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导电 PEDOT 热电材料发展简史

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摘要 热电材料能够直接实现热能与电能的相互转换, 是重要的新型环保能源转换材料之一. 无机半导体材料是当前性能最好的热电材料, 然而由于资源、性能及价格的局限而难以实现大规模工业化应用. 因此, 发展新型高性能热电材料已成为当前重要研究领域. 导电高分子(CPs)作为一种潜在的热电材料, 其研究已有三十余年, 然而在2000年之前, 因其性能不佳而未引起高度关注. 2008年, 聚3,4-二氧乙撑噻吩(PEDOT)热电优值(*ZT*)首次被报道超过10^{-3}, 为发展高性能有机热电材料带来新的曙光. 此后, 大量新技术和方法应用于PEDOT热电性能的改善和提高. 近十年来, PEDOT的*ZT*值迅速从10^{-4}提高到10^{-1}, 使PEDOT成为最有希望的有机热电材料之一. 尽管PEDOT热电材料离实际工业化应用仍有较大差距(*ZT*>1), 但依然是未来有机热电材料中可能获得重大突破的p型有机热电材料. 本文简要归纳了导电PEDOT作为热电材料的优势、发展历程、性能改善的方法及其未来发展趋势.

关键词 有机热电材料, 导电高分子, PEDOT

当前, 全球大约90%的能量是由化石燃料燃烧提供, 其中仅有30%~40%的能量被有效利用, 其余约60%的能量均以废热的形式被直接排放到环境中而损失浪费. 如何有效利用废热, 研究环境友好型能源转换材料, 已成为当前可持续发展的重要挑战之一.

热电材料又称温差电材料, 是一种利用半导体中载流子运动实现热能和电能相互转换的功能材料, 常用于制冷和发电. 热电材料具有良好的节能和环保效应, 可利用废热实现能源的再利用, 得到世界发达国家的高度重视[1,2]. 热电能源转换器件具有独特的优点[3]: (1) 结构简单, 无机械传动部件, 无噪音; (2) 使用寿命超过1×10^5 h; (3) 与传统制冷相比, 无需制冷剂, 不产生有害气体, 无污染; (4) 可灵活调节制冷速度和温度; (5) 可靠性高, 无空间依赖性, 可在各种环境下运行. 热电器件的工作原理主要取决于塞贝克、帕尔贴和汤姆森3种效应, 其效率通常由无量纲热电优值(*ZT*)衡量:

$$ZT=\frac{\sigma S^2}{\kappa}T, \tag{1}$$

其中, σ为材料的电导率, S(或α)是热电势(塞贝克系数), κ是热导率, T为绝对温度. 此外, 功率因子($P=\sigma S^2$或$\sigma\alpha^2$)也是衡量热电材料性能的重要参数. 性能优异的热电材料, 高的热电势用于实现高效的热电转换, 高的电导率可以避免或减少能源转换过程中产生的焦耳热[4], 而低的热导率能有效防止热短路[5].

至今, 高性能热电材料的研究以无机半导体纳米材料为主. 理论预测显示材料纳米化是提高其热电效率的主要途径之一[6], 同时实验研究进而证实纳

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Jiang F X, Liu C C, Xu J K. The evolution of organic thermoelectric material based on conducting poly(3,4-ethylenedioxythiophene) (in Chinese). Chin Sci Bull, 2017, 62: 2063–2076, doi: 10.1360/N972017-00231

米技术(如: 超晶格薄膜、超晶格量子点等)能够有效提高*ZT*值(常温下大于2)[7]. 值得注意的是, 无机纳米材料成功获得高*ZT*值主要是通过减少声子散射从而降低材料的κ值(1.1~1.5 W m^{-1} K^{-1})来实现. 同时, 无机纳米结构所产生的能量过滤效应, 可实现*S*的提高而不影响σ[8,9]. 然而, 无机纳米热电材料的发展受限于资源的短缺以及制备的成本和复杂工艺[3].

导电高分子(CPs, 图1(a))具有来源丰富、价格低廉、易加工等优点, 同时具备固有的低热导率(0.1~1 W m^{-1} K^{-1})和可调的电导率(10^{-8}~10^{4} S cm^{-1})及热电势(10~10^{3} μV K^{-1})[3,10], 为研究和发展新型热电材料开辟了一个新的方向. 本文主要基于当前研究最广泛的聚3,4-二氧乙撑噻吩(PEDOT), 一种最有希望的p型有机热电材料之一, 就其热电性能的发展历程及现状进行综述, 并对其未来的发展做了相应的展望.

1 导电PEDOT的发现

1977年, Alan J. Heeger, Alan G. MacDiarmid和Hideki Shirakawa 3位科学家发现掺杂的聚乙炔(PA)具有金属导电性(10^{3} S cm^{-1})[11], 并因此荣获2000年诺贝尔化学奖. CPs是具有共轭π键长链结构的聚合物, 掺杂(化学术语为氧化)后, 在外电场存在下, 载流子能够沿着共轭π键产生定向迁移, 从而实现电子传递[12]. CPs在防腐、催化、电容、光伏、传感、晶体管等方面均表现出广阔的应用前景[13~16].

自PA之后, 无数新的CPs相继诞生, 如聚苯胺(PANi)、聚吡咯(PPy)、聚噻吩(PTh)及其衍生物等. 近年来, 杂环类聚合物的研究更受青睐, 因为杂环类CPs在应用过程中不易产生有害的分解产物[17]. 然而, 杂环聚合物不溶和不熔的缺陷限制了它们的发展. 为了克服其缺点, 烷基和烷氧基等修饰的杂环聚合物应运而生[18], 尽管这在一定程度上降低了聚合物的电子传递性能.

