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Feature article

Conducting polymer/carbon particle thermoelectric composites: Emerging green energy materials

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ABSTRACT

Being green energy materials, thermoelectric (TE) materials can realize direct energy conversions between heat and electricity, thus have widely applications in both TE generators for energy harvesting and local cooling. Especially, low-quality waste heat can be conveniently used. In the recent several years, there is rapidly growing interest in organic conducting polymer/carbon particle TE composites, which synergistically combine the advantages of both carbon particles and polymer materials. In this review, the recent progress is systematically summarized in the order of the dimensionality of the carbon particles (2D, 1D and 0D) and the type of polymer matrix. Synergistic effect and polymer ordered structure, morphological tuning, devices and flexible films are highlighted. Finally, prospects and suggestions for future studies are presented.

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1. Introduction

Energy crisis is one of the major challenges facing the 21st century. Besides searching for alternative energy sources (such as solar energy, hydrogen energy and biomass energy) to replace the conventional fossil fuels, improving the current efficiency of energy use is a convenient and viable way. Presently, a significant portion of heat energy with low quality is inevitably generated and regrettably wasted in daily life and industrial production [1]. Thermoelectric (TE) functional materials are green energy materials, which can directly convert heat and electricity by use of the mobility of solid internal carriers even under very low temperature gradients relative to environmental temperature. Compared with other common new energy technologies, TE devices have many unique advantages, such as no moving parts, no noise and long operating lifetime, thus have become a very promising candidate to replace traditional energy materials [2,3]. To date, TE materials have been widely used not only in military, aerospace and other high-tech fields, but also in medical thermostats, micro sensors and other civilian areas [4].

Historically, in 1821, Seebeck firstly observed that a temperature difference between two ends of copper wires and bismuth wires could generate a voltage at room temperature, which is commonly referred to as the TE phenomenon [5]. Later in 1834, Peltier found that if an electric current flew through copper and bismuth wires at room temperature, a temperature difference would be produced [6]. These two phenomena are named as the Seebeck effect and the Peltier effect, respectively, which provide a theoretical basis for the applications of TE energy converters and cooling. Fig. 1A shows the working principle of TE equipment (Seebeck effect). When the junctions at the top are heated and those at the bottom are cooled, a temperature difference will occur. The electron/hole pairs are created at the hot end by absorbing heat, then recombine and liberate heat at the cold end. Driven by the mobility of hole/electron, the Seebeck voltage generates between the two ends, resulting in a current flow. Fig. 1B presents the process of TE cooling (Peltier effect). When a voltage is applied across a p–n junction, electron/hole pairs are generated in the vicinity of the junction and flow away, leading to the cooling of the junction on one end and the heating on the other end. TE energy conversion efficiency is generally evaluated by a dimensionless TE figure of merit (ZT), defined as $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ are the Seebeck coefficient or the thermopower, the electrical conductivity, the absolute temperature and the thermal conductivity, respectively. Accordingly, large Seebeck coefficient, high electric conductivity and low thermal conductivity are favourable to achieve high-performance (a high ZT value) TE materials at the working temperature. However, in most cases, due to the strong interdependence of these three parameters, it is extremely difficult to optimize the ZT in homogeneous bulk materials [7]. In the case of similar or low thermal conductivities, a simplified evaluation criterion, power factor ($PF = S^2\sigma$), is often adopted [8].

Currently, inorganic materials, including Bi_2Te_3, PbTe, GeTe and Sb_2Te_3, are still the main focus in TE research [9]. Nevertheless, their practical application is severely limited by the scarcity and expensiveness of their raw materials, the toxicity of the elements and the difficulty of processing [10]. In sharp contrast, organic polymer TE materials display many unique superiorities, for instance, low density, low thermal conductivity, facile processing into versatile forms and adjustable molecular structures, *etc.* [11]. In particular, organic conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy), polyacetylene (PA), polycarbazole (PC) and their derivatives, have exhibited enormous potential for the applications in TE field. Their full names, as well as chemical structures are listed in Table 1. Among them, the instability of PA and the complex preparation procedure of PC restrict their studies and applications to some extent. Therefore, the most extensively studied conducting polymers mainly include PANI [12], PEDOT [13], PTh [14] and PPy [15]. Recently, organic polymer TE materials have achieved significant progress. For example, Pipe et al. [13f]. reported a maximum room temperature ZT value of 0.42 for dimethyl sulphoxide (DMSO)-doped PEDOT:poly(styrene sulfonic acid) (PSS).

In the recent two decades, polymer/inorganic nanocomposites or hybrids have become an important branch in materials science, chemistry, physics and biology, among other fields, because the large interfacial areas and the strong interfacial interactions often lead to significantly enhanced properties and even new functions compared with the corresponding counterparts [16]. However, reviews on organic polymer/inorganic TE composites or hybrids are still rare [17]. So far, carbon particles, especially graphene and carbon nanotube (CNT), have been successfully employed in polymer TE composites, due to their extremely high electrical conductivities that can remarkably improve TE performance. In addition, their large $\pi-\pi$ conjugated systems (formed through fused aromatic rings) and the large specific surface areas greatly promote effective interfacial contacts between carbon particles and conducting polymers, thereby leading to a synergistic effect of property enhancements. On the other hand, the high thermal conductivities of the carbon particles can be mitigated by the wrapping or connection by organic conducting polymers with low thermal conductivities (<1 W m^{-1} K^{-1}). Hence, a novel class of conducting polymer/carbon particle TE composites has received increasing attention. Among previously reported TE composites, carbon particles are mainly used in the forms of graphene, CNT, graphite, carbon fibre and carbon black (CB). In terms of the structural dimensionalities, three categories can be divided, *i.e.* two-dimensional (2D) structure (graphene and graphite), one-dimensional (1D) structure (CNT and carbon fibre) and zero-dimensional (0D) structure (CB). Unfortunately, although conducting polymer/carbon particle nanocomposites have gained remarkable progress and become an important research branch in TE materials, we note that there has been no such review so far.

In this review, we focus on the recent progress of TE composites consisting of conducting polymers and carbon particles with different dimensionalities. First, the advances of the main preparation strategies and TE property are described following the sequence of the dimensionalities of carbon particles, i.e. 2D, 1D and 0D as well as polymer type. Some typical examples of conducting polymer/carbon particle TE composites are listed in Table 2. The main constituents, preparation method, measurement method and