超临界流体协助制备石墨烯及其功能化研究

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摘要 石墨烯, 即单层石墨, 具有独特的二维结构和优异的机械、热学以及电学性质, 自其被发现以来已引起了众多领域研究者的关注. 本文介绍了石墨烯的制备及其功能化的方法, 尤其对利用超临界流体辅助的液相剥离法制备石墨烯进行了详细阐述, 突出介绍了苈基聚合物、苈基小分子衍生物在超临界二氧化碳辅助条件下剥离制备石墨烯及其功能化研究, 并对所制备功能化石墨烯在聚合物基质增强和甲醇燃料电池中的应用研究进行了评述.

关键词

石墨烯
液相剥离
超临界流体
苈基衍生物
燃料电池

石墨烯是由 sp^2 杂化的碳原子以六元环周期排列组成的二维蜂窝状点阵结构, 其厚度仅0.35 nm, 是目前已知二维晶体材料中最薄的一种^[1,2]. 石墨烯的发现, 极大丰富了石墨碳材料家族, 完善了从零维的富勒烯到一维的碳纳米管、二维的石墨烯和三维的石墨完整的体系.

石墨烯的二维结构赋予了其丰富而奇特的现象, 使其表现出众多优良的物理化学性质^[3~6], 如硬度比钻石还高, 强度优于世界上最好的钢铁100倍, 相应的杨氏模量高达1.0 TPa, 断裂强度高达130 GPa. 由于石墨烯内部的大 π 键结构, 使得电子能够在长程离域共轭的表面自由移动, 赋予了石墨烯优异的电学性能. Morozov等人^[4]研究表明, 结构完善的石墨烯中载流子迁移速率可高达 $200000\text{ cm}^2/(\text{V s})$, 优于传统的硅片10倍以上; Balandin等人^[6]首次实验测量了单层石墨烯的热导率, 发现室温下石墨烯的热导率高达 $5300\text{ W}/(\text{m K})$, 明显优于碳纳米管, 是铜热导率的10倍. 除了优异的机械性质、电学性质和热学性质外, 石墨烯同时还具有超常的比表面积(理论值高达 $2630\text{ m}^2/\text{g}$)^[2,7,8]、高透光率(97.7%)^[9]、量子隧道效应和永不消失的电导率等^[10], 这些独特性质引起了化学、物理、材料、生物以及电子领域众多研究者的广

泛关注^[8,11~15].

1 石墨烯的制备与功能化

1.1 石墨烯的制备

近年来有关石墨烯的制备已经取得了富有成效的进展, 其制备方法概括分为自下而上法(bottom-up approaches)和自上而下法(top-down approaches)2大类^[11,16]. 自下而上法, 主要是利用小分子来合成石墨烯, 如化学气相沉积法(chemical vapor deposition, CVD)^[17~23]、SiC外延生长法^[24~28]和有机合成方法^[29~31]. 其中利用CVD法可以获得大面积、高质量的石墨烯, 但是该方法难以实现规模化制备. 利用SiC外延生长同样可以获得大面积、高质量的石墨烯, 但是存在条件苛刻(高温、高真空)、单晶SiC价格昂贵以及石墨烯片难以从基底转移等缺点. 有机合成法常以芳香小分子为起始原料, 经精确的分子设计和严格的合成条件获得具有一定大小和结构的石墨烯, 是可控制备石墨烯的一种重要的方法. 此外还有电弧放电法^[32,33]、剪切碳纳米管法^[34,35]、表面活性剂自组装法^[36]以及还原CO法^[37]等.