为解决PTh溶解性差的问题, 德国贝尔公司在1988年发明了PEDOT[17]. PEDOT是在PTh骨架的β位上取代一个二氧乙撑给电子基团, 不仅降低了空间位阻效应, 同时避免了α-β位缺陷耦合. 为进一步改善PEDOT的可处理性, 聚乙烯基苯磺酸(PSS)被引入PEDOT, 形成了分散性和加工性良好的PEDOT:PSS悬浮液(图1(b)). PEDOT:PSS水溶液表现出许多优异的特点: (1) 良好的成膜性, 可以通过旋涂、打印、喷涂或抽滤等方式制备均匀透明的高质量薄膜[19]; (2) 高σ(~10 S cm^{-1}), 可通过二次掺杂或溶剂处理进而大幅度提高其σ(>1000 S cm^{-1})[20,21]; (3) 杰出的环境稳定性, PEDOT:PSS薄膜可以在100℃下保留1000 h以上, σ几乎不改变[17]; (4) 固有低的κ值(室温下~0.2 W m^{-1} K^{-1})[10]. 近几十年, PEDOT:PSS在发光二极管、晶体管、电致变色、太阳能电池、传感、催化、储存器和能源储存及热电转换领域展示了广泛的应用前景[22~24], 至今国际上每年发表PEDOT相关研究论文

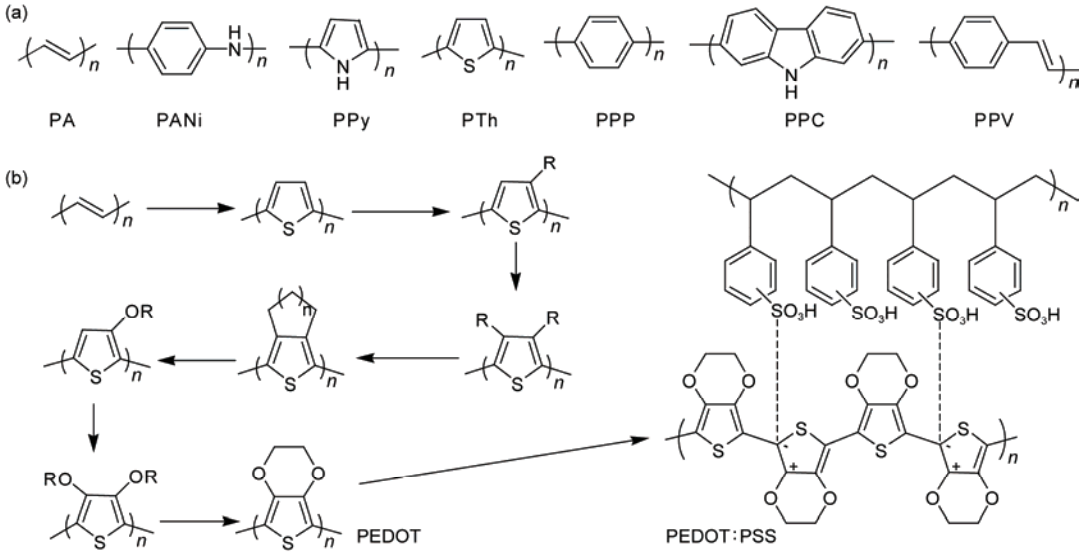

图 1 部分导电高分子结构式(a)与PEDOT:PSS结构示意图(b)

Figure 1 The chemical structure of conducting polymers (a), and the evolution scheme of PEDOT and PEDOT:PSS (b)

超过1000篇，包括多篇综述[17,25~28]和专著(图2)[29,30].

2 PEDOT热电性能的发展

PEDOT良好的电子传输性能、可加工处理性、环境稳定性使其在有机电子材料领域中备受青睐. 在热电材料领域, PEDOT作为典型p型半导体聚合物, 以其固有低的κ和高的σ而引起广泛研究兴趣, 其发展历经了从无到有(表S1), 性能从低到高的艰辛路程(图3), 实现了热电性能的大幅提高, 表现出潜在的应用价值.

2.1 探索阶段(2000年以前)

20世纪80年代初, CPs热电性能的研究主要集中在掺杂度对PA的σ和S的影响方面. 1979年, Park等人[31]首次报道了PA热电性能与掺杂浓度和温度的关系, 发现PA具有巨大的热电势(850 μV K^{-1}). 1984年, Park等人[32]再次发现, 重度掺杂的PA室温下具有类金属的热电行为, 展示了高σ(988 S cm^{-1})和低S(10 μV K^{-1}), 而低掺杂的PA则呈现出低σ(1.7 S cm^{-1})和较高S(35.1 μV K^{-1}). Shakouri和Li[33]系统总结了PA热电性能, 并表示尽管高掺杂PA具有良好的热电性能, 但其稳定性极差. 1993年, Yoon等人[34]发现质子化的PANi室温σ可达300 S cm^{-1}, S仅为10 μV K^{-1}. 1994年, Yoon等人[35]又发现PPy与PANi的S相近, 而热电性能依然不理想. 1995年, Masubuchi和Kazama[36]报道了PTh的σ(100 S cm^{-1})和S(21 μV K^{-1}). 之后, S与T温度的关系研究表明, 不同CPs均呈现类金属的热电行为. 由于PANi, PPy和PTh具有相对较好的稳定性, 其热电性能的研究开始引起关注[37~39]. 1998年, Mateeva等人[40]提出PANi和PPy的σ和S之间存在对数关系, 并给出具体的ZT值(2×10^{-5}). 在该阶段, CPs热电性能的研究重点在于掺杂对电子传输性能的影响和理论的探索方面, 仅少量研究集中在热电P或ZT值.

