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柔性电子技术专刊 • 评述

柔性自修复材料与传感器研究进展

张珽*, 白元元, 孙富钦

中国科学院苏州纳米技术与纳米仿生研究所国际实验室, 苏州 215123
* 通信作者. E-mail: tzhang2009@sinano.ac.cn

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摘要　赋予材料自修复能力是增强设备可靠性、耐用性和功能性的有效途径. 对于柔性电子材料与设备来说, 自修复功能尤为重要. 本文总结了柔性自修复材料与传感器的研究进展. 首先介绍并讨论了自修复聚合物的主要修复机制, 包括本征型自修复和外援型自修复, 并详细介绍了自修复柔性导电材料的研究进展. 在此基础上, 介绍并讨论了自修复柔性传感器, 尤其是自修复柔性力学传感器的构建方法、传感及自修复性能. 最后, 讨论了柔性自修复材料和传感器的现有挑战和解决方案.

关键词　自修复, 柔性电子, 可穿戴电子, 柔性传感器, 柔性导体

1　引言

柔性电子技术是将电子元器件集成在柔性/可延展塑料或薄金属基板上的新兴电子技术. 相对于传统的无机刚性电子器件, 柔性电子器件在适用性、便携性及舒适性等方面具有独特的优势, 是近年来学术界和工业界的研究热点之一 [1,2]. 随着材料科学、信息技术及制造技术的进步, 柔性电子器件向着智能化、多功能化和网络化的方向发展, 同时也对柔性感知技术、能源技术等提出了要求. 近年来, 基于有机聚合物及其导电复合材料的柔性传感器、柔性超级电容器、锂离子电池等取得了较大的研究进展, 并初步应用于可穿戴电子、环境监测、医疗保健等领域 [3~9]. 尽管如此, 在实际应用中, 摩擦、碰撞、弯曲等会不可避免地给柔性电子器件带来划痕、折痕、裂纹等机械损伤, 而这些损伤可能会引起器件电学性能恶化甚至失效, 从而缩短器件使用寿命 [10~12]. 比如, 对于一个以碳纳米管导电网络作为电极的平板电容器, 当电极上产生裂纹后, 由于碳纳米管导电网络被阻断, 电极导电性下降, 导致器件电容值大大减小 [13]; 对于以导电聚合物或者导电材料/聚合物复合材料作为敏感材料的压阻型传感器, 当材料中产生裂纹后, 材料的电阻大大增加, 无法用作传感器的敏感材料 [14,15]; 对于可穿戴电子器件来说, 微小的裂纹在人体运动过程中会持续扩大, 甚至会引起器件断裂、功能失效. 那么, 对

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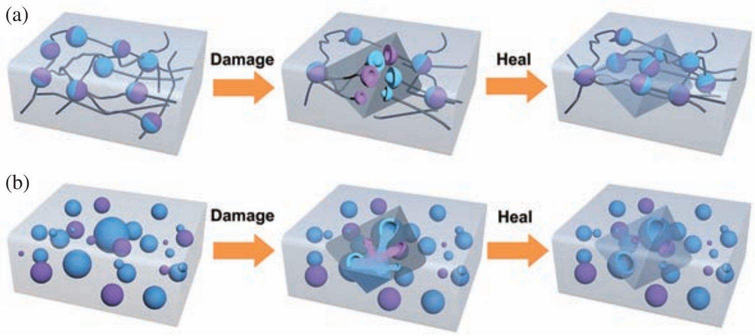

图 1　(网络版彩图) 聚合物自修复机理示意图 [32]**. (a) 本征型; (b) 外援型**

Figure 1　(Color online) Schematic of self-healing mechanism of polymers [32] @Copyright 2017 John Wiley and Sons. (a) Intrinsic; (b) extrinsic

于柔性电子器件来说, 实现裂纹或断面的自修复, 进而修复材料的电性能, 对于修复器件功能、增强器件耐用性以及延长器件使用寿命则具有重要意义.

早期研究表明, 通过埋置修复剂微胶囊/微管或利用动态共价键和非共价键, 多种聚合物材料可以自发地修复其内部的裂纹 [16~18]. 然而, 聚合物材料通常是电绝缘的, 无法用作柔性电子器件的功能材料. 基于此, 近年来, 学者们开始致力于赋予自修复聚合物材料优良的电性能或者研究开发自修复导电材料. 比如, Sun 等 [19]、Pei 等 [20]、Che 等 [21]、Le 等 [13]、Haick 等 [22]、Kim 等 [23, 24] 将金属纳米线、碳纳米管等一维导电材料网络沉积在自修复聚合物衬底上, 利用聚合物衬底的自修复功能实现了材料导电性能的自修复; Bao 等 [14]、Li 等 [25]、Saiz 等 [26]、Zhang 等 [27, 28] 等将导电金属颗粒、石墨烯、碳纳米管等导电材料埋入聚合物基体中制备了自修复导电复合材料; Williams 等 [29]、Aboudzadeh 等 [30]、Feldner 等 [31] 制备了自修复导电聚合物. 随着室温快速自修复聚合物及其导电复合材料取得的巨大突破, 自修复柔性传感器、超级电容器、锂离子电池等自修复柔性器件也取得了较大的研究进展. 最近, Zheng 等 [32] 对面向能量收集和存储器件的自修复柔性材料研究进展作了综述, 这里不再赘述. 本文将对近年来自修复聚合物/复合材料以及相关自修复柔性传感器的研究进展进行总结和讨论. 首先介绍并讨论了本征型和外援型自修复聚合物, 并详细介绍了自修复柔性导电材料的研究进展. 在此基础上, 介绍并讨论了自修复柔性传感器, 尤其是自修复柔性力学传感器的构建方法、传感及自修复性能. 最后, 讨论了柔性自修复材料和传感器的现有挑战和解决方案.

2　自修复材料

聚合物的自修复机制可以分为依靠动态 (可逆) 共价键/非共价键的本征型自修复和内部埋置修复剂微胶囊或微脉管的外援型自修复 [16, 33]. 对于本征型自修聚合物, 其内部的动态共价键/非共价键在外力作用下断裂时, 可以自发地或者在外界刺激 (如热、光照等) 下重新键合, 从而修复损伤 (图 1(a)). 这种修复过程一般可以反复多次进行, 能够有效地延长聚合物的使用寿命. 对于外援型自修复聚合物, 修复剂以微胶囊或微脉管等形式埋入聚合物基体内, 当聚合物受到损伤产生裂纹后, 裂纹的扩展导致微胶囊或微脉管破裂, 释放出修复剂. 修复剂会对裂纹进行简单的物理填充, 或者在预埋于基体中的催化剂 (催化剂也可以微胶囊化, 在基体受到损伤时被诱发释放) 作用下发生聚合反应从而修复裂纹 (图 1(b)). 这种修复过程一般是自发的、不可逆的.

2.1 本征型自修复

本征型自修复利用聚合物内部共价键或非共价键的动态特性 (可逆性) 实现自修复. Diels-Alder (DA) 环加成反应是有机化学中最重要的化学反应之一, 利用其热可逆性可以构建热修复材料[34~39]. 比如, Chen 等[34,35] 利用 DA 反应合成了基于呋喃 – 马来酰亚胺的聚合物, 在 120°C~150°C 左右该聚合物分子间的动态共价键断开, 温度降低时又重新聚合, 从而修复机械损伤. 同样地, 利用 DA 反应, Murphy 等[36] 合成了基于二环戊二烯 (DCPD) 的聚合物, 在 120°C 附近可以实现自修复. 二硫键[40~42]、酰腙键[43,44]、亚胺键[45,46]、碳碳双键[47] 等动态共价键可以用来构建本征型自修复聚合物, 其修复条件可以是热引发, 也可以是光引发. 例如, Canadell 等[41] 通过在环氧基橡胶网络结构中引入二硫键, 构建了在 60°C 下具有热修复功能的聚合物材料, 而 Amamoto 等[42] 在聚氨酯橡胶中引入了二硫化秋兰姆基团, 在可见光照射下, 通过基团中二硫键的断裂及自由重组, 实现材料的自修复. 总的来说, 动态共价键的强度相对较高, 适用于构建力学强度和稳定性较好的自修复材料. 不足的是, 该类自修复材料一般需要外部刺激 (比如热、光照、溶剂) 来实现自修复功能, 并且反应时间较长.