自上而下法是利用物理或化学的方法剥离石墨

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及其衍生物来获得石墨烯,如微机械剥离法^[1,38]、还原氧化石墨烯(GO)法^[13,39-60]、直接液相剥离法^[61-70]等。石墨来源丰富、价格低廉,因此利用该类方法有望实现石墨烯的大规模、低成本制备。微机械剥离法最早是由石墨烯的发现者Novoselov等人^[1]在2004年发明的,该方法能够制备高质量大尺寸的石墨烯,且工艺简单,但是费时费力、产率低。氧化石墨烯还原法制备石墨烯,首先将石墨在强酸和强氧化剂作用下氧化得到氧化石墨,进而通过化学手段将氧化石墨烯还原成石墨烯^[13]。目前,制备氧化石墨的方法主要有3种:Hummers法^[71]、Brodie法^[72]和Staudenmaier法^[73]。其中Hummers法制备出的氧化石墨具有褶皱的片层结构,含氧官能团丰富,在水溶液中的分散性良好。氧化石墨层与层之间的碳原子上引入了大量含氧官能团,其层间距明显增大,层间相互作用力减弱,使得氧化石墨很容易在溶剂中剥离为单层氧化石墨烯。但由于氧化石墨烯含有大量含氧官能团,其共轭结构遭到明显破坏,因此,通过氧化还原方法制备的石墨烯不能用于对石墨烯质量要求较高的电子领域。另外,在利用该方法大量制备石墨烯的过程中容易带来废液污染,肼等还原剂有毒,且易燃易爆,不利于安全生产。

直接溶剂剥离法的原理是将石墨或膨胀石墨分散于特定溶剂中,形成低浓度的分散液,然后利用超声波的剪切空化作用破坏石墨层间的范德华力,将石墨烯从石墨块体上剥离下来。Coleman课题组^[61,64-66,68]首先报道了溶剂剥离制备石墨烯的方法,并进一步研究了溶剂剥离制备石墨烯的影响因素。参照溶剂剥离碳纳米管的方法,首先将石墨粉分散在*N*-甲基-吡咯烷酮(NMP)中,经超声、离心分离后制得单层及少层石墨烯^[62]。研究表明,当溶剂的表面能与石墨烯表面能相匹配时,溶剂与石墨烯之间的相互作用可以平衡剥离石墨烯所需的能量,能够较好地剥离石墨烯的溶剂表面张力为40~50 mJ/m²。对溶剂参数进一步分析发现,剥离石墨的良溶剂需要与Hansen溶解度参数相匹配(色散力溶解参数 δ_D ,极性力溶解参数 δ_P ,氢键结合力溶解参数 δ_H), δ_D ~18.0 MPa^{1/2}, δ_P ~9.3 MPa^{1/2}和 δ_H ~7.7 MPa^{1/2}^[65]。对比研究表明,能够较好底剥离石墨的良溶剂有NMP, *N,N*-二甲基甲酰胺(DMF)等。Hamilton等人^[69]将不同品种的石墨原料(微晶石墨、膨胀石墨、高取向裂解石墨)分散在非极性的邻二氯苯(ODCB)中,经超声、离心分离

后得到了结构完善的非功能化石烯的邻二氯苯溶液,实现了石墨烯在非极性介质中的分散,为石墨烯进一步的功能化及应用开辟了道路。Dhakate等人^[74]同样以膨胀石墨为原料,通过对膨胀石墨进行二次插层处理,经超声剥离,得到了大面积单层或双层石墨烯,产率约为4%~5%(质量百分数,下同)。

与石墨烯结构类似,多环芳烃同样含有大 π 共轭结构,可以通过 π - π 相互作用稳定吸附于石墨烯的表面。An等人^[75]将石墨分散在茚甲酸的甲醇与水的混合溶液中,经超声剥离得到了茚甲酸非共价功能化的单层及多层石墨烯的稳定水溶液。研究表明,茚甲酸通过 π - π 相互作用吸附在石墨烯表面,同时茚甲酸上所带的羧基伸出石墨平面外,使得石墨烯能稳定存在于水溶液中。通过向甲醇溶液中添加水能够提高混合溶剂体系的极性,使得茚甲酸在溶液中的溶解度降低,倾向于向性质相似的石墨片层内部移动,此时,茚甲酸就像“分子楔”一样,楔入石墨片层内部剥离石墨(图1)。