2.2 ZT值10^{-3}阶段(2000~2008年)

2000年之后, 有机热电材料研究依然集中在PANi,

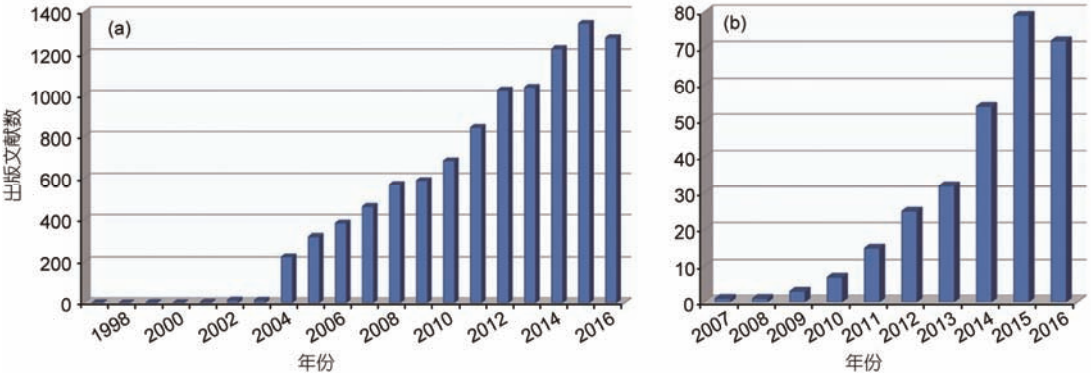

图 2 (网络版彩色)近二十年发表的PEDOT(a)和PEDOT热电(b)相关论文(截至 2016 年 12 月 6 日)

Figure 2 (Color online) Publications on (a) PEDOT and (b) its research papers on thermoelectrics nearly two decades (date from Web of Science on Dec. 6, 2016)

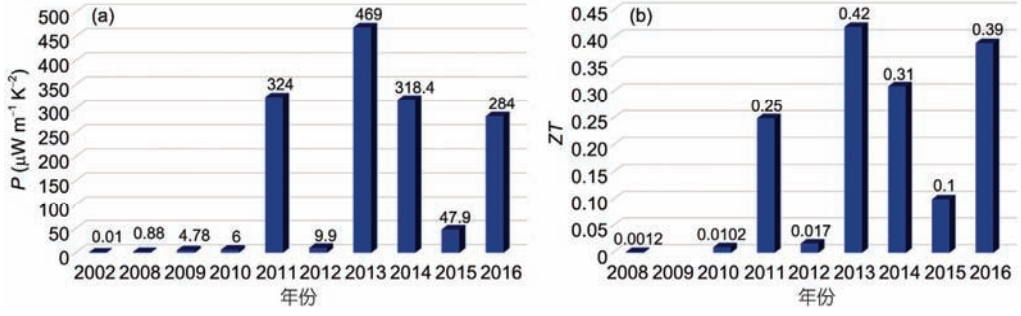

图 3 (网络版彩色)近年来PEDOT基材料的热电功率因子P(a)和ZT值(b)

Figure 3 (Color online) Values of thermoelectric P (a) and ZT (b) for PEDOT-based materials in recent years

PPy, PTh等[41~43], 同时作为明星CPs的PEDOT开始引起广泛关注[17]. 2002年, Kim等人[44]首次报道PEDOT:PSS的S(~12 μV K^{-1}), 在添加适量极性有机溶剂(二甲基亚砜(DMSO)和*N*,*N*-二甲基甲酰胺(DMF))后, 其σ可提高到80 S cm^{-1}, 而S降低甚少(~10 μV K^{-1}). 通常情况下, 由于其材料电子态密度, 传统无机半导体材料σ的提高将伴随S的显著降低[33]. 尽管PEDOT:PSS展示了优越的电子传输性能, 然而热电性能的研究并未引起关注. 2008年, Jiang等人[10]首次系统报道了有机溶剂(DMSO和乙二醇(EG))掺杂PEDOT:PSS的热电性能, 室温下ZT值达1.2×10^{-3}, 具有良好的稳定性, 其性能优于Toshima[42]报道的PANi(1×10^{-3}), 并首次明确其室温κ~0.17 W m^{-1} K^{-1}(κ值随温度降低而减小). 此后, PEDOT:PSS以其良好的环境稳定性、低κ及易调节的电子传输性能开始逐渐引起重视. Levermore等人[45]通过气相聚合的方法制备了高σ(1180 S cm^{-1})的PEDOT, 并将其应用于有机发光二极管. PEDOT优异的σ和环境稳定性, 使其脱颖而出, 为之后高性能有机热电材料研究奠定了基础.

2.3 ZT值10^{-2}阶段(2009~2011年)

自2009年起, 关于PEDOT:PSS导电性能及其机理的报道大量出现[46,47]. Chang等人[48]发现PEDOT:PSS具有高S~888.15 μV K^{-1}, 然而受σ限制, 热电P仅为4.42 μW m^{-1} K^{-1}. 研究表明DMSO掺杂的PEDOT:PSS薄膜, 可实现其高σ~298.52 S cm^{-1}的同时维持S基本不变. 2010年, Scholdt等人[49]利用DMSO气相处理PEDOT:PSS, 实现最高σ~570 S cm^{-1}和S~15 μV K^{-1}, 室温下ZT~9.2×10^{-3}. 同年, Liu等人[50]制备了DMSO掺杂的自支撑柔性PEDOT:PSS薄膜, 并首次实现ZT~1.02×10^{-2}. 大量实验数据表明, PEDOT:PSS可以在不牺牲S和κ的情况下, 通过提高σ实现ZT值的有效增加.

掺杂态PEDOT:PSS的S通常为12~16 μV K^{-1}, 研究高S的PEDOT对提高其热电性能有更重要意义. Taggart等人[51]通过电化学方法沉积了阵列式的PEDOT纳米线, 其S高达122 μV K^{-1}(n型). 对于半导体热电材料而言, σ与S相互对立, 在无机半导体材料中, σ的提高通常伴随S的降低, 反之亦然. 然而, 添加有机溶剂后的PEDOT:PSS其σ大幅提高, 而S基本不变, 这表明同时提高PEDOT:PSS的σ和S可以实现. 2011年, Kong等人[52]利用尿酸处理PEDOT:PSS, 实现了σ(63.13 S cm^{-1})和S(20.7 μV K^{-1})的同时提高. 此后, Liu等人[53]首次通过添加离子液实现了PEDOT:PSS的σ(174 S cm^{-1})和S(30 μV K^{-1})的同时提高, 实现了室温下ZT~1.7×10^{-2}, 随之引发了PEDOT热电性能研究的热潮. Sun等人[54]提出, 在CPs中引入高迁移率的元素调控费米能级, 可以实现σ和S的同时增加. Wang等人[55]采用Holstein模型研究准一维PEDOT:PSS纳米线发现, 其P最大可以达5×10^{4} μW m^{-1} K^{-2}, ZT最高可实现15.2. 此外, 他们指出低维结构的CPs在热电性能上具有潜在的研究价值. 至此, PEDOT热电ZT可稳定达到10^{-2}数量级, 其热电性能已明显优于其他CPs.