近年来, 基于动态非共价键 (包括氢键、π-π 键、离子键、金属配位键等, 又称为超分子键) 的超分子自修复聚合物快速发展, 大量的室温/高效/快速自修复、弹性自修复超分子聚合物相继被报道, Binder 等[48,49] 对自修复超分子聚合物的研究进展作了系列综述. 当超分子聚合物受到机械损伤时, 断裂面上存在大量的动态超分子自由基, 随着聚合物链的运动部分自由基会重新缔合, 从而修复裂纹. 通过调节超分子键的种类、分子缔合常数以及链的运动性等, 不仅可以调节聚合物的修复条件、修复速率/效率, 还可以调节相应聚合物的模量、粘度、流动性等. 对于柔性电子来说, 面向自修复柔性衬底、柔性介质及封装材料等应用的自修复橡胶的发展具有重要意义. Leibler 等[50] 以一元脂肪酸、二元脂肪酸、二亚乙基三胺 (DETA) 及尿素为原料, 采用两步法合成了一种超分子低聚物体系, 通过添加塑化剂降低玻璃化转变温度 (Tg), 该体系在室温下具有类橡胶性能, 其断裂拉伸率超过 500%. 同时, 由于聚合物分子链上的不同官能团之间具有较强的动态氢键作用, 该体系还具有优异的室温 (20°C) 自修复性能, 即修复时间为 15 分钟时, 修复效率 η (= $\frac{f_{\mathrm{HEALED}}-f_{\mathrm{DAMAGED}}}{f_{\mathrm{VIRGIN}}-f_{\mathrm{HEALED}}}$, f 为材料性能) 约为 40%, 而超过 3 小时后, 修复效率可达 100%. 该研究团队还以一元、二元和三元脂肪酸以及 DETA 为原料, 通过简单的调整原料比例的方法合成了室温下具有自修复能力的超分子橡胶[51]. 依据 Leibler 等的研究工作, Zhang 等[52,53] 以羧基功能化的聚二甲基硅氧烷 (PDMS-COOHx)、DETA 和尿素为原料合成了基于 PDMS 单体的自修复超分子橡胶. 超分子自修复橡胶的修复能力与断面分离时间有关, 随着分离时间的延长, 断面上的自由基数量减少, 导致材料的修复能力降低[50,53]. 同时, 聚合物断面的自修复活性对温度非常敏感, 过高的温度会使断面自修复活性降低甚至丧失[54].

本节中提到的一些代表性聚合物自修复性能总结在表 1 中.

2.2 外援型自修复

外援型自修复通过消耗聚合物内部埋置的修复剂来实现自修复. White 等[55] 最早提出了利用修复剂微胶囊实现自主修复的方法. 他们将 DCPD 修复剂封装在微胶囊内, 并埋入环氧树脂基体中. 当环氧树脂受到损伤产生裂纹后, 裂纹的扩展导致微胶囊破裂, 释放出 DCPD, 并因毛细管作用扩展到整个裂纹平面. 在预埋的 Grubbs 催化剂作用下, DCPD 发生开环易位聚合反应, 填充裂纹. 这种方法可以实现自主修复, 效率可达 75%, 但是 Grubbs 催化剂在基体中与环氧树脂中的胺类固化剂接触会失去部分活性, 并且容易团聚. 为解决这一问题, Rule 等[56] 将 Grubbs 催化剂封装在石蜡微球中,

表 1　代表性聚合物自修复性能

Table 1　Summary of the self-healing performance of typical polymers a)

Material	Mechanical strength	Healing mechanism	Healing condition	Healing efficiency (%)	Ref.
3M4F	121 MPa/ Compression	Thermal reversible DA reaction	120°C~150°C (N_2)/2 h→RT	41~50	[34]
2MEP4F	121 MPa/ Compression	Thermal reversible DA reaction	115°C/30 min →40°C/6 h	80	[35]
DCPD based	85 MPa/Compression polymer	Thermal reversible DA reaction	120°C(Ar)/20 h	46	[36]
Epoxy based rubber	0.5 MPa/Stretch	Disulfide bond	60°C/1 h	95	[41]
PU rubber	3.9 MPa/Stretch	Disulfide bond	Visible light/ 24 h	97	[42]
Ru/PBD	0.4 MPa/Stretch	C-C double bond	20 kPa/1 h	100	[47]
CF/polyimine	140 MPa/Bending	Imine bond	121°C/45 MPa	100	[46]
M1-TEGMEMA	–	Acylhydrazone bond	100°C/24 h	100	[44]
Fatty acid based SR	2 MPa/Stretch	Hydrogen bond	RT/3 h	100	[50]
PDMS-$COOH_2$ based SR	0.4 MPa/Stretch	Hydrogen bond	80°C/16 h	100	[53]

a) 3M (maleimide monomor); 4F (furan monomer); RT (room temperature); 2MEP (1, 8-Bis(maleimido)-1-ethylpropane); DCPD (dicyclopentadiene); PU (polyurethane); PBD (polybutadiene); CF (carbon fiber); M1 (acylhydrazone monomer); TEGMEMA (triethylene glycol methylether methacrylate); SR (supermolecular rubber); PDMS (polydimethylsiloxane oligomers); COOH (carboxyl).

大大减少了催化剂的用量, 并将环氧树脂自修复效率提高到 93%; Jackson 等 [57] 将 Grubbs 催化剂封装在 PMMA-PS 微球中, 并用 SiO_2 膜层对催化剂和修复剂微胶囊进行功能化处理, 改善了它们的分散性. 环氧树脂 [58]、PDMS [59] 以及一些有机溶剂 (如氯苯 [60]、异佛尔酮二异氰酸酯 [61] 等), 也可以微胶囊化并作为修复剂用于聚合物的自主修复. 修复剂微胶囊化的方法主要包括原位/界面聚合和熔融分散法 [33]. 原位/界面聚合法是在含有修复剂液滴的水包油型乳液中, 利用原料在液滴界面处发生的原位反应形成壳层, 从而包裹修复剂. 常用的微胶囊壳层原料有尿素 – 甲醛、三聚氰胺 – 甲醛、三聚氰胺 – 尿素 – 甲醛、聚氨酯、聚丙烯酸等. 溶液分散法是在聚合物熔体 (比如石蜡) 中分散修复剂核, 再将熔体乳化形成液滴, 最后通过改变温度或挥发溶剂等方法将液滴固化得到内含修复剂的微胶囊.

修复剂不仅可以封装在微胶囊中, 还可以封装于空心微管中. 不同于微胶囊型自修复, 基于空心微管的自修复材料的构建通常是先将微管以一维、二维或三维网络的方式与基体复合, 再向微管网络中填充修复剂和引发剂 [33]. 因此, 在选择修复剂时要考虑表面润湿性、化学相容性、粘度等, 以提高填充效率. 中空玻璃纤维 (直径一般为 15~60 μm) 常用来制备一维中空网络结构材料 [62, 63], 二维中空网络结构可以通过在一维纤维上打垂直通孔来实现 [64], 而三维中空网络结构则需要结合复杂的加工技术 [65], 比如, 利用墨水直写或 3D 打印技术制备三维网络结构支架, 再将支架浸润在液态聚合物前驱体中并固化, 然后采用溶解等方式去除支架结构从而获得具有三维中空网络结构材料. 这种制备方法可以控制网络结构的形状和连通性, 但是基体材料的选择受限. 基于空心微管的材料自修复机理同微胶囊型自修复材料类似, 不同之处在于空心微管网络结构可以储存大量的修复剂, 其自给能力使得材料具有多次修复功能.

