

石墨烯复合材料的研究进展

匡达, 胡文彬

(上海交通大学 金属基复合材料国家重点实验室, 上海 200240)

摘要: 石墨烯以其优异的性能和独特的二维结构成为材料领域研究热点。本文综述了石墨烯的制备方法并分析比较了各种方法的优缺点, 简单介绍了石墨烯的力学、光学、电学及热学性能。基于石墨烯的复合材料是石墨烯应用领域中的重要研究方向, 本文详细介绍了石墨烯聚合物复合材料和石墨烯基无机纳米复合材料的制备及应用, 并特别讨论了石墨烯/块体金属基复合材料的制备方法和其优异性能。

关键词: 石墨烯; 制备; 性能; 复合材料; 综述

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Research Progress of Graphene Composites

KUANG Da, HU Wen-Bin

(State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China)

Abstract: Graphene has recently attracted much interest in material field due to its unique two-dimensional structure and outstanding properties. Various preparation methods of graphene are briefly compared. The physical and mechanical properties of graphene are then introduced. Graphene-based composite becomes one of the most important research frontiers in the application of graphene. A comprehensive review is presented to introduce the latest progress of the graphene related composites, including graphene-polymer composites and graphene-based inorganic nanocomposites, especially introducing the fabrication methods and outstanding performances of the bulk metal-matrix/graphene composites.

Key words: graphene; preparation; properties; composites; review

2004年英国科学家首次制备出了由碳原子以 sp^2 杂化连接的单原子层构成的新型二维原子晶体—石墨烯, 其厚度只有 0.3354 nm, 是目前世界上发现最薄的材料^[1]。石墨烯具有特殊的单原子层结构和新奇的物理性质: 强度达 130 GPa、热导率约 5000 J/(m·K·s)、禁带宽度几乎为零、载流子迁移率达到 $2 \times 10^5 \text{ cm}^2/(\text{V} \cdot \text{s})$ 、高透明度(约 97.7%)、比表面积理论计算值为 2630 m^2/g , 石墨烯的杨氏模量(1100 GPa)和断裂强度(125 GPa)与碳纳米管相当, 它还具有分数量子霍尔效应、量子霍尔铁磁性和零载流子浓度极限下的最小量子电导率等一系列性质^[2-6]。在过去几年中, 石墨烯已经成为了材料科学领域的一个研

究热点^[7-17]。

为了更好地利用石墨烯的这些特性, 研究者采用了多种方法制备石墨烯。随着低成本可化学修饰石墨烯的出现, 人们可以更好地利用其特性制备出不同功能的石墨烯复合材料。本文将着重介绍石墨烯复合材料特别是块体石墨烯金属基复合材料的最新研究进展。

1 石墨烯的制备

石墨烯的制备从最早的机械剥离法^[1]开始逐渐发展出多种制备方法, 如: 晶体外延生长法、化学气

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作者简介: 匡达(1987-), 男, 硕士研究生. E-mail: dlkda@sina.com

通讯作者: 胡文彬, 教授. E-mail: wbhu@263.net

相沉积法、液相直接剥离法以及高温脱氧和化学还原法等^[18-20]。我国科研工作者较早开展了石墨烯制备的研究工作。石墨烯的研究进展概况如表 1 所示。化学气相沉积法是一种制备大面积石墨烯的常用方法。目前大多使用烃类气体(如 CH₄、C₂H₂、C₂H₄ 等)作为前驱体提供碳源,也可以利用固体碳聚体提供碳源,如 Sun 等^[33]利用化学气相沉积法将聚合物薄膜沉积在金属催化剂基体上,制备出高质量层数可控的石墨烯。与化学气相沉积法相比,等离子体增强化学气相沉积法可在更低的沉积温度和更短的反应时间内制备出单层石墨烯。此外晶体外延生长法通过加热单晶 6H-SiC 脱除 Si,从而得到在 SiC 表面外延生长的石墨烯。但是 SiC 晶体表面在高温过程中会发生重构而使得表面结构较为复杂,因此很难获得大面积、厚度均一的石墨烯^[34-35]。而溶剂热法因高温高压封闭体系下可制备高质量石墨烯的特点也越来越受研究人员的关注^[36]。相比于其他方法,通过有机合成法可以制备无缺陷且具有确定结构的石墨烯纳米带^[37-38]。