2.4 ZT值10^{-1}阶段(2011年以后)

2012年, Yue和Xu[56]发表题为“潜在有机热电材料PEDOT”的综述论文, 系统总结了十余年PEDOT热电材料发展的情况. 与降低晶格热导率的无机热电材料不同, CPs具有固有的低κ, 提高其热电性能的关键在于提高P值. Crispin课题组[57]利用四(二甲氨基)乙烯(TDAE)精确控制PEDOT的氧化程度, 实现室温下热电ZT~0.25, 获得突破性进展. 同时, 他们通过图案化方式编制了PEDOT热电器件, 其输出功率(温差ΔT~10℃)达到0.128 μW, 并指出该装置有望作为能源收集器应用于小型电容器、低功率无线装置或者医疗传感器.

为获得高热电性能的有机热电材料, 电化学和化学处理是提升PEDOT热电性能最常用的方法. 2012年, Bubnova等人[58]提出采用电化学掺杂(利用有机电化学晶体管)控制和测试CPs的氧化程度, 从而实现其热电性能的优化. Takano等人[59]通过实验证实, 在经过EG处理PEDOT:PSS薄膜中, 能有效形成PEDOT晶粒(~4.8 nm), 并大幅提升σ(~600 S cm^{-1}). 2014年, Culebras等人[60]通过电化学方法制备了不同阴离子掺杂的PEDOT薄膜, 并采用水合肼($N_2H_4·H_2O$)处理, 室温下获得P~147 μW m^{-1} K^{-2}和ZT~0.22. Lee等人[61]联合超滤(脱掉不导电的PSS)和$N_2H_4·H_2O$处理(改善导电PEDOT的氧化程度), 使PEDOT:PSS薄膜的P值达到115.5 μW m^{-1} K^{-2}, ZT值为0.2. 此后, 他们再次利用$N_2H_4·H_2O$和DMSO联合处理的方式, 进一步将P值提升至318.4 μW m^{-1} K^{-2}(σ~1310 S cm^{-1}, S~49.3 μV K^{-1}), 室温下ZT值高达0.31[62]. Park等人[63]采用溶液聚合方法合成了高σ的PEDOT薄膜, 通过

电化学方法精确控制氧化程度，最终实现热电*P*值(1270 μW m^{-1} K^{-2})的最大化，弹性的PEDOT热电薄膜器件借助指尖温差实现592±18 μV电压输出.

纯化学处理方法是改善PEDOT:PSS热电性能的另一种有效方式. 2013年以来，利用溶剂处理PEDOT∶PSS优化热电性能得到广泛研究. 这主要因为溶剂处理不仅可以有效提高PEDOT∶PSS的σ(>1000 S cm^{-1})，而且可实现*S*的改善. Luo等人[64]通过添加离子液(EMIMBF_4)和DMSO溶剂处理，大幅提高了PEDOT∶PSS的热电*P*值(38.46 μW m^{-1} K^{-2}). Zhu等人[65]通过低共熔溶剂(DESs)掺杂PEDOT:PSS，实现σ(620.6 S cm^{-1})和*S*(~29.1 μV K^{-1})的同时提高. Wang等人[66]采用气相聚合方法制备了高σ的PEDOT薄膜(944 S cm^{-1})，再通过硫酸处理将σ进而提高到1750 S cm^{-1}，热电*P*值室温下达到~37 μW m^{-1} K^{-2}. 此后，他们改用NaBH_4/DMSO处理获得*ZT*~0.064的PEDOT∶PSS薄膜[67]. 2015年，Xiong等人[68]发明简单的有机溶剂稀释抽滤法，该方法制备的PEDOT:PSS薄膜(膜厚~500 nm)热电性能可稳定达到*ZT*~0.1.

Kim等人[69]采用DMSO和EG溶剂处理旋涂的PEDOT∶PSS薄膜，有效除去了不导电的PSS，成功将其热电*ZT*值提高到0.42. Søndergaard等人[70]使用圆网印花技术制备了0.2 W m^{-2}的PEDOT∶PSS热电器件，使PEDOT∶PSS在实际中的应用得到实现. Wei等人[71]则采用平面印刷技术制备PEDOT∶PSS薄膜并组装三明治式热电器件，获得高达40 mV的开路电压和50 μW的输出功率(Δ*T*~100 K). Zhang等人[72]在常规PEDOT中嵌入PEDOT纳米线(0.2%，质量百分比)，室温下获得*P*~446.6 μW m^{-1} K^{-2}和*ZT*~0.44，实现~0.5 mW m^{-2}的输出功率(Δ*T*~10.1 K). 相对于高性能无机热电材料，PEDOT作为性能良好的有机热电材料已经开始踏上了器件发展的路程，尽管其*S*依然无法与无机材料比拟，然而，其热电性能显著的提升(*ZT*值从10^{-5}到10^{-1}，图3)，让研究者清晰看到它潜在应用的前景(*ZT*>1).

3 PEDOT热电性能的改善

在近十余年研究中，无数方法和技术用于提升PEDOT热电性能，器件组装及应用初见端倪. 然而，PEDOT热电*ZT*值当前尚未满足实际应用要求，其热电性能有待进一步提高，以下内容就其性能提高的方法归纳为4部分.

