功能化石墨烯材料在气体检测方面的应用研究进展

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摘　要　石墨烯是一种具有单原子层厚度的二维蜂窝状碳材料，由于其具有奇异的比表面积效应、光电效应和机械强度等优点，在能源、环境、军事和航天等领域得到了大量的研究。石墨烯材料的功能化可对其结构、物化性质和光电性质等方面进行有益调整，从而拓宽了其对化学物质的检测范围。主要综述了近期利用化学改性、纳米颗粒修饰和聚合物复合方法对石墨烯材料进行功能化改性的研究进展，以及功能化石墨烯材料在提高灵敏度和选择性等气体传感特性方面的应用，并对该领域存在的挑战和前景进行了展望。

关键词　石墨烯，改性，修饰，混合气体检测

Research progress of functional graphene material for gas-detecting application

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Abstract　Graphene，a two-dimensional carbon material only with a structure of honeycomb lattice which having a single-atom-thick layer，has attractive much research in many fields including energy，environment，military and aerospace，due to its fantastic properties of specific surface，photoelectric effect and mechanical strength. Functionalizing endows graphene favorable tailors such as the structure，physicochemical and photoelectrical properties，extending the detecting range of chemical species. It was discussed that the recent advancements in the functionalizing of graphene utilizing the methods of chemical modification，nanoparticle decoration and polymer hybrid，and the applications of functional graphene materials in improved gas sensing properties including sensitivity and selectivity. Finally，the remaining challenges and perspectives of this enticing field were provided.

Key words　grapheme，modification，decoration，hybrid gas-detecting

基于奇特纳米结构的传感单元可对极低浓度的物质进行超高灵敏专一性的检测、且对目标物显示出快速响应和恢复能力，还具有良好的可逆性等优点，因而为开发下一代高性能气体传感器提供了许多机会[1-2]。在纳米结构气体传感系统中，纳米碳材料由于对化学环境的变化显示出高灵敏性和稳定性等特性，在工业生产、环境监测和军事航天等领域显现出广泛的应用前景[3-7]。

石墨烯是一种碳原子以 sp^2 键合，具有单原子层厚度的二维蜂窝状碳材料。由于其拥有非常优异的热力学导电性、超大的比表面积和极大的机械强度等性质，基于石墨烯的传感器已经实现了对大量物质的检测[8-12]。近期，金属及其氧化物功能化的石墨烯由于协同效应显示出高载流子密度、超高稳定性和易与气态物质相互作用等优势，因而在气体传感器方面表现出应用潜力[13-15]。

最近，有研究综述了通过富电子或缺电子分子与石墨烯相互作用进行石墨烯功能化，然而关于功能化石墨烯材料在气体检测方面的报道却很少见[16-22]。鉴于该类材料在气体检测方面的研究兴趣持续增加，笔者主要综述了当前石墨烯材料在化学改性、纳米颗粒修饰和聚合物复合方面的功能化研究及其在检测气体分子，如 NO_2、NH_3、H_2、H_2S 和 CH_3COCH_3 等方面的应用，并对其在气体检测方面的应用前景进行了展望。

1　石墨烯材料功能化与应用

1.1　化学改性石墨烯材料及气体检测

石墨烯材料优秀的气体检测能力主要在于其能经受各种物理化学的环境变化，因此为了保持其电

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性能,同时要易于对其表面结构和化学性质进行调控,原子掺杂、分子浸渍和化学功能化等手段被大量用来开发高性能的石墨烯功能化气体传感器。

石墨烯材料的杂原子掺杂,如N、S、P、B等,目前已经进行了大量的研究应用[23-24]。杂原子掺杂使石墨烯表面活性点位增加,从而提高了目标气体分子吸附量,以致其光电性质产生了更加明显的变化。Niu等[24]通过对氧化石墨烯(GO)和三苯基磷的混合物进行高温退火处理,制备了P掺杂石墨烯高灵敏NH_3传感器。由于NH_3分子与P原子的相互作用,P掺杂石墨烯传感器具有更高的灵敏度、更短的响应和恢复时间。Lv等[25]用一种液体前驱物大面积制备了高质量的B掺杂石墨烯气体传感器,研究发现其对NO_2和NH_3不但具有良好的信噪比,而且相比P掺杂石墨烯传感器灵敏度分别提高了27和105倍。通过高温退火处理含有N和Si的GO和离子液体的混合物而制备的N、Si共掺杂石墨烯气体传感器被证实在NO_2气体中显示出阻抗减小的特性(21×10^{-6}浓度时减少约26%,1×10^{-6}浓度时减少约8.8%),Niu等[26]研究发现N原子掺杂增加了CO_2分子的吸附点位,Si原子掺杂改变了石墨烯的电子排列。最近,Su等[27]使用半胱胺盐改性,制备了还原氧化石墨烯(rGO)-金薄膜电极。相比化学气相沉积法制备的石墨烯传感器,利用该薄膜构造的NO_2气体传感器具有更高的灵敏度。Yoo等[28]利用鞣酸对GO进行功能化和还原,制造了对NH_3检测具有高选择性的气体传感器。相对CH_3CH_2OH等有机分子,NH_3具有较强的还原性,因而传感器表现出更加明显的阻抗变化。