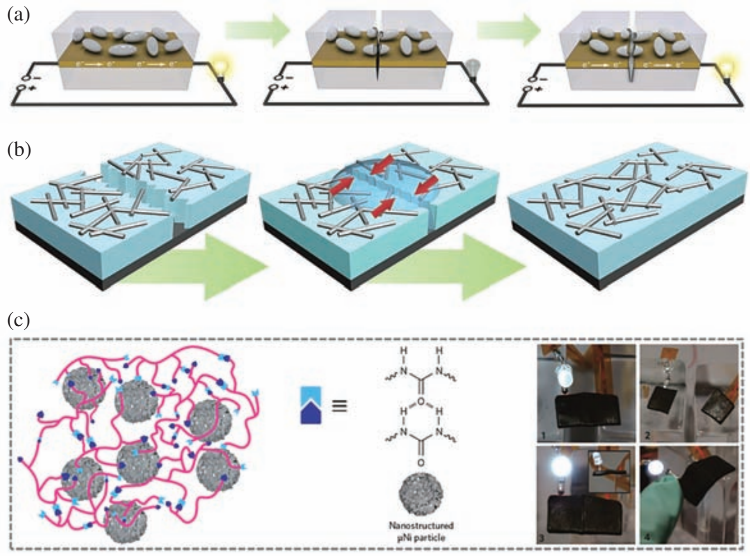

图 2 (网络版彩图) 导电材料/聚合物复合材料自修复示意图. (a) 依靠液态导电材料微胶囊实现金属导体自修复示意图 [67]; (b) 在水的作用下, AgNWs/(bPEI/PAA-HA) 复合材料薄膜自修复示意图 [19]; (c) μNi/L 复合材料微结构示意图及电性能修复过程. 1. 未损伤材料; 2. 完全断裂的材料; 3. 断裂面在 50 kPa 压力作用下接触放置 15 s 后的自支撑材料; 4. 50°C 下修复 5 min 后处于弯曲状态的材料 [14]

Figure 2 (Color online) Schematic of self-healing of conductive material/polymer composites: (a) Schematic of self-healing via embedding liquid conductive materials capsules [67] @Copyright 2011 John Wiley and Sons. (b) Schematic of self-healing of AgNWs/(bPEI/PAA-HA) composite with the aid of water [19] @Copyright 2012 John Wiley and Sons. (c) Schematic of the microstructure of μNi/L composite and the process of electrical self-healing. 1. Undamaged material; 2. completely fractured material; 3. Self-supporting material with its fractured surfaces contact for 15 s; 4. Flexed material after being healed for 5 min, showing its mechanical strength and flexibility [14] @Copyright 2012 Springer Nature

2.3 自修复导电材料

导电材料是电子元器件中不可或缺的电联结材料、电接触材料以及电极材料, 实现导电材料自修复的关键是通过重构导电通路修复其电性能. 利用预埋置的液态金属、碳纳米管墨水等液态导电材料微胶囊或微通道可以实现传统无机金属导体及半导体材料的自修复 [66~69]. 比如, White 等 [67] 在纳米金导线上方沉积一层预埋共晶镓铟 (Ga-In) 液态金属微胶囊的聚合物, 当材料受到损伤后, 通过向裂纹处释放和输送液态 Ga-In 修复导电通路 (图 2(a)). 对于印刷电子来说, 基于导电墨水的电子电路中导电颗粒之间存在聚合物粘结剂, Moore 等 [70] 以有机溶剂微胶囊为修复剂, 利用微胶囊破裂后溶剂对粘结剂的溶解作用实现导电颗粒的重新分布, 并进一步实现电路电性能的自修复. 利用修复剂微胶囊可以实现导电材料的快速自主修复, 但是通常只能实现一次或若干次修复.

近年来, 将无机导电材料与聚合物复合, 利用聚合物的自修复驱动导电材料实现电性能自修复成为研究热点. 复合方式主要可以分为两大类, 一类是将金属纳米线、碳纳米管等一维导电材料网络沉积在自修复聚合物衬底上 [13,19~24,71,72], 比如, Sun 等 [19] 将聚乙烯吡络烷酮 (PVPON) 修饰的银纳米线 (AgNWs) 沉积到支化聚乙烯亚胺 – 聚丙烯酸 – 透明质酸 (bPEI/PAA-HA) 聚电解质多层膜 (PEM) 衬底上制备了柔性自修复导电材料. 如图 2(b) 所示, 在水的作用下, PEM 薄膜溶胀并通过重构离子键修复裂纹, 同时, 由于 PEM 衬底表面的羧酸基团和 AgNWs 上的吡咯烷酮基团之间存在较强的氢键作用, AgNWs 会随着 PEM 的溶胀移动并重新接触, 实现电性能的自修复. 另一类是将导电金属颗

粒、石墨烯、碳纳米管等导电材料埋入聚合物基体中[14, 22, 25~28]. 比如, 在 Leibler 等[50, 51] 研究工作的基础上, Bao 等[14] 以二聚酸、三胺和尿素为原料合成了由氢键连接的超分子聚合物 L, 通过将镍纳米结构微粒 (μNi) 引入 L 基体中制备了电导率为 40 S/cm 的 μNi/L 复合材料. 由于 L 基体内存在大量的动态氢键, μNi/L 具有优异的力学自修复性能, 同时由于 μNi 表面包裹一层氧化层薄膜, 能够与超分子聚合物产生氢键相互作用, μNi/L 复合材料还具有优异的电学自修复性能 (图 2(c)). Saiz 等[26] 将蜂窝状 rGO 浸入含有 B_2O_3 的 PDMS 液体中, 并在 200°C 下原位聚合得到了电导率到达 90 S/cm 的 rGO/PBS 复合材料. 由于 rGO 被束缚在 PBS 内部, 并且 PBS 超分子聚合物内存在大量的动态硼 – 氧配位键和氢键, 将断裂的复合材料在室温下接触放置 10 分钟, 其力学性能和电学性能可分别修复 80% 和 90%. 可以看出, 利用无机导电材料/聚合物复合材料构建自修复导电材料的关键在于采用化学修饰或半嵌入等方式使得导电材料和聚合物之间具有良好的相容性 (包括分散性、界面结合力等).

作为柔性离子导电材料, 导电聚合物在柔性电子领域具有广泛的应用, 包括电子皮肤、柔性超级电容器、柔性触摸屏[73~77] 等. 导电聚合物的自修复可以通过动态共价键/非共价键来实现, 比如, Williams 等[29] 利用氮杂卡宾和过渡金属制备了一种基于热可逆化学键的有机金属聚合物, 在 200°C 加热条件下或 150°C/二甲亚砜溶剂蒸汽条件下具有自修复功能; Aboudzadeh 等[30] 利用一元/二元羧酸和二/三烷基胺制备了一种基于动态氢键的超分子离子聚合物, 在 50°C 加热条件下或室温氮气氛围下具有自修复功能; Feldner 等[31] 利用醋酸铜 – 草酸 (CuA-Ox) 制备了基于金属配位键的超分子金属凝胶体系, 在微小压力作用下具有自修复功能.

总的来说, 导电材料可以通过埋置修复剂微胶囊、与自修复聚合物复合以及引入动态共价键/非共价键等方法来实现自修复. 尽管如此, 制备同时具有优异的电学性能 (比如大电导率)、力学性能 (比如强度高、柔性好) 和自修复性能 (比如修复效率高、速度快、条件温和) 的导电材料仍具有挑战性.

3　自修复柔性传感器

柔性传感器是发展智能化柔性电子设备的核心器件之一. 该部分总结并讨论了基于柔性自修复聚合物/复合材料的柔性自修复物理和电化学传感器 (见表 2[78~92]), 并重点讨论了典型柔性自修复传感器的构建方法、传感及自修复性能, 以及它们在人体活动监测领域的应用.