与上述自下而上的合成方法不同,自上而下的方法可提高石墨烯产率并且易于制备。如简单易行的化学剥离法和氧化石墨还原法,后者已成为实验室制备石墨烯最简单的方法。而接下来发展的溶剂剥离法比氧化还原法毒性小,并且不会破坏石墨烯的结构。除化学还原法外,也可通过电化学方法将

石墨氧化物还原成石墨烯^[39-41],但该法制备得到的石墨烯中 C 和 O 原子比值较低。此外,微波法也被用来制备石墨烯,如 Chen 等^[32]首先将氧化石墨烯(GO)分散到 N-N-二甲基乙酰胺与水(DMAc/H₂O)的混合溶剂中,然后将混合反应液进行微波热还原,得到的石墨烯电导率是氧化石墨烯的 10⁴ 倍。北京科技大学的吕岩等^[42]利用电弧法制备出了具有开放介孔结构的石墨烯,其比表面积为 77.8 m²/g、中孔率高达 74.7%,可作为电极材料。

2 石墨烯的优异性能

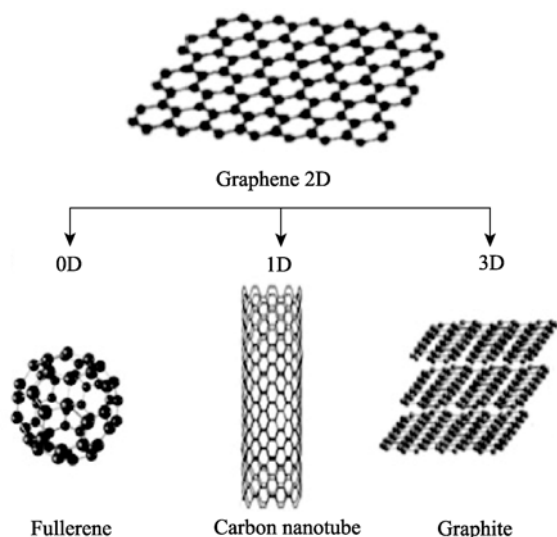
单层石墨烯及其衍生物如图 1 所示^[43]。它是由键长 0.141nm 的碳六元环构成的两维周期蜂窝状点阵结构,石墨烯可以卷曲成零维的富勒烯、一维的碳纳米管或者堆垛成三维的石墨。

2.1 电学特性

石墨烯最重要的性质之一就是它独特的载流子特性和无质量的狄拉克费米子属性^[1, 44]。石墨烯的价带和导带部分相重叠于费米能级处,是能隙为零的二维半导体,载流子可不通过散射在亚微米距离内运动^[1, 45],为目前发现的电阻率最小的材料^[46-47]。石墨烯内部电子输运的抗干扰能力很强,其电子迁移率在室温下可超过 15000 cm²/(V·s)^[46],而当载流子密度低于 5×10⁹ cm⁻²时,低温悬浮石墨烯的电子迁

表 1 石墨烯的制备方法概况
Table 1 Various methods for preparation of graphene

Methods	Conditions	Characteristics	Ref.
CVD	Carbon source: CH ₄ Substrate: Cu;Ni; Si/SiO ₂ Temperature: 1000℃	Homogeneous single-layer graphene films	[21-22]
PECVD	Carbon source: CH ₄ Substrate: Si/SiO ₂ Temperature: 650℃	High-quality, large-area graphene with 1-3 layers	[23]
Epitaxial growth of graphene	Substrate: 6H-SiC(0001) Temperature: 1280℃	Grain size: up to 50 μm long, 1 μm wide	[24]
Solvothermal	Reagents: Na and C ₄ Cl ₆ Temperature: 300℃	1-3 graphene layers with low density of defects	[25]
Organic synthesis	Thermal fusion of polycyclic aromatic hydrocarbons at 1100℃	Conductivity for a 30 nm thick on quartz is 20600 S/m	[26]
Chemical exfoliation	Number of layers(3-4) controlled by changing the exfoliation temperature	Electrical conductivity: 10 ⁸ S/m	[27]
Chemical reduction of GO	Reduction agent: hydrazine hydrate	Sheet thickness: 1nm	[28]
Liquid exfoliation of graphite	In supercritical DMF for less than 15 min	Single layer graphene	[29]
Electrochemical reduction	Cyclic voltammetric reduction of a graphene oxide colloidal solution	Enhanced electron transfer properties	[30]
		Improved electrical conductivity: 1.43×10 ⁴ S/m	[31]
Microwave radiation	Reduced by microwaves in a solution of DMAc/H ₂ O	Its electrical conductivity is about 10 ⁴ times than that of GO paper	[32]