1.2 金属纳米颗粒-石墨烯修饰材料及气体检测

石墨烯作为一种P型半导体,被吸附气体分子电子效应的不同将诱导其电导率产生差异。虽然基于石墨烯的气体传感器具有较高的灵敏度,但在面对组成复杂的样品时却暴露了低选择性的缺点。金属和金属氧化物颗粒功能化的石墨烯,由于相互协同效应作用对混合材料电子性质的调节,成为潜力较大的增强气体灵敏度和选择性的传感材料[29-36]。

Kaniyoor等[29]开发了Pt等贵金属修饰的石墨烯气体传感器,发现在对空气中H_2(含量为4%,wt,质量分数,下同)进行检测时,Pt-石墨烯传感器比Pt-多壁碳纳米管传感器在灵敏度方面提高了2个数量级。Chung等[32]研究了纳米Pd颗粒修饰石墨烯传感器在室温下对H_2的传感特性,发现更低功函数氢化钯的形成增加了电子从Pd向石墨烯的转移,从而展现出更加灵敏的阻抗变化。Pak等[33]使用Pd修饰石墨烯传感器实现了对H_2的检测,由于H_2分子快速吸脱附,该传感器在1000×10^{-6}浓度H_2下90%的响应时间为60s,同时在N_2环境中80%的恢复时间为90s。Li等[30]采用交流双电泳方法开发的Pd修饰rGO实现了对NO气体的高灵敏检测,在室温下检测范围为$2\times10^{-9}\sim420\times10^{-9}$,在检出下限时恢复时间约为1000s。Gutes等[31]利用还原电势不同制备了贵金属功能化的石墨烯气体传感器,其中Pt-石墨烯传感器由于较强的S—Pt键而恢复时间较长。采用蚀刻印刷技术,Huang等[37]制备了Ag纳米颗粒修饰的磺酸化石墨烯,在50×10^{-6}浓度NO_2气体中室温下74.6%的响应时间为12s,恢复时间为20s,同时由于该材料机械强度高和质量轻等特点而有望实现对NO_2的在线监测。

虽然金属氧化物具有优异的气体传感特性,然而操作温度高和选择性低等缺点限制了其实际应用,但是与石墨烯材料复合后产生的协同作用却对气体分子选择性和灵敏度有了非常大的提高。通过密度泛函理论计算,Mohammadi-Manesh等[38]对室温下H_2S气体分子在纯石墨烯片、Cu-石墨烯片和CuO-石墨烯片上的吸附机理、态密度和电荷分布以及电导率进行分析,研究发现CuO-石墨烯传感器对H_2S气体检测具有更高的灵敏度。Bai等[39]使用原位微波热处理方法制备了WO_3功能化的rGO气体传感器,WO_3-rGO异质界面的相互协同作用赋予了该材料表面更多的电子和更快的电子迁移速度,因而在110℃下对10^{-6}浓度级的H_2S气体表现出更优的灵敏度和选择性、更短的响应和恢复时间。利用Cu_2O表面对H_2S分子的高活性吸附和石墨烯的高效电子转移作用,Zhou等[13]使用室温下稳定的Cu_2O功能化石墨烯片对H_2S进行了测定。相比于H_2、CH_4和NH_3等气体分子,该材料对H_2S的灵敏度增加了至少5倍。Mao等[34]设计了SnO_2-rGO气体传感平台,发现其在1%浓度NH_3和100×10^{-6}浓度NO_2混合气体中对NO_2有较强的传感特性(相比单独rGO材料,NO_2灵敏度提高30%以上)。Liu等[35]在GO上原位生长ZnO后再化学还原GO,发现在相同浓度(5×10^{-6})的NO、CO和Cl_2中,该材料对NO_2显示出优异的灵敏度与选择性以及更短的响应和恢复时间。采用微波辅助加热和退火处理两步工艺,Meng等[40]利用Cu_2O纳米棒修饰的石墨烯材料实现了对NH_3的检测,相