3.1 掺杂度优化

由于较低的载流子浓度，本征CPs具有低的σ[3]. 不同掺杂程度的CPs，表现出广泛变化的σ(10^{-9}~10^5 S cm^{-1})和*S*(10~10^3 μV K^{-1})[33,73]. 不同于绝缘聚合物(sp^3杂化)，导电聚合物主链上的碳原子是sp^2杂化(反式PA结构，图4(a))，其带宽通常在1~4 eV，属于典型的半导体材料，且载流子(电子或空穴)容易注入. 载流子通过π轨道有效传输，而聚合物主链结构不发生变化. 当CPs引入额外的载流子后，其主链上易形成孤子、极化子和双极化子(图4(b))，从而实现载流子在聚合物链上和链间的传输[74]. 不同掺杂程度的CPs，具有类似无机半导体或金属的行为. 通常，掺杂度越高，CPs的σ越高，相反其*S*则越低. 这是因为高掺杂度将导致费米能级向导带靠近，从而降低载流子传输的能量[3,73]. 如果要实现高热电*P*值，必须获得σ和*S*之间的平衡. 因此，有效优化和控制CPs的掺杂度是改善有机热电材料性能的主要途径之一，而化学掺杂和电化学掺杂是当前两种最主要的方式.

化学掺杂优化方式主要是通过还原剂或富电子物质诱导化学的还原反应从而改变PEDOT的掺杂度. 2011年，Bubnova等人[57]将气相聚合制备的PEDOT暴露在TDAE蒸气中，使PEDOT链的电子结构发生变化，通过精确时间调控PEDOT的氧化程度，在氧化度为22%时实现了*P*值最大化(324 μW m^{-1} K^{-2}). 从图5中可以明显观察到，PEDOT的σ和*S*与氧化度(<40%)呈截然相反的变化趋势. Lee等人[62]采用N_2H_4/DMSO溶液精确调控对甲苯磺酸(TSA)掺杂的PEDOT∶PSS薄膜(~160 nm)，实现高σ~1310 S cm^{-1}和*S* ~49.3 μV K^{-1}. Wang等人[67]则利用NaBH_4/DMSO调控，将PEDOT∶PSS的热电*P*值提升至98.1 μW m^{-1} K^{-2}. Zhu等人[75]利用NaOH/DMSO精确优化PEDOT∶PSS的掺杂度，同样获得了提高的*P*值(30.04 μW m^{-1} K^{-2}). 此外，Kong等人[76]发现，pH对PEDOT∶PSS热电性能影响较大，随着pH的增加，其*S*呈现增加趋势.

电化学是优化PEDOT氧化度的另一种有效方法. 电化学是通过改变电解质溶液中对阴离子的类型和氧化电位，从而实现其掺杂度的变化. Culebras等人[60]采用电化学沉积方法制备了对阴离子(ClO_4^-，PF_6^-等)掺杂的PEDOT薄膜，通过有效控制电化学还原电位和处理时间，成功优化了热电*P*值(从40增加到150 μW m^{-1} K^{-2}). 通过调控PEDOT氧化度而优化热电性能，已得到大量实验的验证，而且获得了理论

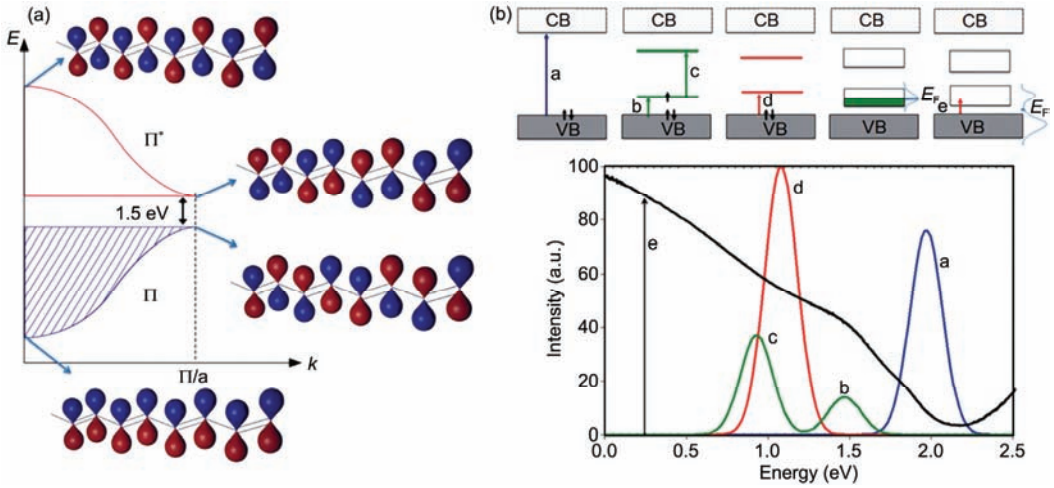

图 4 (网络版彩色)(a) 反式聚乙炔分子轨道π键价带和导带键合能量示意图; (b) 不同掺杂程度导电聚合物的电子结构: 中立态、极化子、双极化子、多极化子和双极化子[73]

Figure 4 (Color online) (a) Energy dispersion of the valence and conduction p-bands for trans-polyacetylene. The bonding scheme of the molecular orbitals is seen as a combination of atomic 2*pz* orbitals pointing perpendicular to the skeleton of the polymer chain. (b) Electronic structures of polymer chains at various oxidation states from left to right: a neutral chain, a chain carrying a polaron, a chain carrying a bipolaron, a chain or assembly of chains with a high concentration of polarons (intrachain or interchain polaron network), a chain or assembly of chains with a high concentration of bipolarons (intrachain or interchain bipolaron bands). The optical spectrum of these species is illustrated at the bottom[73]