图1 单层石墨烯及其衍生物示意图^[43]Fig. 1 Schematic diagrams of graphene and its derivatives^[43]

移率首次被发现可以接近 $200000 \text{ cm}^2/(\text{V}\cdot\text{s})$ ^[48]。单层石墨烯中载流子迁移率几乎不受化学掺杂和温度的影响^[49]，另外，石墨烯中电子载体和空穴载流子的半整数量子霍尔效应可以通过电场作用改变化学势而被观察到^[45-46]，而 Novoselov 等^[50]在室温条件下就观察到了石墨烯的这种量子霍尔效应。Burghard 等^[51]发现化学还原的多层氧化石墨烯薄片的电导率在 $0.05\sim 2 \text{ S/cm}$ 之间，其室温下的场效应迁移率为 $2\sim 200 \text{ cm}^2/(\text{V}\cdot\text{s})$ 。

2.2 光学特性

单层悬浮石墨烯的白光吸收率是 2.3%，而且吸收率随着层数的变化呈线性增加^[6]。Gusynin 等^[52]发现石墨烯的透明度只取决于其精细结构常数。康奈尔大学的 Dawlaty 等^[53]运用超快光学泵浦-探针光谱研究了 SiC 上生长石墨烯的载流子动力学和相对弛豫时间。他们发现首先出现一个快速的弛豫瞬态：70~120 fs，随后是一个变慢的弛豫过程：0.4~1.7 ps，二者分别与石墨烯的载流子-载流子带内扫描过程和载流子-声子带间扫描过程有关。Wang 等^[54]运用红外光谱发现可通过电子选通技术对多层石墨烯的带间跃迁和光跃迁进行控制。

2.3 热学特性

根据所测石墨烯薄片尺寸的不同，单层悬浮石墨烯的室温热传导率可达到 $3000\sim 5000 \text{ W}/(\text{m}\cdot\text{K})$ ^[55]，此特性可被用来解决纳米电子学中的热耗散问题，尽管有人指出与悬浮石墨烯接触的基体会影响测量值，Seol 等^[56]证明在无定形 SiO_2 上生长的石墨烯，其热传导率仍可达到 $600 \text{ W}/(\text{m}\cdot\text{K})$ ，而热传导率的降低是由于声子穿过石墨烯-硅界面时的耗散和强烈

的界面散射，尽管如此，石墨烯的热导率仍是如今在电子领域广泛应用的铜的 2 倍和硅的 50 倍。

2.4 力学特性

Lee 等^[3]运用原子力显微镜纳米压痕技术测试了独立支撑的多层石墨烯的力学性能，他们发现石墨烯的断裂强度为 42 N/m ，而超窄石墨烯薄带的杨氏模量约为 7 TPa ^[57]，是目前已知的最牢固的材料。此外，Hao 等^[58]运用量子力学研究了锯齿形石墨烯和扶手型石墨烯的断裂机理，他们发现两种石墨烯模型都是从最外层碳原子层开始断裂。而 Frank 等^[59]通过运用悬臂梁实验发现单层石墨烯可以承受不同角度的轴向压力。Schniepp 等^[60]也运用原子力显微镜观察了功能化石墨烯薄片的弹性变形行为，在反复折叠石墨烯薄片后，其曲折线都出现在同一位置，这种现象是由薄片上已经存在的扭结和缺陷导致的。