3.1　自修复柔性物理传感器

柔性物理传感器能够将力、热、声等物理信号转换成电信号, 近年来, 利用柔性物理传感器实现对人体活动和健康状况的实时监测成为研究热点, 其中, 研究最多的是柔性力学传感器和温度传感器[4]. 将一维导电材料网络沉积在自修复聚合物上可以构建自修复平板电容式力学传感器. 比如, Lei 等[13] 利用热可逆 DA 反应制备了自修复 MT/S-CCTO 复合材料, 进一步通过在复合材料上下表面沉积单壁碳纳米管 (SWNT) 导电薄膜制备了柔性平板电容. 将该平板电容用刀片割出裂纹 (50 μm 宽) 后在 150°C 条件下处理 30 分钟, 其电容值和拉伸率可以分别修复到初始值的 89% 和 86%. 在 10 次重复割裂 – 修复过程后, 其电性能修复效率仍有 82%. 该平板电容可以作为柔性应变传感器用于检测手指的弯曲, 并且展现出良好的自修复性能. 可以看出, 这种平板电容式力学传感器通过聚合物介质层的自修复来实现电极导电性能的自修复, 如 2.3 小节所述, 其关键在于增强电极材料和聚合物之间的

表 2　柔性自修复传感器代表性研究成果

Table 2　Summary of typical research about flexible self-healing sensors[a)]

Material	Healing mechanism	Healing condition/efficiency	Application	Ref.
MDPB-TDF/ S-CCTO	Self-healing of SWNT driven by thermal reversible DA reaction	105°C/30 min: electrical∼89%; mechanical∼86%	Capacitive force sensor	[13]
μNi/L	Hydrogen bond	50 kPa/15 s: electrical∼90% 50°C/10 min: mechanical∼100%	Piezoresistive force sensor	[14]
rGO/PBS	B-O dative bond & hydrogen bond	RT/10 min: electrical∼90%; mechanical∼80%	Piezoresistive force sensor	[26]
SWNT/ PVA-borax	Hydrogen bond	RT/3.2 s: electrical∼98%	Piezoresistive force sensor	[78]
m-PCL/GO/ AgNWs	Hydrogen bond	80°C/3 min: electrical∼80%; mechanical∼100%	Piezoresistive force sensor	[79]
CNT-Fe^{3+}/PDA@ENR	Metal coordination bond	RT/24 h: electrical∼100%; mechanical∼89.3%	Piezoresistive force sensor	[80]
CNTs@(PEI@CNC)/ XNBR	Hydrogen bond	Hot-press: electrical∼100%; mechanical∼83%	piezoresistive force sensor	[81]
C-CNC@GA@Ca^{2+} @CNTs/ENR	Hydrogen & metal coordination bond	RT/30 s: electrical∼100%; mechanical∼90%	Piezoresistive force sensor	[82]
C-CNC@CT@CNTs/ENR	Hydrogen bond	RT/15 s: electrical∼100%; mechanical∼100%	Piezoresistive force sensor	[83]
Amylopectin hydrogel	Hydrogen bond	RT/3 s: electrical∼99.3%; RT/5 min: mechanical∼98.4%	Piezoresistive force sensor	[84]
PVA-PEDOT: PSS	Hydrogen bond	80°C → −20°C: electrical∼100%; mechanical∼85%	Piezoresistive force sensor	[85]
PVA-PVP/CNC-Fe^{3+}	Ionic coordination bond	RT/5 min: electrical∼100%; mechanical∼100%	Piezoresistive force sensor	[86]
κ-carrageenan/PAAm	Thermal-reversibleg κ-carrageenan	90°C/20 min: electrical∼99.2%; mechanical∼100%	Piezoresistive force sensor	[87]
PEG-PAA	Metal coordination & Hydrogen bond	RT/2 h: electrical ∼100% RT/12 h: mechanical∼96.8%	Piezoresistive force sensor	[88]
PANI-PAA-PA	Hydrogen bond & electrostatic interaction	Slight pressure/24 h: electrical∼99%; mechanical∼99%	Piezoresistive force sensor	[89]
Graphene/PU	Thermal reversible DA reaction	Microwave/5 min→65°C/5 h: electrical∼75%; mechanical∼100%	Piezoresistive force sensor	[90]
PAA-Fe^{3+}/DCh-PPy	Ionic interaction	RT/1 min: electrical∼96% RT/2 min: mechanical∼100%	Piezoresistive force sensor	[15]
PDMAA-PVA/rGO	Hydrogen bond	RT/12 h: electrical∼89.6%; mechanical∼100%	Piezoresistive force sensor	[25]
SWNT/L	Hydrogen bond	RT/1 h: electrical∼100%	Temperature sensor	[91]
P(BMA-co-LMA)/MWNT	C-C double cond	60°C/3 h: electrical∼98%; mechanical∼94%	Temperature sensor	[92]
MWNT/PEM	Hydrogen bond & electrostatic interaction	Water/30 min: electrical ∼91%; mechanical∼100%	Gas sensor	[21]

a) S-CCTO (surface-modified CaCu3Ti4O12); MDPB (1, 1'-(methylene di-4, 1-phenylene) bismaleimide); TDF (2, 2'-(Thiodimethylene) difuran); PBS (polyborosiloxane); PVA (polyvinyl alcohol); m-PCL (poly(3-caprolactone) microspheres); PDA (polydopamine); ENR (epoxidized natural rubber); PEI (polyethyleneimine); C-CNC (carboxyl cellulose nanocrystals); XNBR (carboxylated nitrile rubber); GA (gelatin); CT (chitosan); PEDOT:PSS (poly(3, 4-ethylenedioxythiophene):polystyrene sulfonate); PVP (polyvinyl pyrrolidone); PAAm (polyacrylamide); PEG (polyethylene glycol); PAA (poly(acrylic acid)); PANI (polyaniline); PA (phytic acid); DCh (double-bond decorated chitosan); PPy (polypyrrole); PDMAA (poly(N, N-dimethylacrylamide)); P(BMA-co-LMA) (poly(butyl methacrylate-co-lauryl methacrylate)); PEM (polyelectrolyte multilayer)

相容性.

对于导电材料/聚合物复合材料, 当填料含量超过逾渗值后, 材料具有导体特性; 当填料含量低于和接近逾渗值时, 材料通常具有压阻特性, 即材料电阻在外力作用下会发生变化. 利用这种性质, 再结合聚合物的自修复特性可以构建柔性自修复导体和压阻式力学传感器. 例如, Bao 等[14] 将导电 μNi 引入自修复超分子聚合物 L 中制备了具有优良导电性的柔性自修复 μNi/L 复合材料, 可以用作自修复柔性导体 (图 3(a)). 在室温及微小压力作用下, 材料的电性能在 15 秒内即可修复 90%, 而在 50°C 下处理 10 分钟后, 材料的力学性能可完全修复 (图 3(b) 和 (c)). Bao 等通过减小 μNi 的含量使得 μNi/L 具有压阻性, 构建了自修复压阻式弯曲传感器和触觉传感器, 可以分别实现角度 (0°∼70°) 和压力 (0∼400 kPa) 检测 (图 3(d) 和 (e)). Bao 等还利用自修复 μNi/L 柔性导体、弯曲/触觉传感器以及发光二极管 (LED) 组成了简单的电子皮肤电路, 分别贴附在铰接式木质机器人的肘部和掌部 (图 3(f)), 实现了对机器人肘部弯曲程度以及掌部所受压力的检测.

Bao 等的研究工作展示了自修复柔性导体和力学传感器在可穿戴电子皮肤领域的应用雏形, 当然, 该自修复电子皮肤电路仍有一些不足之处, 比如, 电路中的部分导线仍采用了不具有自修复能力的传统导线, 这也是目前文献报道的柔性自修复传感器普遍存在的问题. 此外, 导电材料/聚合物复合材料的电阻容易受外界的污染而发生变化, 进而影响传感器的性能, 封装则是解决这一问题的有效途径. Lee 等[78] 将压阻型 SWNT/PVA-borax 凝胶复合材料封装在两层弹性体之间制备了超弹性应变传感器 (拉伸率 >1000%). 该传感器可以嵌入手套、衣服或贴附在皮肤上, 实现了对人体大尺度动作的监测 (图 4). 该传感器的敏感层 SWNT/PVA-borax 凝胶复合材料具有优异的自修复性能, 不足的是, 其弹性体封装材料不具有自修复功能, 从而限制了传感器整体的自修复功能. 总体来说, 在选择封装材料时, 力学柔性、电绝缘性以及自修复性能是需要考虑的关键因素.

除了自修复导电材料/聚合物复合材料以外, 自修复导电聚合物通常具有优异的柔性、拉伸性和压阻特性, 常用作自修复柔性应力/应变传感材料[15,85,88,89]. 最近, Xing 等[15] 将导电 PPy 接枝到双键修饰的壳聚糖 (DCh) 上, 再与 Fe^{3+} 和 PAA 共聚制备了 PAA-Fe^{3+}/DCh-PPy 导电水凝胶 (图 5(a)). 由于 PAA 分子链上的 COOH 基团、PPy 表面的 N-H 基团和 Fe^{3+} 之间存在动态非共价离子键, 该水凝胶具有优异的自修复性能, 即室温下其力学性能可在 2 分钟内实现 100% 自修复, 而其电学性能在 30 秒内可实现 90% 自修复, 1 分钟内可实现 96% 自修复 (图 5(b) 和 (c)). 该柔性自修复水凝胶具有压阻特性, 即其电导率随着外加压力的增大而增大. 利用这一特性结合 3D 打印技术, Xing 等制备了柔性可穿戴应变传感器, 进一步结合智能手机构建了人体活动实时监测系统 (图 5(d) 和 (e)). Xing 等的工作展示了先进加工技术 (比如 3D 打印技术) 在构建小型化柔性自修复传感器方面的重要作用, 也初步验证了利用智能终端设备实现无线传感的可行性.