1.2 石墨烯的功能化

结构完整的石墨烯表面呈惰性,与其他物质的相互作用较弱,并且石墨烯片层之间存在一定的范德华力,容易聚集,这给石墨烯的进一步研究和应用造成了很多困难。为了提高石墨烯在溶液和基体中的分散性,必须对石墨烯进行适当的修饰。功能化恰是实现石墨烯分散、溶解和成型加工的重要手段。目前,石墨烯的功能化主要分为共价键功能化和非共价键功能化。

1.2.1 共价键功能化

在氧化石墨烯和化学还原的石墨烯表面存在大量的含氧活性官能团,如羟基、羧基、环氧官能团等,Veca等人^[76]通过石墨烯表面上的羧基与聚乙烯醇(PVA)分子链上的羟基之间发生酯化反应,实现了PVA对石墨烯片的共价键功能化。PVA功能化的石墨烯在水相和有机溶剂实现了良好的分散。

1.2.2 非共价键功能化

石墨烯的非共价键功能化主要通过 π - π 相互作用、氢键作用以及聚合物和表面活性剂包覆物理吸附来实现。含有大共轭 π 结构的芳香族小分子^[77,78]以及含有共轭聚合物主要通过 π - π 相互作用实现对石墨烯的非共价键修饰。在非共价修饰中,通过聚合物等大分子的包覆也是实现石墨烯溶解性和稳定性的重

图1 (网络版彩色)(a) 芘甲酸的分子结构. (b) 芘甲酸在石墨表面形成稳定的 π - π 相互作用. (c) 在极性介质水和震动条件下, 芘甲酸分子向石墨层间渗入的示意图. (d) 单层或少层石墨烯与石墨的分离^[75]

Figure 1 (Color online) (a) Molecular structure of 1-pyrenecarboxylic acid. (b) A PCA molecule can form a stable π -stacking bond with graphitic surfaces. (c) Schematic illustration of the penetration of 1-pyrenecarboxylic acid into the layers of graphite in a polar medium (H_2O) and with agitation. (d) The separation of single, double, or few-layer graphene flakes from graphite^[75]

要方法.

在氧化石墨烯还原过程中, 随着石墨烯共轭结构的恢复, 其疏水性增加, 因此还原后的石墨烯很容易团聚析出. 为提高还原后石墨烯的分散稳定性, Xu等人^[77]向氧化石墨烯水溶液中添加芘丁酸(PB), 然后在碱性环境下利用肼还原即得到了PB-非共价修饰的石墨烯稳定分散的水溶液(图S1), 石墨烯片之间由于静电排斥的作用而相互排斥. 通过对所得物质的吸收和荧光光谱分析得出芘丁酸与石墨烯通过 π - π 作用结合, 对比没有添加芘丁酸的体系发现还原后的石墨烯发生明显聚集析出(图S1).

在非共价修饰中, 通过聚合物等大分子的包覆也是实现石墨烯溶解性和稳定性的重要方法. Li等人^[79]利用聚[(间苯乙炔)-共聚-(2,5-二辛氧基对苯乙炔)](PmPV)与石墨烯之间的 π - π 作用, 制备了PmPV非共价修饰的石墨烯纳米带, 该纳米带在1,2-二氯乙烷(DCE)中分散良好. 对比实验表明, 没有添加PmPV聚合物的混合体系得不到石墨烯纳米带. 另外, Li等人^[80]还利用四丁基铵(TBA)对酸插层的可膨胀石墨再次进行插层处理, 然后分散在溶有磷脂-聚

乙二醇(DSPE-mPEG)的水溶液中, 经超声剥离得到了在水溶液中均匀分散的DSPE-mPEG包覆石墨烯. 将DSPE-mPEG修饰的石墨烯从水溶液中离心分离出来能再分散到其他的有机溶剂中, 如DMF(图S2).

Qi等人^[81]利用一种双亲性圈-棒-圈结构的共轭三嵌段共聚物PEG-OPE(结构如图S3(a)所示)为稳定剂修饰还原氧化石墨烯. PEG-OPE中共轭的刚性棒通过 π - π 作用附着于还原氧化石墨烯表面, 亲脂的侧链以及亲水的环则伸出石墨烯表面外, 形成双亲性的外层, 利于石墨烯在低极性的有机溶剂以及水溶性的高极性有机溶剂中的分散.

