PERSPECTIVES

CHEMISTRY

Organic thermoelectrics for green energy

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INTRODUCTION

Driven by the increasing demand for electricity, a burning desire in scientific fields is to harvest electricity from renewable energy using a green route. Thermoelectric materials can meet this requirement because their heat–electricity conversion ability not only enables direct energy harvesting from waste heat and natural heat resources, but also the fact that more than 90% of the energy we use comes from thermal processes and more than 60% of the produced energy is lost as waste heat [1,2]. The energy-conversion efficiency of a thermoelectric material is determined by the figure-of-merit ZT, which is defined by the equation $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. A key point of thermoelectric research is therefore to develop thermoelectric materials with high electrical conductivity and Seebeck coefficient, while possessing low thermal conductivity. Since the observation of Seebeck effect in 1821, inorganic thermoelectric materials have made great achievements with maximum ZT over 2. However, the energy conversion efficiency of thermoelectric devices is still not sufficient for wide power generation applications such as large-scale power plants. One possible way to break this limitation is to develop their unique and indispensable applications.

The realization of flexible applications represents one of the most important development trends of thermoelectrics. Organic materials possess excellent flexibility in comparison with conventional thermoelectric materials, which constitute their particular advantages in flexible applications (Fig. 1) [3,4]. Furthermore, benefitting from striking developments in organic electronics since the 1970 s, organic materials have been widely considered, with the unique features of fine-tuned electrical properties via molecular design, solution processability and light weight. More importantly, the low thermal conductivity of organic materials offers potential for possessing high thermoelectric performance, especially at low temperatures of ≤400 K. The combination of these features makes organic thermoelectrics an emerging interdisciplinary research frontier, which can open up new opportunities for thermoelectrics with their inorganic counterpart.

ORGANIC THERMOELECTRICS: AN EMERGING FIELD EXPERIENCING RAPID DEVELOPMENT

After a few early studies on the Seebeck coefficient of organic materials in the last century, organic thermoelectrics did not attract wide interest before 2010. Ten years ago, there were usually fewer than 10 papers published each year (Fig. 2a). In contrast, the number of organic thermoelectric publications has grown exponentially, reaching 70 in 2015 alone. A similar trend is observed in the citation pattern, with more than 1400 citations registered in 2015, whereas the number in 2005 was less than 50 (Fig. 2b). The number of papers and citations is anticipated to increase further in the years to come, suggesting that organic thermoelectrics is attracting an increasing

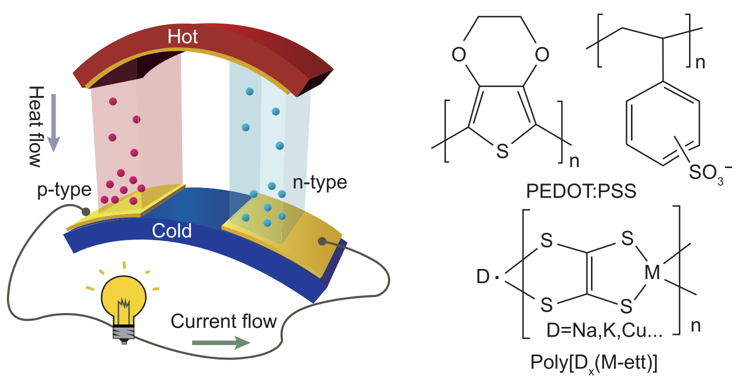

Figure 1. Working principle of a flexible thermoelectric generator and representative organic thermoelectric materials. A thermoelectric generator generally consisted of *p*- and *n*-type thermoelectric materials connected in series through conducting plates. In a temperature gradient, holes (*p*-type) and electrons (*n*-type) tend to diffuse from the hot side to the cold side, and accumulate on the cold side to produce a thermoelectric voltage via the Seebeck effect.

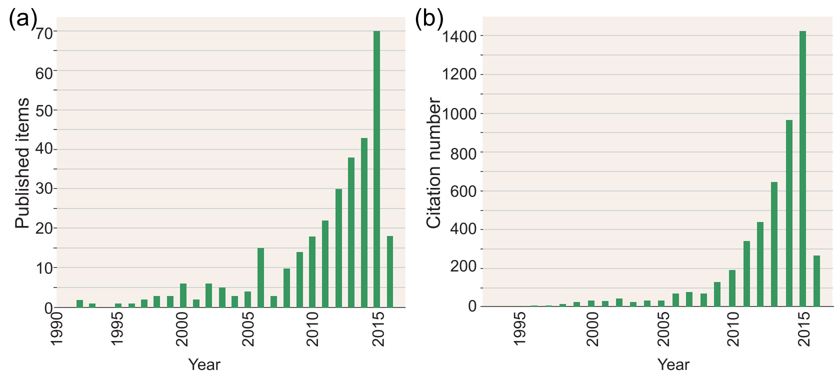

Figure 2. (a) The publication numbers of papers (without patents) and (b) citations on organic thermoelectric materials in recent years. Data retrieved from Web of Science using the keyword 'organic thermoelectric material' on 23 March 2016.

number of researchers and experiencing rapid developments. A wide range of interests are contributing to the formation of a community in this developing field. An international conference dedicated to organic and hybrid thermoelectrics (ICOT2016) was recently held in Japan to review recent achievements of organic thermoelectrics, to discuss the trends in their development and to encourage more enthusiastic efforts.