对于柔性温度传感器, 热释电聚合物聚偏二氟乙烯 (PVDF) 及其与三氟乙烯的共聚物 (P(VDF-TrFE))、纳米金属材料、CNT 等是常用的温敏材料. 目前, 尚未有关于自修复 PVDF 及 P(VDF-TrFE) 的报道, 而纳米金属材料、CNT 等与自修复柔性聚合物复合后可具备电学自修复性能[22,91,92]. 比如, Chen 等[91] 将羧基化的 SWNT 引入超分子聚合物 L 中制备了柔性自修复热敏 SWNT/L 复合材料. 超分子聚合物 L 由动态氢键连接, 赋予 SWNT/L 良好的自修复性能, 而 SWNT 和 L 之间由共价键连接, 赋予 SWNT/L 良好的电性能. 当温度升高时, 聚合物分子链的伸展运动使得 SWNT 间的接触性变好, 复合材料电阻率降低, 从而实现温度传感 (图 6).

3.2 自修复柔性电化学传感器

柔性气体传感器、离子传感器等柔性电化学传感器在环境监测、人体健康监测等领域具有广泛的

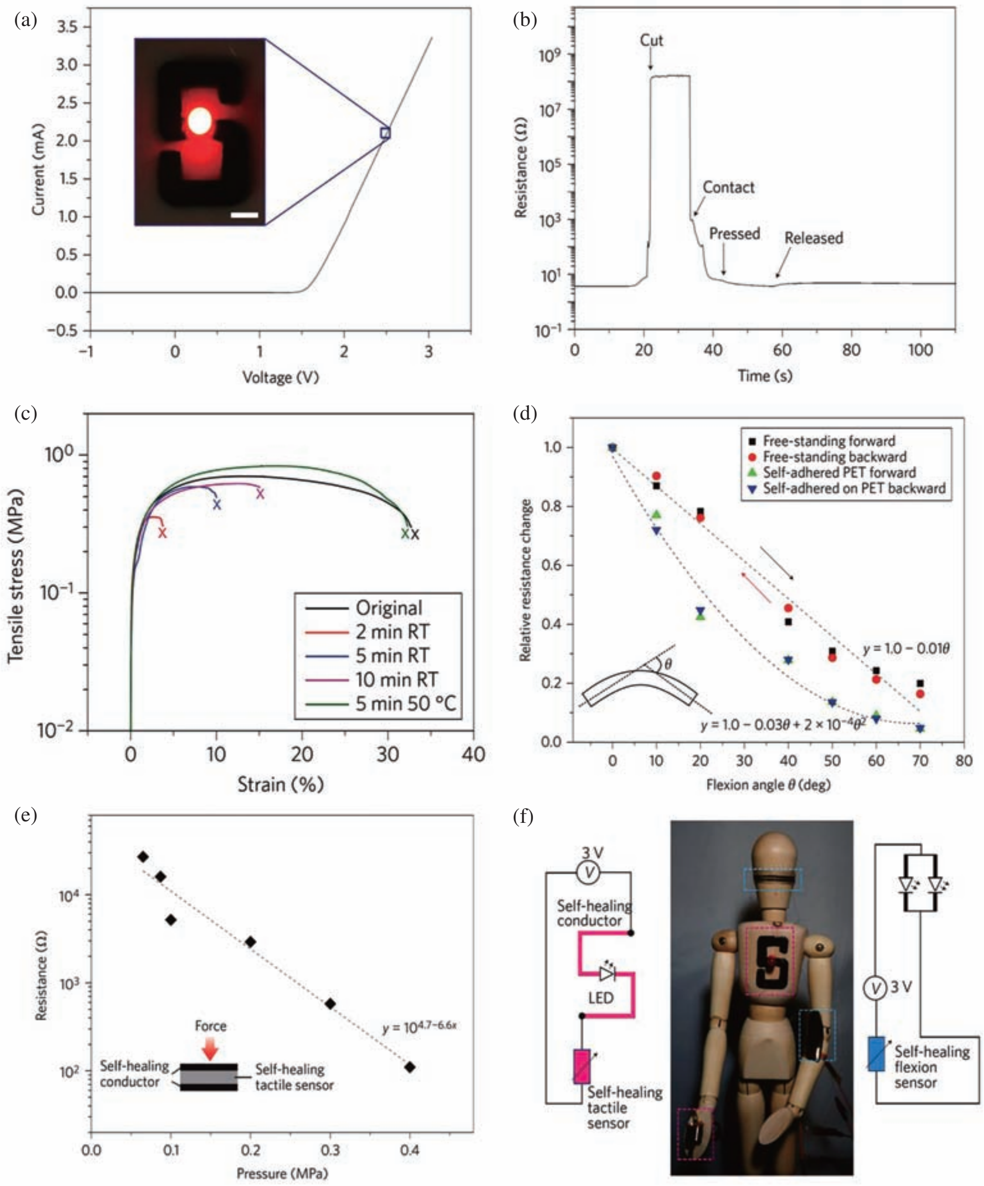

图 3 (网络版彩图) 基于 μNi/L 复合材料的自修复压阻式力学传感器[14]. (a) 以 μNi/L 复合材料为导线的商用 LED 的电流 – 电压曲线, 插图为电路在 2.5 伏电压下的光学照片 (比例尺, 10 mm); (b) 和 (c) μNi/L 复合材料 (b) 电学和 (c) 力学自修复性能; (d) 基于自支撑 μNi/L 薄膜以及粘附在聚对苯二甲酸乙二酯 (PET) 衬底上的 μNi/L 薄膜的弯曲传感器的电学响应; (e) 平板结构触觉传感器的电学响应及其线性拟合, 插图为传感器的结构示意图; (f) 基于 μNi/L 复合材料的自修复传感器电路示意图以及肘部和掌部分别贴附了弯曲传感器和触觉传感器电路的铰接式木质机器人的光学照片

Figure 3 (Color online) Self-healing piezoresistive force sensor based on μNi/L composite[14] @Copyright 2012 Springer Nature. (a) Current-voltage curve of a commercial LED using self-healing μNi/L composite as conducting wire. Inset: optical photograph of the circuit taken at 2.5 V (scale bar, 10 mm). (b) and (c) Self-healing of the (b) electrical and (c) mechanical performance of μNi/L composite. (d) Electrical response of the flexion sensors based on μNi/L composite in free-standing modes and self-adhered modes on PET substrate. (e) Electrical response of the parallel-plate structured tactile sensor based on μNi/L composite. (f) Self-healing flexion and tactile sensor circuit schematic and the optical photograph of a fully articulated wooden mannequin with its elbow and palm region mounted with the flexion and tactile sensor circuits