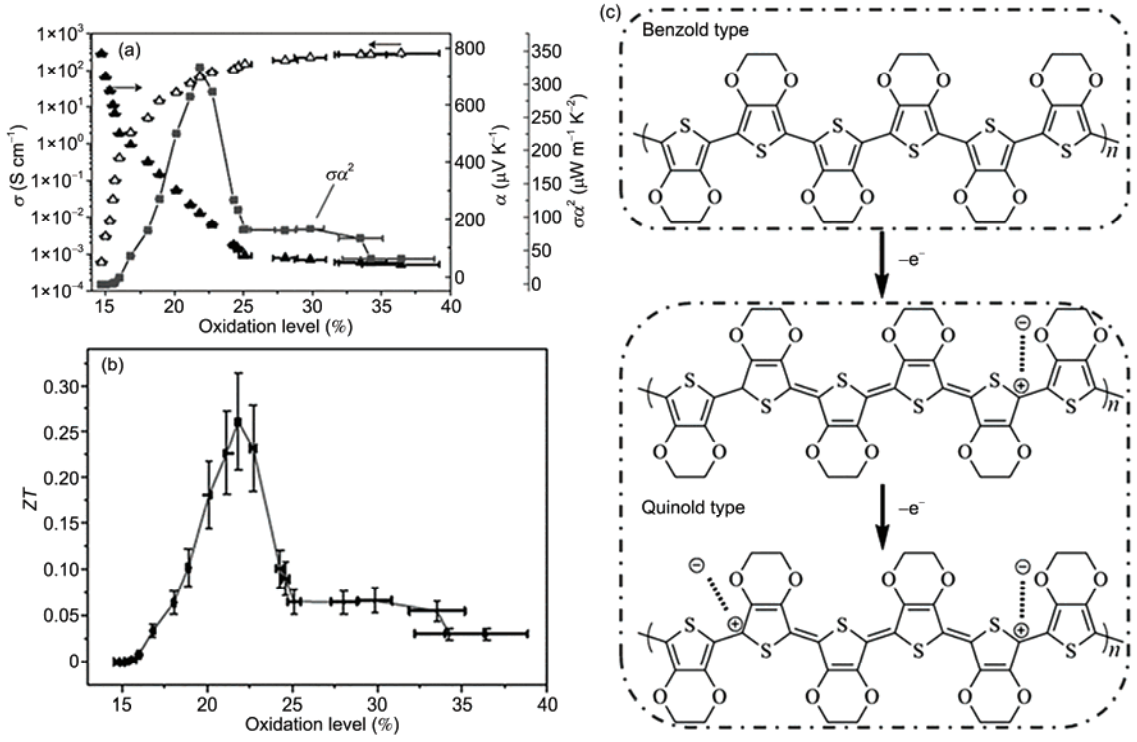

图 5 (a) 热电性能随PEDOT氧化度的变化情况; (b) 室温下PEDOT热电优值*ZT*与其氧化度的变化关系[57]; (c) PEDOT从苯型结构到醌型结构的变化

Figure 5 Thermoelectric properties (a) and *ZT* values (b) versus oxidation level of PEDOT[57]. (c) Structure conversion of PEDOT from benzoid to quinoid type

研究的支持. Zhang等人[77]通过密度功能理论研究表明, PEDOT的氧化度不仅受掺杂的影响, 其分子的几何结构也随之变化. 当掺杂度为12.5%时, PEDOT展示σ和S的同时提高. 通过优化掺杂度提高PEDOT的

热电P值，已得到多数研究者的证实，该方法对于其他CPs热电性能的调控同样有效[78~80].

在优化CPs掺杂度的过程中，载流子浓度的变化直接影响其σ. 然而，若能较好地平衡CPs的σ和S，能有效改善CPs的热电性能. 依据热电P值公式，提高CPs的S，其效果明显优于改善σ. 对于降低CPs的掺杂度而提高其S，可以通过以下公式进行解释[81]:

$$S(T)=\frac{1}{eT}\frac{\int[E_{\mathrm{F}}(T)-E]\delta\sigma(E)\mathrm{d}E}{\int\delta\sigma(E)\mathrm{d}E}, \quad (2)$$

该公式适用于能带和跳跃传输，其中E_{F}是费米能级，$\delta\sigma(E)$为能级E的微分电导. 假设单极载流子仅在一个较窄能级(E_{T})层上传输，以上方程可进一步简化为

$$S(T)=\frac{E_{\mathrm{F}}(T)-E_T}{eT}, \quad (3)$$

因为能极差$E_{\mathrm{F}}(T)$–E_T关系到载流子浓度(氧化度)，载流子浓度的降低将增大能极差，从而提高S. 然而，掺杂效应对载流子传输的影响目前尚未明确，密度功能理论常应用于有机半导体材料掺杂机制的研究[82]. Shi等人[83]首次利用第一性原理从分子水平上揭示掺杂效应对PEDOT热电传输性能的影响，尤其是电荷载流子散射. 结果表明，随着掺杂度的增加，PEDOT由半导体(苯型结构)向半金属(醌型结构)转变(图5(c))，掺杂态PEDOT以电离杂质散射为主，而低掺杂度的PEDOT其热电性能优于重度掺杂的. 因此，如果要提高CPs的热电P值，通过有效掺杂度优化载流子密度非常重要[84].

3.2 形貌构象优化

PEDOT是一种优异的CPs,与聚阴离子聚合物PSS易形成水溶性良好且稳定的PEDOT∶PSS体系. 因此，PEDOT∶PSS的电导率不仅取决于其氧化度的高低，还与其分子形貌和构象有着密切联系. Kim等人[44]认为，添加高介电常数极性溶剂将导致PEDOT∶PSS中抗衡离子和载流子之间的屏蔽效应，从而降低PEDOT中正电荷与PSS中负电荷之间的库仑作用，最终提高空穴的调频速率，而不改变PEDOT∶PSS掺杂浓度. 2003年，Jönsson等人[85]提出不同看法，他们发现有机溶剂可以改变PEDOT:PSS的形貌结构，其σ的增加在于表面绝缘层PSS的减少和导电PEDOT晶粒的形成. 2004年，Ouyang等人[86]研究指出，有机溶剂带有极性基团的多少对PEDOT∶PSS的σ有重大影响，偶极子之间的相互作用会驱使PEDOT在固体膜中的构象从卷曲型(苯型链结构为主)变化为线型(醌型链结构为主)，导致PEDOT链上载流子的离域，最终使电子传输性能得以提高. Xiong等人[68]利用有机溶剂(高沸点和低沸点)稀释抽滤的方法，进一步证实PSS的去除可以有效提高PEDOT∶PSS薄膜的σ(1500 S cm^{-1})，最终实现PEDOT∶PSS热电性能ZT值稳定达0.1(室温下)，在空气中保存3个月，其性能基本保持不变. 同样，Mengistie等人[87]利用抽滤的方法并借助乙酸处理获得高σ的PEDOT∶PSS薄膜(1900 S cm^{-1})，ZT值达到0.32，且发现乙酸处理效果明显优于EG和甲醇. 通过溶剂添加或处理提高PEDOT∶PSS的热电性能，主要在于提高其σ. 这是因为溶剂的添加可以改变导电PEDOT链的构象，而溶剂处理过程则是有效脱掉PEDOT∶PSS中绝缘的PSS，以上两种方式均可以降低PEDOT中电子传输的能量势垒. 通过溶剂添加或处理的方式提高PEDOT∶PSS热电P值已经实现高σ(>2000 S cm^{-1})[19,88]，其S没有明显变化(掺杂度并未发生变化)为改善其热电性能带来新机遇.