2 超临界流体协助石墨烯的制备与功能化

2.1 超临界流体的性质

超临界流体(supercritical fluid, SCF)是指温度及压力均处于临界点以上的流体^[82](图2). 在超临界流体中液体与气体的分界消失, 超临界流体的物理性质兼具液体性质与气体性质, 其密度要比气体大2个数量级, 接近液体的密度; 黏度比液体小, 但扩散

图2 (网络版彩色)物质的相图^[82]

Figure 2 (Color online) The phase diagram of the substance^[82]

速度比液体快约2个数量级, 有较好的流动性和传质性能; 其介电常数随压力而急剧变化. 同时, 超临界流体也具有区别于气体和液体的特点: 在临界点附近, 流体的密度对温度和压力十分敏感, 尤其是压力, 微小的变化就能使流体的密度发生巨大的改变, 从而导致流体的多项性质, 如黏度、介电常数、扩散系数和溶解能力产生巨大改变. 因此, 通过调节压力和温度可以控制超临界流体的物理化学性质^[83]. 在众多超临界流体中, 超临界CO₂在实际生产和研究过程中使用的最多, 这是因为超临界CO₂除了具有高的扩散性和渗透性外, 还具有相对较低的临界值温度(304.1 K)和临界压力(7.38 MPa), 而且其化学性质不活泼、无毒、无臭、无味, 成本适中, 能够反复利用.

2.2 纯超临界流体剥离石墨烯的研究

超临界流体由于其低黏度、低表面张力、高扩散

系数和良好的表面润湿性, 使其成为向层状材料间浸润和膨胀的良溶剂^[84,85]. 超临界CO₂在层状材料剥离方面的应用已有相关报道^[84,86-88], 同时由于超临界CO₂对有机分子的溶解能力, 其也可以作为一种有效的“夹带剂”携带某些小分子渗入到材料内部, 实现层状材料的插层以及修饰^[88,89]. 最近的研究显示, 超临界流体可以帮助制备石墨烯, Rangappa等人^[90]报道了利用超临界流体(乙醇, NMP, DMF)一步剥离制备石墨烯的方法. 首先将石墨经超声均匀分散到相应的溶剂中, 然后将分散液置于高压反应釜中, 快速升温至超临界状态, 反应1 h后能获得90%~95%小于8层的石墨烯片, 其中单层石墨烯的含量占6%~10%(图3).

Liu等人^[91]首先利用超临界DMF对膨胀石墨进行剥离处理得到了少层石墨烯(few layer graphene, FG), 然后对FG再次超临界DMF处理, 经分离后即获得了单层石墨烯, 并研究了超临界流体条件对剥离效果的影响(图S4).

Pu等人^[86]报道了利用超临界CO₂气体插层石墨制备石墨烯的方法, 首先将石墨在超临界CO₂中浸润30 min, 然后将其在含有十二烷基磺酸钠(SDS)的水溶液中快速放气使石墨膨胀剥离, SDS能够阻止石墨烯片层的重新堆积. 该法所得石墨烯产率可达30%~40%, 具有操作简便、成本低的优点, 但是制备出的石墨烯片层较多(~10层). Jang等人^[92]在前期工作的基础上, 进一步利用超临界乙醇和茛磺酸钠(1-PSA)剥离石墨, 实现了石墨烯的一步法剥离和修饰. 茛磺酸钠不仅能够阻止石墨烯的重新聚集, 还有利于剥离的进行. 研究发现随着茛磺酸钠用量的增加, 石墨的剥离效率明显提高. 当茛磺酸钠与石墨的碳原子比为1:1时, 所得单层或双层石墨烯的产量可

图3 (网络版彩色)纯超临界流体剥离石墨制备石墨烯的过程示意图^[90]

Figure 3 (Color online) Scheme showing the SCF exfoliation of graphite crystals to graphene^[90]