The tremendous progresses of organic thermoelectrics are also evidenced by the realization of high ZT, a key parameter of thermoelectric materials [5–12]. Take polymer-based thermoelectric materials, for example; poly(3,4-ethylenedioxythiophene) (PEDOT) is the most widely investigated p-type organic thermoelectric material [4,5]. Precise control of the chemical doping of PEDOT via polystyrene sulfonic acid (PSS) has resulted in a ZT value of 0.42. In comparison with p-type materials, the most successful achievement of n-type organic thermoelectric materials is the development of poly[Kx(Ni-ett)] by our group [6,7]. With 1,1,2,2-ethenetetrathiolate (ett) as the linking bridge, the electrochemically deposited poly[Kx(Ni-ett)] film exhibited a maximum ZT of 0.3 at room temperature. Significant progress has also been made in organic/inorganic hybrid materials [8,9]. An interesting example is tetrakis(dimethylamino)-ethylene (TDAE)-treated PEDOT:PSS/CNT hybrids, which exhibited a ZT value of 0.5. It is worth noting that these performances are comparable to that of many inorganic thermoelectric materials at room temperature, and even superior thermoelectric performance can be expected after systematic optimization in the near future.

ORGANIC THERMOELECTRICS: A CHALLENGING AREA WITH A BRIGHT FUTURE

Despite these achievements, organic thermoelectrics is undoubtedly in its initial development stage with many fundamental challenges. How can state-of-the-art organic thermoelectric materials be explored? What is the intrinsic mechanism of organic thermoelectric materials? Where are the unique applications of organic thermoelectrics? To date, nobody can answer these open questions clearly. Overcoming these challenges, which involve engineered studies of materials, theories and devices will remain critical tasks for a long time.

Material engineering in six aspects is essential to boost further development of organic thermoelectrics: (i) optimization of classic materials such as PEDOT and poly[Kx(Ni-ett)] in order to pursue superior performance; (ii) efficient screening of promising materials from numerous organic semiconductors and conductors to accelerate the exploration of high-performance thermoelectric candidates; (iii) design and synthesis of novel materials by the utilization of well-revealed structure–property relationships; (iv) development of organic/inorganic hybrid materials by incorporating advantages of organic and inorganic candidates in low thermal conductivity and high electrical conductivity, respectively; (v) exploration of novel doping methods to fine-tune the energy levels and densities of the states; and (vi) modulation of micro-/nano-structures to achieve optimized performance and to get new insights into organic thermoelectric materials. Breakthroughs in these studies may boost the development of organic thermoelectrics in an unexpected manner.

From a theoretical point of view, an understanding of the structure–property relationship towards rational molecular design is of vital importance. To meet this critical requirement, focus attention must be devoted to computational modelling of the relationships between molecular structures, energy levels, condensed structures and thermoelectric performance. Moreover, the systematic studies of the complicated physical processes, including charge transport, phonon transport, phonon scattering and their combined effect, also deserve increasing interest. ZT is defined by the equation $ZT = S^2\sigma T/\kappa$. A key point of thermoelectric research relies on the trade-off relationship between S, σ and κ. An in-depth understanding of these mechanisms and relationships is expected to further advances in experimental activities.

Organic thermoelectric devices will emphasize the performance evaluation of thermoelectric materials and demonstration of their specific applications. A straightforward way to evaluate the thermoelectric performance is via the construction of thermoelectric modules with high-output power by utilizing designed device architectures and optimized interfaces. Fabrication of flexible and low-cost power generators, which is promised by organic thermoelectrics, is a more challenging task. It typically requires integration of a huge number of p-type and n-type legs using printing techniques, whereas these integration methods are not well established.

Exploration of novel/multi-functional applications of organic thermoelectric devices can extend their use beyond power generators and refrigerators. Photothermoelectric (PTE) elements and flexible sensors have attracted attention, as evidenced by our demonstrations of flexible PTE light detectors and temperature–pressure sensors [13,14]. These functional applications allow the construction of wearable power generators, portable refrigerators, flexible detectors and artificial e-skins, which is not easy to achieve with inorganic thermoelectric materials.

In summary, organic thermoelectrics has emerged as a cutting-edge research field and recently experienced rapid development. Many original innovation opportunities still lie ahead in the study of organic thermoelectric materials, mechanisms, devices and applications. Although there is still a long way to go for realizing their true benefits, organic thermoelectrics has a bright future.

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GEOSCIENCES

Asia dust production ramped up since latest Oligocene driven by Tibetan Plateau uplift

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Eolian dust is an integral component of the Earth system dynamics, participating in a range of physical, chemical and biogeological processes of the Earth system at various temporal and spatial scales [1] (Fig. 1). Great advance has been achieved in recent years in understanding eolian dust cycles through instrumental investigations and numerical modeling as well as tracing geological records [1]. The Asian dust cycle is one of the major dust systems on Earth, playing important roles in many processes and exerting impacts well beyond the region [2]. From a geological perspective, the production, emission, transportation and deposition of Asian dust are closely associated with regional tectonic-geomorphic-climatic configurations, and thus preserving valuable archives for deciphering regional tectonic and climatic history. Among others, uplift of Tibetan Plateau and aridification of Asian interior is of great interest and global relevance.

ASIAN DUST FROM SOURCE TO SINK

It is a general consensus that the source area of Asian dust lies in its arid interior, the evolutionary history of which has attracted extensive attention in the last few decades [3]. In the case of the Taklimakan Desert, provenance analysis suggests that it contributes profoundly to global dust cycles at present, and must have done so in the geological past [1]. As such the formation of the Taklimakan Desert marks a major environmental event in central Asia during the Cenozoic. Determining when and how the desert formed holds the key to better understanding the tectonic–climatic linkage in this region. Much recent sedimentological investigation on the Cenozoic successions within and along the margin of the desert, constrained by radioisotopic dating of volcanic ash/lahars preserved in the sequences, has suggested the Taklimakan Desert came into existence by at least latest Oligocene