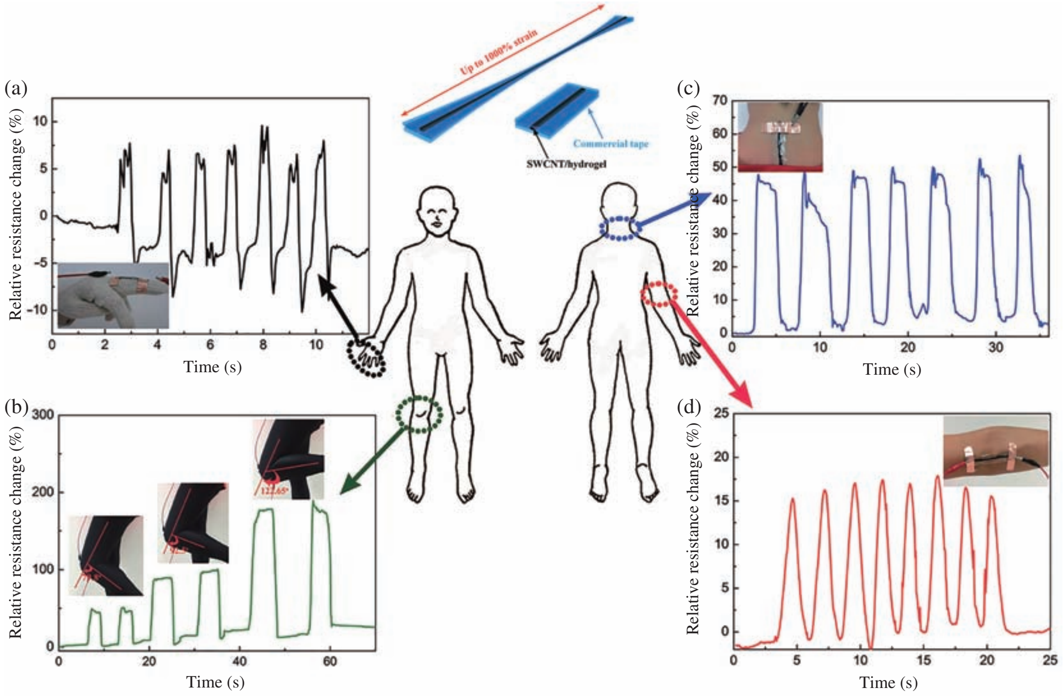

图 4 (网络版彩图) 基于自修复 SWNT/PVA-borax 凝胶复合材料的超弹性应变传感器对人体活动的实时监测[78]. (a) 手指屈伸运动; (b) 膝盖弯曲运动; (c) 颈部屈伸运动; (d) 肘关节屈伸运动

Figure 4 (Color online) Real-time monitoring of human motions using the superelastic strain sensor based on self-healing SWNT/PVA-borax hydrogel composite[78]. (a) Bending and release of the finger; (b) bending of the knee; (c) bending and release of the neck; (d) bending and release of the elbow

应用前景[93~96], 近年来, 关于自修复柔性电化学传感器的研究日益增加[21,22,97~99]. 最简单的方法是将纳米金属薄膜、碳纳米管等敏感材料沉积在自修复柔性衬底上实现电阻型柔性自修复电化学传感器, 例如, Chen 等[21] 将 MWNT 导电网络沉积在聚电解质多层薄膜 (PEM) 衬底上制备了自修复柔性气体传感器 (图 7(a)). PEM 由氢键和静电相互作用连接, 在水滴作用下 30 分钟后可以实现自修复 (图 7(b) 和 (e)). MWNTs 由羟基、羰基、环氧基等含氧官能团修饰, 与 PEM 表面的胺基之间存在氢键和静电相互作用, 使得 MWNTs 能够随着 PEM 的运动重新接触, 从而实现电性能自修复. 该自修复柔性传感器对 NH_3 有较好的检测性能. 室温下可检测 5~100 ppm 的 NH_3, 并且在受到多次损伤并进行自修复后灵敏度变化不大 (图 7(f) 和 (g)). 该传感器结构简单、透光性好, 但是检测限较高而灵敏度较低. Katz 等[97] 以自修复聚甲基丙烯酸羟乙酯/聚乙撑二胺混合聚合物 (PHPMA/PEI 1:1) 为介质层、炭黑为栅电极制备了自修复有机场效应晶体管 (OFET). PHPMA/PEI 介质层在室温下十几分钟内可实现力学性能的完全修复, 而炭黑珊电极电性能需要经过较长时间 (约 1000 分钟) 来实现自修复, 并且电阻率比初始值略有增加 (从 4.5 $\Omega\cdot$cm 增大到 36 $\Omega\cdot$cm), 尽管如此, 源电流仍可修复到初始值的 76% (栅压为 -5 V). 该自修复 OFET 可以作为自修复柔性电化学传感器用于 NH_3 检测, 其检测限低至 0.5 ppm. OFET 是印刷电子中常用的器件结构, 在柔性电子器件、大规模和超大规模集成电路中具有重要的应用[100,101]. 然而, 目前文献报道的研究工作大多只能实现 OFET 介质层的自修复[102,103], Katz 等首次实现了 OFET 中介质层和栅电极层的自主修复, 是构建完全自修复印刷电子器件研究中的一大进步.

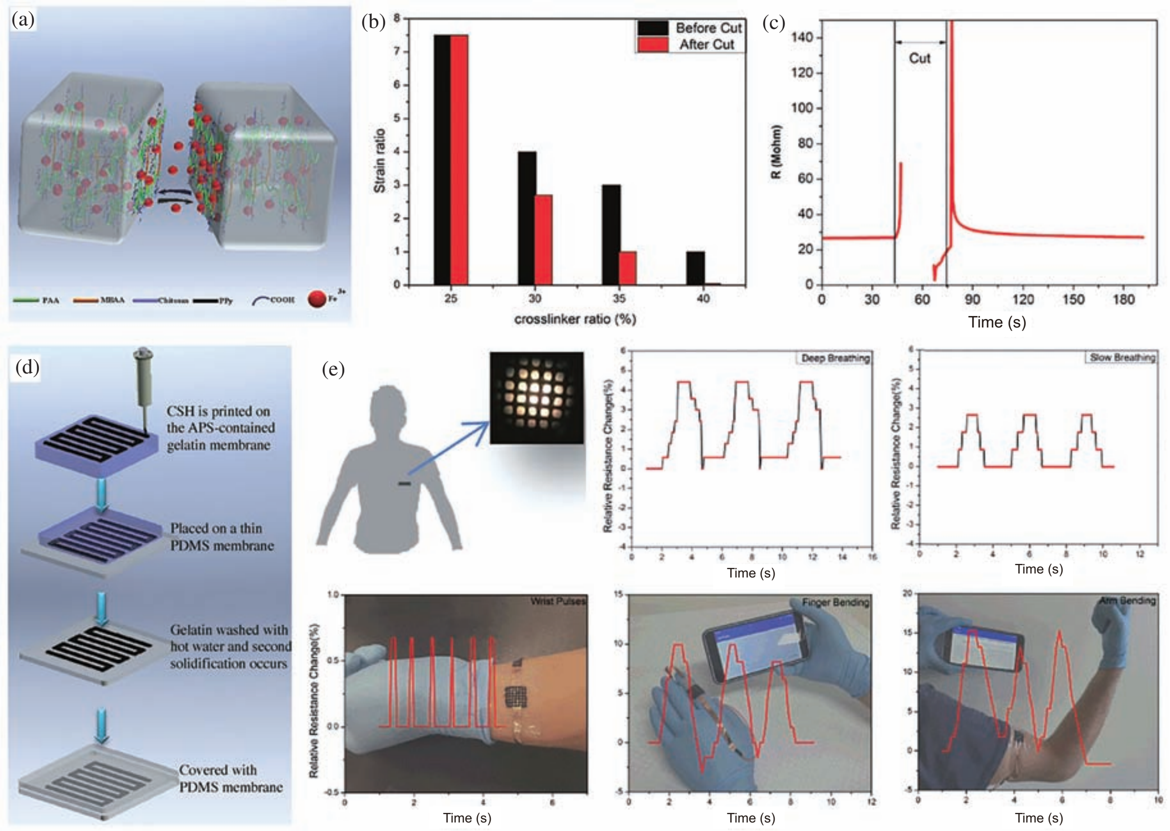

图 5 (网络版彩图) 基于导电聚合物的自修复压阻式应力/应变传感器[15]. (a) 自修复机制示意图; (b) 力学性能自修复效率; (c) 电学自修复性能; (d) 3D 打印法制备可穿戴传感器过程示意图; (e) 基于可穿戴传感器和智能手机的人体活动实时监测系统

Figure 5 (Color online) Self-healing piezoresistive stress/strain sensor based on conductive polymer[15] @Copyright 2017 John Wiley and Sons. (a) Schematic of the self-healing mechanism; (b) self-healing efficiency of mechanical property; (c) electrical self-healing property; (d) schematic of the preparation of wearable sensor via 3D printing technique; (e) real-time human motion monitoring system based on the wearable sensor and smart phone