达到60%(图S5)。

2.3 超临界流体复合体系剥离制备功能化的石墨烯

2.3.1 芘基聚合物体系制备功能化的石墨烯

含有共轭结构的多环芳香族物质能与共轭的石墨之间产生 π - π 相互作用,从而实现对石墨烯表面的修饰.本课题组^[89,93,94]以超临界 CO_2 为挟带剂,将芘基聚合物作为分子楔和改性剂来直接剥离和功能化石墨烯,从而得到了稳定分散的不同芘基聚合物修饰的石墨烯溶液.石墨的剥离是在溶剂、芘基聚合物以及超临界 CO_2 之间的多重相互作用下协同实现的.芘基聚合物剥离修饰石墨烯有以下几个优点:(1)赋予碳纳米材料独特的性能,如溶解性^[95]、刺激响应性^[96]和生物相容性^[97]等;(2)芘基聚合物连接的聚合物分子链可以与不同的聚合物本体有很好的相容性^[98],有利于作为聚合物复合材料的添加剂.采用2种具有不同分子量的芘基聚合物(pyrene-PEG和pyrene-PCL)来剥离制备石墨烯,根据芘基聚合物连接的聚合物分子链的

不同,将pyrene-PEG/石墨烯体系制备得到的石墨烯分散在水中,将pyrene-PCL/石墨烯体系制备得到的石墨烯分散在二甲基亚砜(DMSO)中。

图4给出了用芘基聚合物和超临界 CO_2 剥离制备的石墨烯溶液的数码照片和透射电子显微镜(TEM)照片以及选区电子衍射照片.由于PEG分子链的亲水性和PCL分子链的亲油性使得剥离制备的石墨烯分别在水溶液和DMSO溶液中形成均匀的分散液(图4(a)).图4(b)~(i)是剥离制备的石墨烯TEM照片以及选区电子衍射照片.图4(f)~(i)显示剥离制备的石墨烯呈现典型的六角对称的蜂窝状结构,并且晶面 $\{1100\}$ 的衍射强度大于 $\{2110\}$ 的衍射强度($I\{1100\} > I\{2110\}$),证明所制备的呈现典型的六点对称衍射为单层石墨烯.从TEM结果中可以看到制备的石墨烯主要分为3种:(1)如图4(b)~(e)所示的单层石墨烯;(2)少层(2~3层)的石墨烯(图5(a)~(d));(3)重新堆砌形成的无规的多层石墨烯(图5(e)~(h)).另外发现一些石墨烯的电子衍射图呈现2个六点对称的衍射花样图案(图5(h)插图),这是由剥离后的石墨烯层重新无

图4 (a) 石墨烯溶液的数码照片: (a1), (a2) pyrene-PEG_{2K} 和 pyrene-PEG_{5K}/石墨烯水溶液; (a3), (a4) pyrene-PCL₁₉ 和 pyrene-PCL₄₈/石墨烯的DMSO溶液; (b)~(e) 对应于(a1)~(a4)溶液的TEM照片; (f)~(i) 对应于(b)~(e)的选区电子衍射照片^[89]

Figure 4 (a) Digital photographs of graphene dispersions: (a1), (a2) Dispersion of graphene sheets in water by non-covalent functionalization of pyrene-PEG_{2K} and pyrene-PEG_{5K}, respectively; (a3), (a4) dispersion of graphene sheets in DMSO by non-covalent functionalization of pyrene-PCL₁₉ and pyrene-PCL₄₈, respectively. (b)~(e) TEM images of the exfoliated graphene sheets corresponding to (a1)~(a4), respectively. (f)~(i) Electron diffraction (ED) patterns of the exfoliated graphene sheets corresponding to (b)~(e), respectively^[89]

图5 Pyrene-PEG_{2K}, pyrene-PEG_{5K}, pyrene-PCL₁₉ 和 pyrene-PCL₄₈ 剥离制备的 2 层和 3 层石墨烯(a)~(d)和无规的多层石墨烯(e)~(h). (h)内插图是相应的选区电子衍射照片^[89]

Figure 5 (a)~(d) bilayer and trilayer graphene sheets and (e)~(h) disordered small and multilayer graphene sheets, which are prepared by non-covalent functionalization of pyrene-PEG_{2K}, pyrene-PEG_{5K}, pyrene-PCL₁₉ and pyrene-PCL₄₈, respectively. The inset in (h) is the corresponding ED pattern^[89]

规堆砌形成的.