对较大的比表面积、较高的电导率和气体吸附性能是高灵敏度、快速响应与恢复的重要保障。最近,石墨烯基三元功能化材料作为气体传感材料也得到了大量研究和探索。Wang 等[41]利用水热法制备了 CuO-ZnO/石墨烯复合材料,发现由于 CuO 和 ZnO 之间在石墨烯表面存在大规模的纳米 p-n 结,该材料对 CH_3COCH_3 分子表现出较高的灵敏度和选择性。Cui 等[42]在低温下制备了 In 掺杂 SnO_2 修饰的石墨烯传感器,研究揭示 In 掺杂诱导了在 SnO_2 纳米晶表面产生更多的氧离子族物质,从而增加了 NO_2 分子吸附量,提高了灵敏度和选择性。

1.3　聚合物-石墨烯复合材料及气体检测

自从发现碳纳米管和导电聚苯胺(PANI)能提高气体传感性能后,聚合物-石墨烯气体传感材料得到了大量研究[43-44]。Huang 等[45]用 PANI 修饰的 rGO 气体传感器对 NH_3 进行检测,发现相对于单独石墨烯和 PANI 传感器,在 NH_3 浓度 50×10^{-6} 时灵敏度分别提高了 10.4 和 3.5 倍,rGO 片和 PANI 纳米粒子间的联合作用提高了传感器的灵敏度、选择性和稳定性。Parmar 等[46]在不同温度下比较了 PANI 和 PANI-石墨烯薄膜对甲苯分子的传感性能,发现在 50℃下 PANI-石墨烯薄膜整体显示出了更短的响应时间和更快的恢复能力。利用石墨烯和聚 3-己基噻吩混合材料优异的表面形貌和电子 π-π 堆积作用,Ye 等[47]实现了对 NH_3 的检测,相比单独石墨烯材料的灵敏度提高了约 30%,响应时间减少了 75%,恢复时间缩短了 20%。Xie 等[48]制备了聚 3-己基噻吩-石墨烯气体传感器,利用石墨烯二维材料比表面积大、石墨化碳原子对 NO_2 分子的吸附特点以及聚 3-己基噻吩膜对 NH_3、SO_2、CO、CO_2 和 H_2S 分子的选择性过滤,实现了 NO_2 高灵敏度检测。

Mishra 等[49]依次在光纤上包覆了一层 Cu 膜、聚甲基丙烯酸甲酯层和聚甲基丙烯酸甲酯与石墨烯混合材料,制备了表面等离子体共振的光纤气体传感器,对 NH_3 测试发现其共振波长发生了红移,表现出高灵敏度、高再现性和检测范围宽等优点。Hong 等[50]在 Pd 修饰的石墨烯材料上包覆了一层聚甲基丙烯酸甲酯膜,发现由于该膜对 CO、NO_2 或 CH_4 分子的选择性过滤,在对 2%浓度 H_2 检测时该材料 66.37%的响应时间为 1.81min,恢复时间为 5.52min。利用石墨烯高比表面积和聚 3,4-乙烯二氧噻吩多孔导电聚合物在石墨烯表面分布均匀的特点,Yang 等[51]制备了聚 3,4-乙烯二氧噻吩-rGO 传感器对 10^{-9}浓度 NH_3 实现了高灵敏度和选择性检测。Seekaew 等[52]采用喷墨打印技术开发了聚 3,4-乙烯二氧噻吩和聚苯乙烯磺酸盐修饰石墨烯气体传感器,由于石墨烯材料比表面积效应和 π 电子网络作用,对 NH_3 检测具有较高的选择性和灵敏度。

2　结语与展望

全球日益严重的环境问题促使全世界科学家们不断探索新型高效的气体传感技术,以实现对各种气体物质的监测。石墨烯材料独特的二维结构带来巨大的比表面积效应和超高的电导率,在气体传感器方面得到了较大的应用。通过不同物质间的协同效应,化学掺杂、金属、金属氧化物和聚合物功能化石墨烯气敏材料在选择性和灵敏度等方面显示出更优异的性能。但是目前功能化石墨烯气体传感材料还存在以下几方面的问题有待进一步研究:(1)石墨烯结构和组成的微观刻意调控值得进一步探索;(2)需进一步深入研究目标分子与石墨烯材料、石墨烯材料各组分界面间的作用机理,以开发具有更高检测性能的传感器;(3)使用密度泛函等理论计算工具,寻找更多种类的石墨烯功能化材料,设计开发满足高选择性、低检测浓度和使用环境广泛的气体传感器。

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