomplished by various research groups. Foremost objective of this paper is to highlight the recent research advances on CNT and graphene filled thermoelectric (TE) materials for the replacement of inorganic semiconductors. Fundamentally, for polymer composite based thermoplastic (TP) materials, a thermally nonconductive but electrically connected nano-structured network should be established.

Contents

1. Introduction . . . 654
2. How to improve TE efficiency? (Key question) . . . 657
3. Thermoelectric properties: polymer materials vs current thermoelectric . . . 657
4. Carbon nanotube as conducting filler for thermoelectric application . . . 657
5. Recent trends in CNT filled polymer composite thermoelectric application . . . 660
   5.1. PVAc/CNT composite . . . 660
   5.2. PANI/CNT composite . . . 662
   5.3. PEDOT: PSS/CNT composite . . . 662
   5.4. Polylactic–graphite–CNT composite . . . 663
   5.5. PVDF/CNT composite . . . 663
   5.6. Poly (3-hexyl thiophene) (P3HT)–MWCNT composite . . . 663
   5.7. Nafion/CNT composite . . . 663
6. Graphene filled polymer composite: another efficient futuristic thermoelectric material . . . 663

Abbreviations: AIBN, azoisobutyronitrile; BTU, British thermal unit; CNT, carbon nanotube; CPC, conductive biopolymer nanocopmposite; CSA, chlorosulfonic acid; $CuBiS_3$, copper bismuth sulfide; CVD, chemical vapor deposition; DMF, dimethyl formamide; DOC, sodium dioxicholate; DWCNT, double wall carbon nano tube; *E*, electric field; EIA, energy information administration; GA, gum arabic; GN, graphene nanosheet; GNP, graphene nanoplatelets; HRSEM, high resolution scanning electron microscopy; *i*, electric current density; $LaSrCuO_3$s, lithium strontium copper oxide; $LiSrCoO_3$, lithium strontium cobalt oxide; MWCNT, multiwall carbon nanotube; NMP, N-methyl pyrrolidone; P3HT, poly(3-hexylthiophene-2,5-diyl); PANI, polyaniline; PE, polyethylene; PEDOT, poly(3,4-ethylenedioxythiophene); PHAE, polyhydroxyaminoether; PMMA, poly(methyl methacrylate); PSS, poly(styrenesulfonate); PVA, polyvinyl alcohol; PVAc, polyvinyl Acetate; PVDF, polyvinyldene fluoride; *q*, heat current density; S, Simen; SDBS, sodium dodecyl benzene sulfonate; SWCNT, single wall carbon nanotube; TCPP, mesotetra (4-carboxyl phenyl)porphirine; TE, thermoelectric; TEG, thermoelectric generator; TW, terawatt; V_c, critical volume fraction of CNT; ZT, thermoelectric figure of merit; λ, thermal conductivity; σ, electrical conductivity; μV, microvolt

* Corresponding author. Tel.: +91 20 2591 2225.
** Corresponding author. Tel.: +91 3222 281758.
*** Corresponding author. Tel.: +91 20 2591 2212.
E-mail addresses: abhidey_bkn@yahoo.com (A. Dey), santanuchat71@yahoo.com (S. Chattopadhyay), maskhan@hemrl.drdo.in (M.A. Shafeeuulla Khan).

http://dx.doi.org/10.1016/j.rser.2015.09.004
1364-0321/

6.1. Graphene as conducting filler for thermoelectric application . . . 663
6.2. PANI/Graphene filled composite . . . 665
6.3. PEDOT:PSS–Graphene filled composite. . . . 665
6.4. Graphene nanoribbons (GNRs) . . . 668
7. Conclusions and outlook . . . 668
References . . . 668

1. Introduction

In 2007, global civilization consumed 495 quadrillion British thermal units (BTUs) [1], which is equivalent to an average power of 16.6 Terawatts (TW). The energy need of the planet is continuously growing mainly due to population growth and the rapid economic development. The Energy Information Administration (EIA) of the U.S. Department of Energy predicts that the mean global energy consumption will rise to 49% (or 1.4% per year), from 495 quadrillion BTU in 2007 to 739 quadrillion BTU by 2035. These numbers are definitely a cause for alarm, not only because it will be a challenge to supply energy on this scale, but also the majority (85%) of energy is currently generated by burning of fossil fuels [2,3]. Along with the questions about the long-term sustainability of non-renewable fuels, there are serious concerns about the consequences of the combustion of fossil fuels. The burning of fossil fuels creates a large amount of carbon dioxide (CO_2), a known greenhouse gas that contributes to the phenomenon of global warming [4]. In near future, carbon-free alternative energy sources need to be implemented on a massive scale to avoid the crisis of climate change by stabilizing CO_2 levels at reasonable target values. The technical analyses [5,6] indicate that 10–30 TW of carbon-free primary power technology will need to be in place by 2050 to meet modest CO_2 stabilization goals. Thus, the majority or even the entirety of our global energy consumption needs to be supplied by sources that do not emit CO_2. There are many solutions to meet this challenge in a sustainable fashion [7]. Nuclear fission technology is well-established and has the potential to play a partial role in meeting the terawatt challenge. However, in addition to serious concerns about nuclear waste, development of nuclear weapons, and long plant start-up times, energy from fission may be limited in this scale by the abundance of suitable nuclear fuel [8]. To implement at least 10 TW of carbon-free energy by 2050, we need to resort to other forms of energy.