图6是基于芘基聚合物和超临界CO₂剥离制备石墨烯的机理图. 首先石墨粉和芘基聚合物加入到DMSO溶剂中超声, 由于 π - π 相互作用使芘基聚合物吸附在石墨表面, 而聚合物分子链伸向溶剂(图6(b)). 由于石墨层之间强的范德华力, 吸附的芘基聚合物和悬挂的聚合物链不足以剥离石墨烯并使其分散在溶液中. 超临界CO₂的低黏度、高扩散性和零表面张力使得CO₂易渗透进石墨层之间, 并易携带芘基聚合

物插入石墨层之间. 当芘基聚合物/石墨体系处于超临界CO₂条件时, 超临界CO₂渗透进石墨层之间, 同时由于芘基聚合物在CO₂中的溶解度低, 超临界CO₂的通入导致DMSO对芘基聚合物的溶剂效应降低(抗溶剂效应), 芘基聚合物在溶液中的溶解度降低. 芘基聚合物为了最小化其与CO₂的相互作用, 倾向于作为分子楔插入石墨层之间, 与石墨内层形成 π - π 相互作用(图6(c)). 插入到石墨层之间的芘基聚合物增大了石墨层之间的距离并阻止石墨烯的聚集. 最后

图6 (网络版彩色)基于芘基聚合物和超临界CO₂剥离制备石墨烯的示意图^[89]

Figure 6 (Color online) Scheme showing the exfoliation process of graphene sheets from graphite based on pyrene-polymer and supercritical CO₂^[89]

通过超声,制备了茈基聚合物修饰的石墨烯溶液(图6(d)),石墨烯表面的茈基聚合物作为稳定剂使得石墨烯在不同的溶液中分散稳定。

茈基聚合物修饰的石墨烯在纳米复合材料中具有广泛的应用潜力.本课题组^[89]研究了PCL/石墨烯和苯乙烯(PS)/石墨烯纳米复合材料.图7是纯的聚合物和石墨烯基复合材料的差示扫描量热图(DSC).对于PCL体系,PCL/石墨烯复合材料的结晶温度(T_c)、熔融温度(T_m)和结晶度(X_c)相对于纯的PCL都有显著的增加(图7(a)).在石墨烯含量仅为1%时,PCL的结晶温度提高10℃;在石墨烯含量为5%时,PCL的结晶度也增加近10%.同样地,对于PS体系,当石墨烯含量仅为1%时,PS的玻璃化转变温度(T_g)提高近10℃(图7(b)).说明石墨烯表面的功能化使得石墨烯与聚合物本体之间的结合力增强,因此赋予石墨烯基复合

图7 (网络版彩色)DSC图谱.(a1) 纯PCL;(a2) 1%的PCL/石墨烯纳米复合材料;(a3) 5%的PCL/石墨烯纳米复合材料;(b1) 纯PS;(b2) 1%PS/石墨烯纳米复合材料.内插图是相应的热压复合膜的数码照片^[89]

Figure 7 (Color online) Non-isothermal DSC scans of pure PCL (a1), 1wt% PCL/graphene nanocomposite (a2), 5wt% PCL/graphene nanocomposite (a3), pure PS (b1) and 1wt% PS/graphene nanocomposite (b2). Inset of (a) and (b) show photographs of the corresponding hot-pressed composite films^[89]

材料优异的热学性能。

2.3.2 茈基小分子衍生物体系制备功能化的石墨烯

除了上述介绍的茈基聚合物功能化修饰石墨烯外,本课题组^[93]还利用超临界 CO_2 制备了茈及另外3种小分子茈基衍生物(茈甲酸、茈丁酸和茈胺)非共价键修饰的石墨烯,并进一步通过密度泛函理论(vdW-DFT)研究了它们与单层石墨烯和处于石墨烯层间的相互作用能。