3 石墨烯复合材料

基于石墨烯的复合材料是石墨烯应用领域中的重要研究方向，其在能量储存、液晶器件、电子器件、生物材料、传感材料和催化剂载体等领域展现出了优良性能，具有广阔的应用前景^[61]。目前石墨烯复合材料的研究主要集中在石墨烯聚合物复合材料和石墨烯基无机纳米复合材料^[62]上，而随着对石墨烯研究的深入，石墨烯增强体在块体金属基复合材料中的应用也越来越受到人们的重视，本文将特别介绍其最新的研究进展。

3.1 石墨烯聚合物复合材料

根据石墨烯与聚合物的相互作用方式不同，可将石墨烯聚合物复合材料分为石墨烯填充聚合物复合材料、层状石墨烯聚合物复合材料和功能化聚合物复合材料^[63]。

3.1.1 石墨烯填充聚合物复合材料

石墨烯是可替代碳纳米管的理想填充物，其分散性和与聚合物基体的相互作用是影响复合材料制备的两个关键因素，制备方法主要有溶液混合^[64-65]、熔融共混^[66-67]和原位聚合等^[68-74]。

Zhao 等^[75]通过溶液混合制备了石墨烯含量为 1.8vol% 的聚乙烯醇(PVA)复合材料并研究了其力学性能，他们发现复合材料的抗拉强度提高了 150%，杨氏模量提高了 10 倍左右。而 Vadukumpully 等^[76]也通过溶液混合制备了石墨烯/聚氯乙烯复合材料，他们发现 2wt% 的石墨烯填充物使得复合材料的杨氏模量提高了 58%、抗拉强度提高了 130%，而石墨

烯的引入也提高了聚合物的玻璃化转变温度。不难发现利用溶液混合法制备的石墨烯填充复合材料中石墨烯分散性较好,复合材料具有较高的力学性能。然而该方法需要使用昂贵的分散液并且不能得到单层石墨烯分散液,与之相比,熔融共混法更加简单经济并且能制得增强效果更好的复合材料。例如 Zhang 等^[67]利用熔融共混制备出了聚对苯二甲酸/石墨烯复合材料,他们发现石墨烯的填充大大提高了复合材料的电导率,含有 3.0vol% 石墨烯的复合材料电导率可以达到 2.11 S/m。然而大多数工业级聚合物的高粘度阻止了熔融共混法在石墨烯/工程塑料复合材料中的应用,而原位聚合法则不存在这种缺陷。最近, Huang 等^[77]运用原位聚合法制备了导电性能良好的聚烯烃/石墨烯纳米复合材料,石墨烯含量 1.2vol% 的复合材料电导率为 3.92 S/m,而石墨烯含量为 10.2vol% 时,电导率可达到 163.1 S/m。Fabbri 等^[78]也通过原位聚合制备了聚对苯二甲酸丁二醇酯(PET)/石墨烯复合材料,结果表明石墨烯含量的增加显著提高了复合材料的热稳定性却没有影响 PET 的结晶温度。此外 Longun 等^[79]利用动态力学分析法研究了石墨烯/聚酰亚胺复合材料的橡胶态高弹模量,他们发现石墨烯含量为 28.08vol% 时,复合材料橡胶态高弹区的模量增加了 4000 倍。而 Kandanur 等^[80]研究了石墨烯/聚四氟乙烯复合材料的润滑性能,他们发现 10wt% 的石墨烯使得复合材料的稳态磨损率降低了 75%。

3.1.2 层状石墨烯聚合物复合材料

与石墨烯随机分散在聚合物基体的石墨烯填充复合材料不同,石墨烯衍生物也可与聚合物复合形成层状结构材料,其可应用于定向负载承重膜和光伏器件等领域中^[62]。例如 Kulkarni 等^[81]利用 LB 膜法在导电介质多层膜上逐层沉积氧化石墨烯(GO)薄片,8vol% 含量氧化石墨烯的复合薄膜,其弹性模量从 1.5 GPa 增加到 20 GPa。Zhao 等^[82]利用同样的方法制备了力学性能良好的 PVA-GO 多层膜。在光伏器件的应用中, Li 等^[83]将 GO 薄膜和聚(3-乙基噻吩)(P3HT)/苯基 C61 丁酸甲基酯(PCBM)混合物逐层沉积在铟锡氧化物(ITO)上,其中 GO 层负责空穴的传输,使得该光伏设备具有极高的效率值,制备过程如图 2 所示。