3.3 自修复柔性多功能传感器

多功能化是智能传感器的发展趋势, 也是实现器件小型化的有效途径之一. 最近, Haick 等[22] 基于自修复聚氨酯 (PU) 衬底、自修复聚氨酯/银微粒 (PU/μAg) 复合材料电极、有机分子修饰的金纳米颗粒 (AuNP) 薄膜敏感层制备了自修复柔性多功能传感器, 可以实现对应力/应变、温度和挥发性有机物 (volatile organic compound, VOC) 正辛醇的检测 (图 8). 柔性 PU 衬底依靠内部的动态二硫键和氢键实现自修复: 对于 150 μm 宽的裂纹, 在室温下经过 16 小时可自主修复 (图 8(b1)~(b4)); 当 PU 完全断裂时, 其力学性能在室温下 48 小时内可修复 90%. 将导电 μAg 颗粒引入 PU 二醇聚合物中, 当 μAg 的体积分数超过渗流阈值 (26%~30%) 时, PU/μAg 复合材料具有较好的导电性 (电导率为 0.7×10^5 S/m), 可以作为电极. 对于 100 μm 宽的裂纹, 在室温下经过 30 分钟可自主修复 (图 8(c1)~(c4)). 在自修复 PU/μAg 电极之间沉积 AuNP 薄膜, 当 PU 衬底实现自修复时, AuNP 之间重新接触, 实现电学性能的修复 (图 8(d1)~(d4)). 当衬底弯曲/拉伸、环境气氛变化或者温度变化时, AuNP 薄膜的电阻会发生变化, 从而实现对应力/应变、环境气氛或温度的检测 (图 8(e)~(h)).

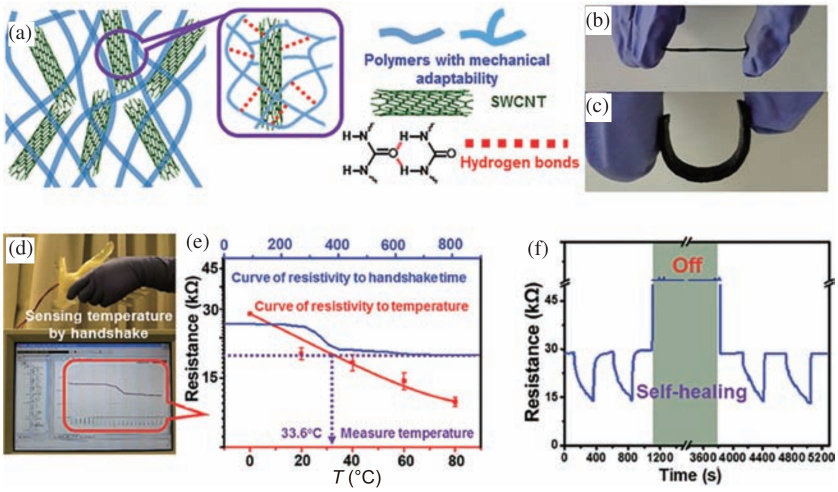

图 6　(网络版彩图) SWNT/L 复合材料 [91]. (a) 结构示意图; (b) 和 (c) 光学照片; (d) 和 (e) 温度传感性能及测试光学照片; (f) 电学自修复性能

Figure 6　(Color online) SWNT/L composite [91] @Copyright 2016 John Wiley and Sons. (a) Schematic of the structure; (b) and (c) optical photographs; (d) and (e) temperature sensing performance and the optical photographs showing the measurement procedure; (f) electrical self-healing performance

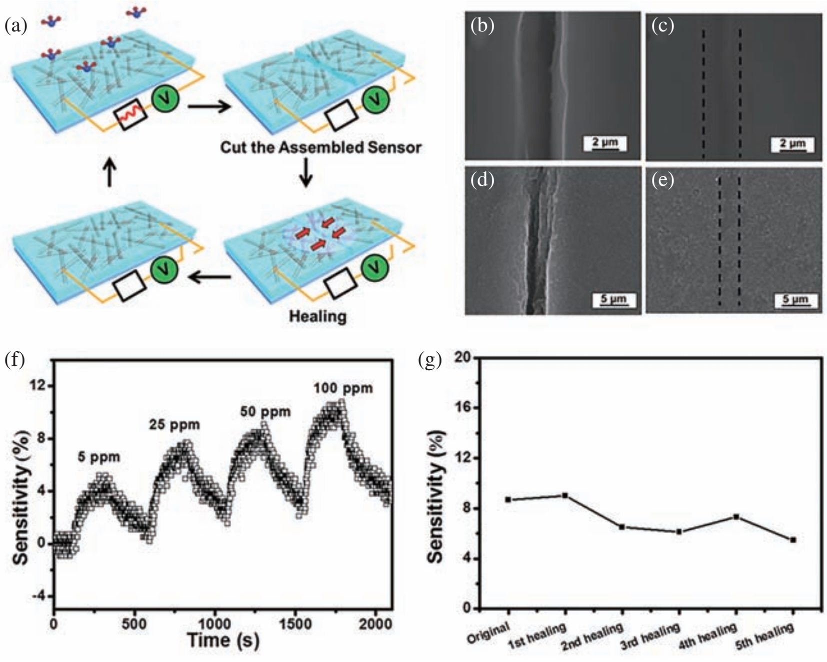

图 7　(网络版彩图) 基于 MWNT/PEM 复合薄膜的自修复柔性气体传感器 [21]. (a) 自修复过程示意图; (b)～(e) 裂纹在自修复前后的微观形貌; (f) 对 NH_3 的检测性能; (g) 多次自修复后对 25 ppm NH_3 的检测性能

Figure 7　(Color online) Self-healable flexible gas sensor based on MWNT/PEM composite film [21] @Copyright 2015 John Wiley and Sons. (a) Schematic showing the self-healing procedure of the gas sensor; (b)–(e) SEM images of MWNT/PEM film with a cut before and after being healed; (f) electrical self-healing property; (g) the sensing sensitivity of MWNT/PEM film to 25 ppm NH_3 after healing for different times

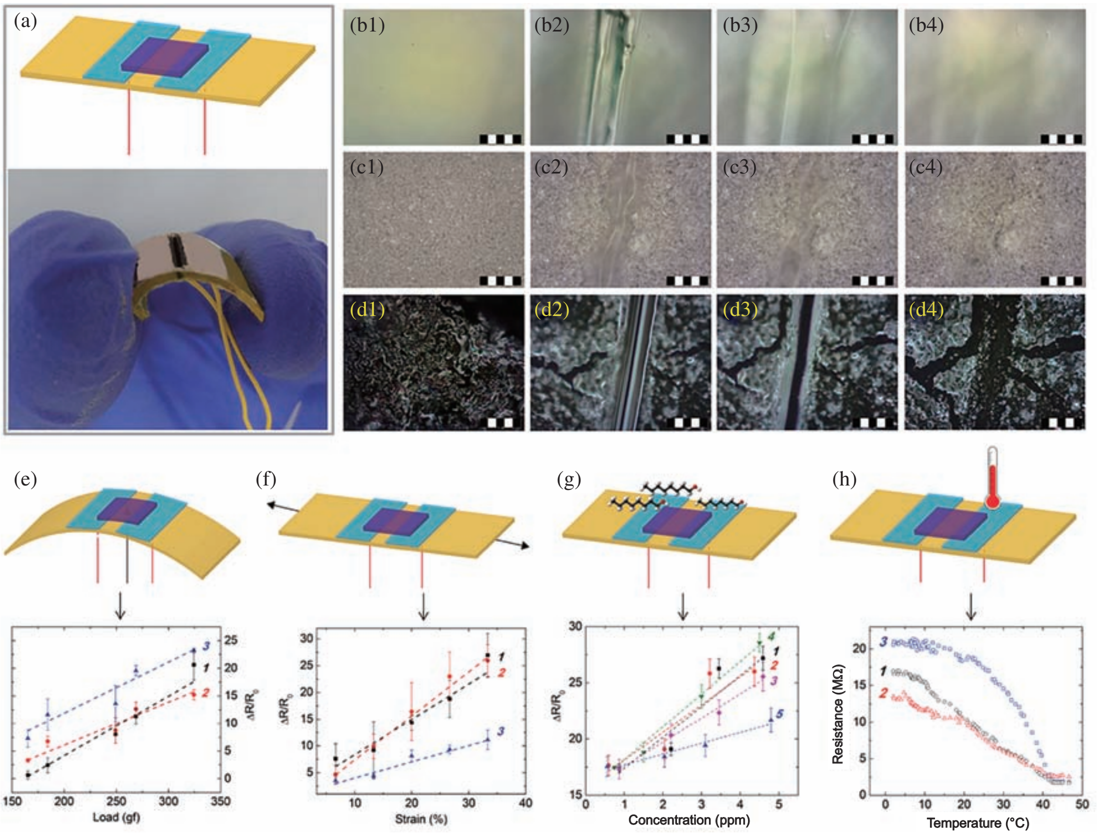

图 8 (网络版彩图) 自修复柔性多功能传感器 [22]. (a) 器件结构示意图及光学照片; (b1)~(b4) PU 衬底自修复过程的微观形貌; (c1)~(c4) PU/μAg 复合材料自修复过程的微观形貌; (d1)~(d4) AuNP 薄膜自修复过程的微观形貌; (e) 器件对弯曲形变的电学响应; (f) 器件对拉伸形变的电学响应; (g) 器件对 VOC 正辛醇的电学响应; (h) 器件对温度变化的电学响应