在实验和理论研究的基础上,本课题组^[94]对茈胺非共价键修饰的石墨烯上负载金属Pt纳米粒子,研究该复合材料用于甲醇燃料电池上的潜在应用,实验流程如图8所示.研究结果显示茈胺修饰的石墨烯纳米片(PA-GNS)表面上的氨基可以作为Pt纳米粒子成核和生长的活性位点,从而增强了石墨烯纳米片和Pt纳米粒子间的相互作用。

本课题组^[94]进一步对GNS和PA-GNS上负载的Pt纳米粒子的形貌、尺寸以及在载体上的分散进行了TEM表征.图9是GNS/Pt和PA-GNS/Pt的TEM图像以及相对应的Pt粒子的尺寸分布的柱状图.100个随机选择的Pt粒子用来分析Pt粒子的尺寸分布.沉积在GNS上Pt粒子的粒径分布在2~6 nm,GNS/Pt中Pt的平均粒径为4.0 nm.对于PA-GNS/Pt(图9(d)和(e)),Pt的平均粒径为3.0 nm,较GNS/Pt要小很多.因为PA-GNS上存在大量的氨基,这些氨基作为Pt纳米粒子成核的活性位点并限制粒子的长大^[99],图9(d)内插图展示的是面心立方Pt的(111)晶面,其晶格间距为0.22 nm^[100].Pt纳米粒子的尺寸和在载体上的分布情况与其甲醇氧化的电催化活性密切相关^[101].

将PA-GNS/Pt作为直接甲醇燃料电池(DMFCs)

图8 (网络版彩色)石墨烯纳米片/铂和茈胺修饰的石墨烯纳米片/铂纳米复合材料的制备示意图^[94]

Figure 8 (Color online) Schematic illustration of the synthesis of graphene nanosheets/Pt composite and 1-pyrenamine (PA) modified graphene nanosheets/Pt composite, respectively^[94]

图9 GNS/Pt 和 PA-GNS/Pt 的低倍 TEM(a)和(d)以及高倍 TEM(b)和(e)图片及其相对应的 Pt 纳米粒子尺寸分布的柱状图(c)和(f). (d)中的插图为 PA-GNS/Pt 的高分辨 TEM 图像^[94]

Figure 9 Low-, high-magnification TEM images and corresponding histograms of Pt particle size distributions of the GNS/Pt (a), (b) and (c) and PA-GNS/Pt (d), (e) and (f). The inset of (d) is an HRTEM image of PA-GNS/Pt^[94]

的催化剂, 对其电催化活性进行了测试研究. 催化剂的电化学活性面积 (ECSA) 与其催化活性密切相关^[102], 图 10(a) 是不同样品在 N_2 饱和的 0.5 mol/L H_2SO_4 溶液中的循环伏安 (CV) 曲线, 扫描电压范围为 0.2~1.0 V(vs Ag/AgCl 电极), 扫描速率为 25 mV/s. ECSA 值由 CV 曲线中负向扫描的氢吸附电量 (扣除双电层充电电量) 计算得出^[102,103]. PA-GNS/Pt, JM-C/Pt 和 GNS/Pt 的 ECSA 值分别为 82.9, 64.0 和 42.7 m^2/g . PA-GNS/Pt 具有最大的 ECSA 值, 这与 PA-GNS/Pt 上 Pt

粒子在 PA-GNS 载体上的高度分散、更小粒径和窄的尺寸分布相一致^[104]. ECSA 值表明 PA-GNS/Pt 具有最高的催化活性, 有利于电化学反应.

进一步测量了 GNS/Pt 和 PA-GNS/Pt 在甲醇氧化反应中的电催化性能, 并与 JM-C/Pt 进行了对比. 图 10(b) 所示的是 GNS/Pt, PA-GNS/Pt 和 JM-C/Pt 在 0.5 mol/L H_2SO_4 + 1 mol/L CH_3OH 溶液中的甲醇氧化反应的 CV 曲线, 测试在室温下进行. 所有的催化剂都显示出了相似的 CV 曲线, 位于 0.7 V(vs Ag/AgCl) 附