3.3 低维有序结构

基于以上改善PEDOT热电性能的方式(掺杂度和形貌构象优化)，可以归纳为两点：(1) 在S基本不变的情况下，PEDOT:PSS可获得较高的σ; (2) 提高PEDOT-Tos(Tos: 对甲苯磺酸离子)的S(55 μV K^{-1})，同时完成高的σ(1500 S cm^{-1}). 2012年, Takano等人[59]研究发现，通过EG添加和后期处理的方式可以有效提高PEDOT晶型结构，将PEDOT:PSS的σ提高了2个数量级，同时指出PEDOT单晶结构有利于提高其σ. 2014年, Bubnova等人[89]提出要同时实现高σ和大S的PEDOT，研究其分子有序排列是一种更有效的方式，可以有效实现其σ和S的同时增加. 对于固态无定型的聚合物，由于分子链排列结构无序，导致其费米能级处在局域态之间[90]. 然而，对于有机分子晶体，较短的链间间距容易导致相邻链π电子密度的重叠，从而促进电子波函数离域[91]. Mott公式陈述了S与[d(ln$N(E)$)/dE]$_{E=E_{\mathrm{F}}}$的比例关系，在无定型的极化子系统中，E_{F}取决于局域态，E_{F}处态密度由于接近极小值而无法发生明显改变. 相比之下，有序结构局域能级能够消除态密度，导致态密度不对称性得到放大，最终使S变大[89]. Yue等人[92]研究了形貌对PEDOT(常规、纳米粒子、纳米棒、纳米管和纳米线)的热电性能的影

响, 发现提高的链取向更有利于降低链间载流子跳跃势垒. Cho等人[93]联合气相聚合和纳米转印技术, 成功制备了超高σ~8797 S cm^{-1}的PEDOT单晶纳米线. 由于CPs链间载流子迁移率受聚合物链的排列和晶态的严重影响, 高σ的PEDOT强烈依赖于它的结晶度[94]. 单晶PEDOT具有诸多优点, 如无晶界存在的有序聚合物链、良好的界面接触和极低的电荷陷阱, 可以实现更优越的电子传输性能[93]. 实验和理论研究同时表明[83,95], 热电输运在有序晶体中具有高度的各向异性, 由于聚合物分子链方向具有大的P值和低的晶格κ(堆叠和层状方向), 有序结构的无定形聚合物纳米纤维有望实现较大的热电优值.

3.4 纳米复合

尽管CPs的热电P值可以通过诸多方法进行调控, 然而其S依然与无机热电材料有较大差距. 纳米复合的方式已被公认为最好的改善材料性能的途径之一. 良好的复合可以联结两种或多种材料的优势, 避免某一种材料性能的缺陷, 从而有效改善材料的热电性能. PEDOT具有固有的低κ和容易优化的σ等优点, 其缺点在于较低的S. 为了有效改善PEDOT的热电性能, 各种PEDOT基复合材料已经被研究, 并取得了一定的效果[73,96].

当前, 热电性能最好的当属无机热电材料, 主要以碲化铋基纳米材料为主(室温下ZT~2.4[97]). 利用无机材料高的S, PEDOT基复合材料通常呈现以下优点: (1) 相对于无机材料, κ明显降低, 主要取决于复合界面处的声子散射[98]; (2) PEDOT不仅可以作为保护层防止无机材料的氧化, 而且可以有效地连接无机纳米材料, 从而实现良好的接触[99]; (3) 在复合界面处, 低能量载流子将遭受强烈的散射, 产生能量过滤效应, 从而提高PEDOT的S[100]; (4) 与无机材料相比, PEDOT基复合材料展示了更好的柔韧性[101]. 基于以上优势, PEDOT基复合热电材料得到广泛研究, 如Te/PEDOT:PSS[99,101], Bi_2Te_3/PEDOT:PSS[102,103], PbTe/PEDOT:PSS[104], Ag_2Te/PEDOT:PSS[105], SnTe/PEDOT:PSS[106], MoS_2/PEDOT:PSS[107]等. 同样, PEDOT与石墨烯[108,109]、碳纳米管[110,111]、CPs[112,113]等复合材料也备受研究关注. 石墨烯和碳纳米管以其较高的载流子迁移率而被视为与PEDOT复合的最佳选择之一, 它们之间存在较强的π-π相互作用, 不仅可以提高复合材料的载流子迁移率, 还可以维持载流子浓度不变, 从而实现σ和S的同时提高, 最终实现高的热电P值[3]. 尽管当前PEDOT基复合材料已展示了较高的热电性能(Te/PEDOT:PSS[101], ~284 μW m^{-1} K^{-2}和SnTe/PEDOT:PSS[106], ~386 μW m^{-1} K^{-2}), 然而更多努力仍然需要投入在同时提高σ和S的研究上, 此外新技术和理论的研究有待进一步深入和完善.