Figure 8 (Color online) Self-healing flexible multifunctional sensor [22] @Copyright 2015 John Wiley and Sons. (a) Schematic of the device structure and its optical photograph; SEM images of the microstructure of (b1)–(b4) PU substrate, (c1)–(c4) PU/μAg composite, and (d1)–(d4) AuNP film with a cut showing the self-healing procedure; (e) electrical response to bending deformation; (f) electrical response to stretching deformation; (g) electrical response to VOC n-octanol; (h) electrical response to temperature variation

在该工作的基础上 Haick 等 [98] 采用 5 种不同的有机小分子对 AuNP 薄膜进行功能化, 同样以自修复 PU/μAg 作为电极, 在自修复 PU 衬底上制备了多个传感模块, 实现了对压力及正常人体呼吸/皮肤中产生的十一种挥发性有机物代谢产物的检测, 有希望用于人体健康监测 (图 9). Haick 等的工作没有排除人体呼吸/皮肤中水分子的影响, 相应地, 未来用于人体健康监测的传感器系统需要集成水分子含量或湿度检测传感器, 并需要集成相关柔性电路以实现各传感器的独立及协同工作.

4 结论与展望

自修复功能对于增强柔性电子材料与设备的可靠性、耐用性和功能性具有重要的意义. 这篇文章总结了本征型和外援型自修复聚合物及柔性自修复导电材料的研究进展; 总结并讨论了柔性自修复应力/应变传感器、温度传感器和电化学传感器的构建方法、传感和自修复性能, 以及在可穿戴电子领域

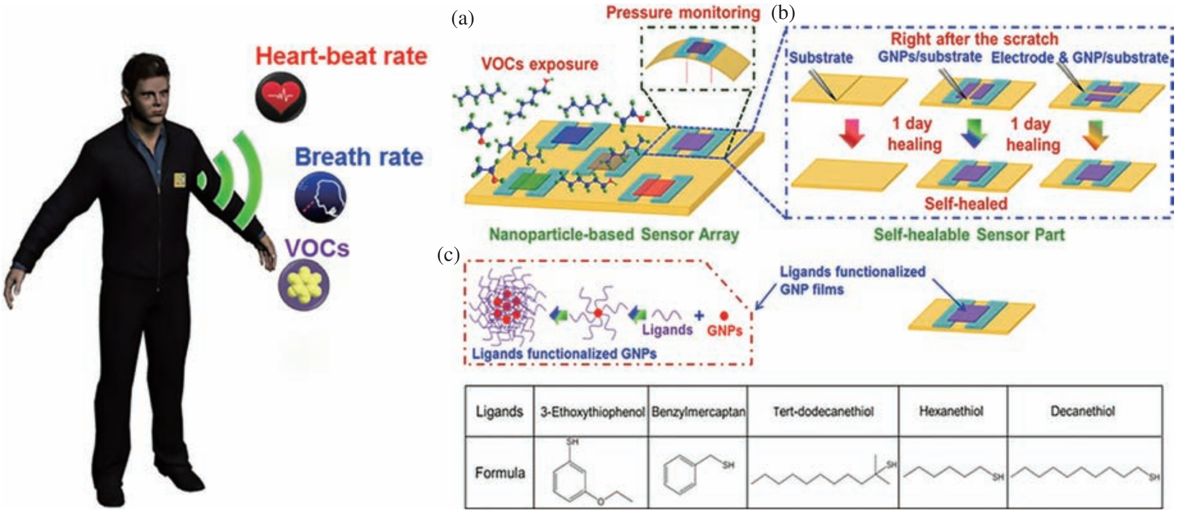

图 9　(网络版彩图) 面向人体健康监测应用的自修复柔性多功能传感器整体实验策略示意图 [98]. (a) 结构示意图; (b) 功能化 AuNP 的分子结构示意图; (c) 3 种损伤模式下传感器的自修复演示

Figure 9　(Color online) The overall experimental strategy relating to the flexible self-healable multifunctional sensor for human health monitoring application [98] @Copyright 2016 American Chemical Society. (a) Schematic of the structure; (b) schematic of the molecular structure used for the functionalization of AuNP; (c) demonstration of the self-heal of the sensor under 3 different damage modes

的应用. 目前, 柔性自修复材料及传感器件的发展仍处于早期阶段, 未来仍存在许多问题与挑战, 比如, 相对于无机金属及半导体材料来说, 柔性聚合物/复合材料的电学性能仍然较差, 柔性传感器件的可靠性、灵敏度、精确度等较差, 很难满足实际应用要求; 柔性传感器尺寸较大, 很难集成到电路板中. 这些也是柔性电子发展中的瓶颈问题 [4~6]. 现阶段, 纳米金属和半导体薄膜可以同时具有良好的柔性和优异的电学性能, 仍是柔性电子领域不可替代的功能材料和电极材料 [104~107]. 不足的是, 纳米金属和半导体薄膜的室温自修复还只能依靠自修复聚合物衬底来实现, 极大地限制了自修复柔性电子器件的发展. 针对上述问题, 未来应致力于提高自修复柔性聚合物及其复合材料的电学性能, 并着重发展实现纳米金属和半导体薄膜本征自修复的方法. 在柔性电子器件方面, 快速/反复自修复、器件小型化、多功能化以及生物相容性等仍是需要重点关注的问题, 其中, 3D 打印等先进加工技术将成为实现柔性自修复器件小型化的重要手段 [87,108,109].

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Recent advances in flexible self-healing materials and sensors

Ting ZHANG*, Yuanyuan BAI & Fuqin SUN

i-Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123*, China*
* Corresponding author. E-mail: tzhang2009@sinano.ac.cn

Abstract Endowing devices with the self-healing capacity is an effective approach to enhance their reliability, durability, and functionality, especially for flexible electronic materials and devices. This article reviews the developments in the field of flexible self-healing materials and sensors. This review first introduces the self-healing mechanism of intrinsic and extrinsic polymers, and the advances in self-healing flexible conductive materials are discussed briefly. Then, the fabrication techniques, sensing performance, and healing performance of the newly developed flexible self-healing sensors, especially the flexible self-healing force sensors, are described in detail. Finally, the existing challenges and some possible solutions for flexible self-healing materials and sensors are discussed.

Keywords self-healing, flexible electronics, wearable electronics, flexible sensors, flexible conductor

Ting ZHANG was born in 1978. He received the Ph.D. degree in chemical engineering from the University of California, Riverside, USA, in 2007. Currently, he is a professor at the Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences (CAS), Suzhou, China. In 2017, he was selected by the Jiangsu Natural Science Foundation as a distinguished young scientist. His research interests include nanomaterials and micro-/nano-sensors, flexible electronics, and micro-manufacturing technology.

Fuqin SUN was born in 1993. He received the B.S. degree in electronic information engineering from Qufu Normal University, China, in 2016. Currently, he is pursuing his M.S. degree in electronics science and technology from the University of Science and Technology of China. His research interests are in the area of flexible sensors, implantable materials, and devices.

Yuanyuan BAI was born in 1987. She received the Ph.D. degree in electronics science and technology from Xi'an Jiaotong University, China, in 2016. Currently, she is a post-doctoral research fellow at the Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences (CAS), Suzhou, China. Her research interest is in the area of flexible materials, sensors, and actuators.