图10 (网络版彩色)GNS/Pt, PA-GNS/Pt 和 JM-C/Pt 在 0.5 mol/L H_2SO_4 溶液(a)和 0.5 mol/L H_2SO_4 + 1 mol/L CH_3OH 溶液(b)中的 CV 曲线. 扫描速率 25 mV/s^[94]

Figure 10 (Color online) CV for GNS/Pt, PA-GNS/Pt and JM-C/Pt in 0.5 mol/L H_2SO_4 solution (a) and 0.5 mol/L H_2SO_4 + 1 mol/L CH_3OH solution (b) at a scan rate of 25 mV/s^[94]

近的前扫峰来自甲醇氧化,位于0.5 V(vs Ag/AgCl)附近的逆扫峰来自于含碳中间物种的氧化^[105]. PA-GNS/Pt前扫峰的质量比电流密度为365.6 mA/mg,远高于商品化JM-C/Pt(260.6 mA/mg),是GNS/Pt(85.6 mA/mg)的4.3倍. PA-GNS/Pt在甲醇氧化反应中催化活性的增强可以归由以下几点原因:(1) 芘胺的引入提高了Pt纳米粒子在GNS上的分散性,同时限制了Pt粒子的生长,使其尺寸更小, Pt粒子具有更多的活性位点^[101];(2) 非破坏性的芘胺非共价功能化方法有效地保护了GNS的固有性质,如高的电子传导性^[106];(3) 与GNS/Pt电极相比, PA-GNS/Pt样品中含有足够的氨基基团,可以提高甲醇在催化剂表面上的浸润性和可利用率^[103].

3 结论和展望

二维石墨烯由于其优异的电学、机械、热学和光

学性能,在电子器件、纳米复合材料、传感器、生物医药等领域具有广泛的应用前景. 利用超临界流体技术制备石墨烯及其功能化材料是一个重要且新颖的方法. 超临界CO₂的黏度、密度、介电常数、溶剂化能力、扩散系数等物理化学性质随温度和压力的变化十分敏感,在不改变化学组成的前提下,其性质可连续进行调节,为研究化学环境对石墨烯制备路径的影响提供了便利. 与传统制备石墨烯基纳米杂化材料的方法相比,超临界流体性质的可调性也为石墨烯的功能化提供了方便,同时可实现石墨烯基纳米杂化材料的形貌调控,为其在能源储存与转化、生物电子器件领域的应用提供了基础.

在未来研究中,如何将高分子、金属、金属氧化物纳米粒子和石墨烯的特性充分相结合,设计和制备出多功能化的石墨烯基纳米杂化材料,并推广其应用将成为研究的重点.

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Production and functionalization of graphene with the assistance of supercritical fluids

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Graphene, a monolayer of graphite, has attracted increasing attention since its discovery because of its unique two-dimensional (2D) structure, excellent mechanical, thermal and electronic properties. Currently, great effort has been carried out for the preparation and function of graphene, as well as its use in the energy conversion field, such as fuel cells. In this article, we review the recent achievements in the preparation and functionalization of graphene. The methods of the preparation and functionalization of graphene by liquid-phase exfoliation with the assistance of supercritical fluids are stated in detail. In particular, we focus on the one-step fabrication and functionalization of graphene based on pyrene-polymers and small molecule derivatives of pyrene by liquid-phase exfoliation with the assistance of supercritical carbon dioxide (scCO₂). Moreover, we introduce the study of the resulting graphene's application in the enhancement of polymer matrix and the direct methanol fuel cells (DMFCs).

graphene, liquid-phase exfoliation, supercritical fluids, pyrene-derivatives, fuel cells

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补充材料

- 图 S1 还原氧化石墨烯和 PB-功能化石墨烯的水(0.1 mg/mL)分散液照片
- 图 S2 液相中化学法制备单层石墨烯
- 图 S3 PEG-OPE 修饰还原氧化石墨烯
- 图 S4 超临界 DMF 中剥离可膨胀石墨制备多层石墨烯和单层石墨烯的示意图
- 图 S5 1-PSA 辅助超临界乙醇剥离石墨制备石墨烯的示意图

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