As a first step to circumvent today's energy challenges, sought for renewable energy resources are inevitable. The most promising renewable energy resources are the solar energy. Huge amount (120,000 TW) of energy is striking to the earth's surface round the clock by means of solar energy which can be useful to satisfy the global energy demand [3,8]. To cultivate the solar energy, three steps are necessary like capture, conversion and storage [9]. Development of thermoelectric materials with high figures of merit (ZT) is one of the challenging areas of research for the utilization of solar energy. Table 1 represents a comparison of the amount of energy (TW) produced from different forms of energy resources [10].

Alternatively, the growing need for surrogate and portable sources of energy has motivated significant effort to develop new forms of energy-conversion and storage devices. Ambient energy is mostly dominant in the mechanical and thermal forms [11] and their conversion into electrical energy could play a key role in developing technologies such as remote access electronics, self-powered sensors and other medical devices. There is increasing need for self-sufficient power sources for wireless sensors and electronics that can extend device performance beyond what is available from conventional batteries. Considerable attention has been focused on thermal energy as a potential source of energy which is widely available in the environment and can be converted to electrical energy using TE or pyroelectric (PE) modules [5,13]. The vast majority of TE devices have been operated under larger temperature gradient conditions (>50 K). Thermal gradients in the environment are directly converted to electrical energy through the TE effect. TE devices consisting of n- and p-type materials electrically joined at two ends having gradient of temperatures. The generated voltage and power is relative to the temperature differential and the Seebeck coefficient (S) of the TE materials. Large thermal gradients are essential to produce practical voltage and required power. Assessment of the coefficient of performance (COP) referring to the thermoelectric figure of merit, the characterization of the cooling capacity has been addressed by Enescu et al. in the form of review [12].

Table 1
Comparative study of different forms of energy sources.

Sl. no	Energy resources	Amount of energy (TW)
1.	Hydroelectric resources	≤ 0.5
2.	All tides and ocean current in the world	≤ 2.0
3.	Wind power (Globally extractable)	2–4
4.	Solar energy	120,000

TE materials are very useful for conversion of heat into electricity, i.e. recovery of electricity from waste or unused heat. The major challenge lies in the fact that how a small gradient of temperature with respect to the environmental temperature can be efficiently harvested. Fig. 1 schematically depicts the conversion of waste heat to electricity by the TE system. The main disadvantage is the low efficiency of the existing TE devices. If the ZT or efficiency of the TE can be increased, these devices can be a feasible solution of the TW energy problems [11,13]. Therefore, improvement of figure of merit or efficiency is a key issue in the allied areas of research. In this review article, our endeavor is to present a consolidated review of recent work on state-of-the-art thermoelectric composites. Several generalized reviews [14–23] of various composite TEs are already available, but here we primarily focus on CNT/graphene based polymeric composites as new generation TE materials [24].

The limited supply of natural fuels and adverse public opinion on nuclear energy led to look for alternative resource of energy and consequently this has become an important subject of research in global scenario. TE system is very promising for conversion of heat into electricity, i.e. harvesting of electricity from waste heat with small gradient of temperature compared to the environmental temperature [25,26]. This device is very reliable with reduced noise level and maintenance free long term operation due to the absence of moving segment and simpler leg type structure [27,28]. Additionally, it is very much useful for mobile power generators and cooling systems.

Three major fundamental effects viz.: (a) Peltier effect where temperature gradients generates from electrical energy, (b) Seebeck effect where electricity generates due to temperature differences and (c) Thomson effect where the heat is changed to temperature gradient in a single conductor while an electric current pass through it. These effects are fundamentally related to the characteristics of TE [29–31] and it is illustrated in Fig. 2. TE module is basically an assembly of ‘p’ type (electron deficient) and ‘n’ type (electron rich)