4 展望

有机热电器件是未来新能源材料应用和发展的主导方向, 尤其为柔性器件的发展带来良好的机遇. 一个完整的热电器件是由p型和n型两部分半导体材料组成, 发展高热电性能p型和n型有机材料是组装热电器件的基础. 当前, 国内n型有机热电材料的研究处于起步阶段, 中国科学院化学研究所在n型有机热电材料已取得较大进展[114~116], 大量努力依然需要投入设计和制备新型分子结构的n型有机热电材料.

相对于n型有机热电材料, 在近十余年的努力下, PEDOT在有机热电材料领域研究中, 以其优异的热电性能获得了举足轻重的地位, 其热电ZT值从10^{-4}到10^{-1}, 3个数量级的提高已经使其成为当下最受欢迎的p型有机热电材料之一. 然而, 当前高热电性能的PEDOT(ZT>0.1)主要依赖于其高的σ. 如何同时获得高σ和大S, 仍是高性能PEDOT(ZT>1)热电材料发展的最大障碍. 基于现有研究, 已有大量新技术和方法应用于PEDOT热电性能的提高, 继续研究高热电性能PEDOT材料或许可以从以下几点开展[2,84,117,118]. (1) 发展低维PEDOT晶体制备技术, 建立新的理论模型和测试方法, 研究有序晶体结构和分子链排列对PEDOT热电性能的影响, 重点研究同时提高σ和S的有效途径及其电子传输的理论原理, 包括对PEDOT分子链热电性能的研究; (2) 研究新物质掺杂以及掺杂方法对PEDOT电子传输的影响, 精确调控PEDOT的氧化度, 进一步有效实现σ和S的同时提高, 从而获得大的热电P值; (3) 在维持PEDOT现有高电导率(>2000 S cm^{-1})的情况下, 除现有的复合、溶剂处理等方法外, 发展新方法或途径提高S; (4) 增加PEDOT链的共轭长度和提高链的排列取向, 研究新型多晶聚合物, 增加载流子迁移率; (5) 选择更加合理的纳米复合材料, 发展新复合制备技术, 深入研究和探讨复合结构对材料热电输运性能的影响机制; (6) 发展柔性PEDOT热电器件制备技术, 扩大PEDOT在实际中的应用, 包括热电新能源、热电制冷、热电传感等.

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Summary for “导电 PEDOT 热电材料发展简史”

The evolution of organic thermoelectric material based on conducting poly(3,4-ethylenedioxythiophene)

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Thermoelectric (TE) material, as one of new energy materials, is regarded as one of the most important energy-saving materials, which can directly achieve the interconversion between heat and electricity. Presently, inorganic semi-conductors are considered to be the best thermoelectric materials. However, the development of new thermoelectric material has attracted great attention owing to the scarce resource and limited performance of inorganic thermoelectric materials. As the discovery and wide application of conducting polymers (CPs), organic thermoelectric materials have come into the sights of people over the past 30 years. The development of CPs as a promising thermoelectric material has gained great attention over the past decades. Various CPs have been developed and investigated on thermoelectric performance such as polyacetylene (PA), polyaniline (PANi), polypyrrole (PPy), polythiophene (PTh) and their derivatives since 1989. Among numerous CPs, poly(3,4-ethylenedioxythiophene) (PEDOT) shows many superior properties compared to others due to its excellent environmental stability, water solubility, easy processibility, and high electrical conductivity, which brings new strategy for studies of high performance organic thermoelectric materials. The conductive PEDOT combined with an insulating poly(styrenesulfonate) (PSS) can form a stable aqueous PEDOT:PSS with a good film-forming property and has been regarded as one of the most potential thermoelectric material. In 2008, the thermoelectric performance of PEDOT:PSS pellets were reported systematically for the first time. Although its thermoelectric figure-of-merit (ZT) was as low as 10^{-3}, it was one of the highest values for CPs at that time. Soon afterwards, the thermoelectric performance of the free-standing PEDOT:PSS film achieved a ZT value as high as 10^{-2} in 2010. During these years, great attention focused on the derivatives of PTh, polyselenophene (PSh), PANi, and polycarbazole (PCz). Since 2010, PEDOT:PSS has come into sight of researchers in the world. The past few years witnessed great development of thermoelectric performance of conducting PEDOT:PSS (ZT ~10^{-1}). In recent ten years, the thermoelectric figure-of-merit (ZT) of PEDOT has been enhanced by three orders of magnitude from 10^{-4} to 10^{-1} as one of the most promising organic thermoelectric materials. Presently, the enhanced thermoelectric performance for PEDOT concern in the increased electrical conductivity via an easy method, especially for PEDOT:PSS. A large electrical conductivity of PEDOT:PSS thin film more than 3000 S cm^{-1} has been achieved by adding an organic solvent or post-treatment with organic solvents, acid, and ionic liquids. Compared to inorganic thermoelectric materials, PEDOT:PSS can achieve a high electrical conductivity without an obviously decreasing Seebeck coefficient. A further improvement of thermoelectric performance for PEDOT:PSS has been devoted to the optimization of Seebeck coefficient via the pH value adjustment, the reduction of the oxidized level of conductive PEDOT, or composite with inorganic thermoelectric materials. A large thermoelectric power factor has become a reality. Although there are large gaps from actual industrial application for thermoelectric PEDOT (ZT>1), yet most efforts focus on the high performance PEDOT. A large number of new techniques and methods have been developed to improve the thermoelectric performance of PEDOT. This review pays the attention to the advantages and characteristics, development history, and performance improvement of PEDOT as a promising organic thermoelectric CP from discovery to development. In order to achieve a high performance thermoelectric PEDOT, more attention should be paid to the development of low dimensional PEDOT crystal, control of oxidized level, extension of conjugated chain length of PEDOT, new preparation method and techniques, and the effects of crystal structure on electron transport properties as well as the flexible PEDOT thermoelectric devices in the future. Additionally, it is necessary to keep up with the development of n-type organic thermoelectric materials.

organic thermoelectrics, conducting polymer, PEDOT

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