3.1.3 功能化石墨烯聚合物复合材料

石墨烯及其衍生物也可通过聚合物修饰的共价或非共价功能化形成功能化石墨烯聚合物复合材料。石墨烯衍生物的功能化主要是通过聚合物官能团和氧化石墨烯表面的含氧官能团发生反应。

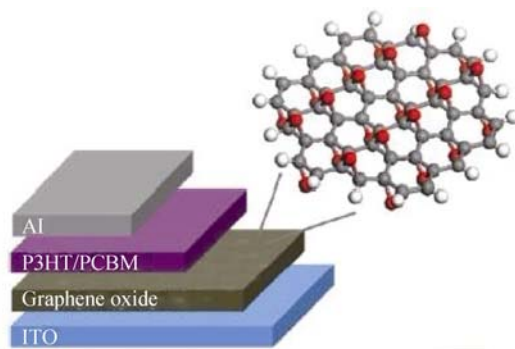


图 2 光伏器件结构示意图^[83]

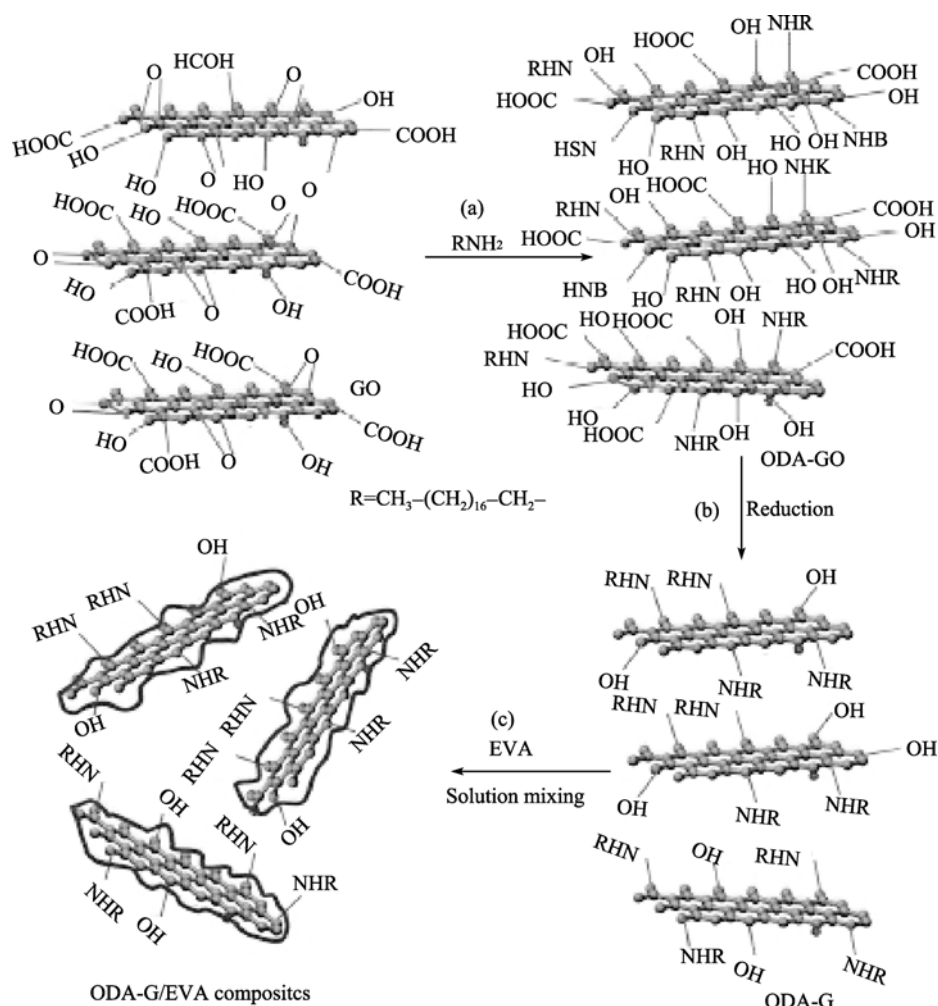
Fig. 2 Schematic illustration of the photovoltaic device structure consisting of the following: ITO/GO/P3HT:PCBM/Al^[83]

而发生反应的共价界面可以提高复合材料的力学和热学性能。最近, Cai 等^[84]研究了聚甲基甲酸乙酯(PU)功能化石墨烯复合材料,他们发现 PU 和 GO 的共价界面起到了应力传递的作用,从而提高了复合材料的力学性能,如杨氏模量提高了 7 倍、硬度提高了 50%。Wang 等^[85]制备了功能化石墨烯环氧树脂复合材料,他们同样发现了共价功能化后的石墨烯界面使得复合材料的抗拉强度提高了 45%。Kuila 等^[86]研究了功能化石墨烯醋酸乙烯(EVA)共聚合物复合材料的力学性能,他们用十八烷基胺(ODA)作为石墨烯的表面改性剂,然后与 EVA 共混制成共聚合物复合材料,如图 3 所示。他们发现复合材料的抗拉强度提高了 74%、热稳定性提高了 42℃。此外, Nanjundan 等^[87]研究了功能化石墨烯复合材料良好的导电性能,他们发现石墨烯的加入使得共聚合物复合材料的室温电导率达到了 22.5 S/cm。

而非共价功能化是通过范德瓦尔斯力、静电相互作用和 π - π 堆积作用对石墨烯表面进行修饰而不改变它的化学结构,此方法可提高复合材料的电学、光学特性和可溶性^[88]。例如 Yang 等^[89]利用 π - π 堆积非共价修饰的石墨烯薄片制备了多功能聚合物纳米复合材料,研究发现功能化石墨烯的引入提高了复合材料的储能模量、玻璃化转变温度和电导率。

3.2 石墨烯基无机纳米复合材料

将无机材料(金属纳米材料、半导体和绝缘纳米材料)分散在石墨烯纳米层表面可合成石墨烯基无机纳米复合材料。无机纳米粒子可减小石墨烯片层间的相互作用,而石墨烯与特定纳米粒子相结合,使该类复合材料在催化剂、光学等领域具有广泛的应用前景^[90-93]。目前研究的无机纳米粒子主要包括金属纳米粒子: Au^[94-99]、Ag^[100-103]、Pd^[104]、Pt^[105]、Ni^[106-107]、Cu^[108-109]、Ru^[110]、Rh^[111]; 金属氧化物纳米粒子: TiO₂^[112-117]、ZnO^[118]、SnO₂^[119-120]、

图3 ODA-G/EVA 复合材料的制备过程示意图^[86]Fig. 3 Schematic depiction for the preparation of functionalized graphene and its composite with ethylene vinyl acetate co-polymer^[86]

MnO_2 ^[121-122]、 Co_3O_4 ^[123-125]、 Fe_3O_4 ^[126-130]、 NiO ^[131-134]、 Cu_2O ^[135-136]、 RuO_2 ^[137]、 SiO_2 ^[138]；硫化物纳米粒子： CdS ^[139]、 $CdSe$ ^[140]。表2概括了制备石墨烯无机纳米材料的典型方法和相关应用。本文主要按照制备方法的不同将石墨烯基无机纳米复合材料进行分类。

3.2.1 化学还原法

化学还原法是目前制备石墨烯基金属纳米材料较常用的方法。一些贵金属的前驱体，如 $HAuCl_4$ 、 $AgNO_3$ 、 K_2PtCl_6 和 H_2PdCl_6 可被抗坏血酸、 $NaBH_4$ 等还原剂在石墨烯表面还原。上海交通大学的 Xu 等^[100]利用氨水还原 $AgNO_3$ 和 GO 的混合液制备了 Ag 纳米粒子石墨烯薄膜，所得复合材料具有很好的反射率和延展性。Spreeprasad 等^[101]也运用化学还原法制备了银/石墨烯复合材料，他们发现该材料对 $Hg(II)$ 具有很好的吸附性从而可应用在水净化领域。

此外，金属氧化物如 Cu_2O 、 SnO_2 、 MnO_2 、 NiO 等也可通过化学还原在 GO/rGO 表面生成。如南京理工大学的徐超等^[136]利用醋酸铜和氧化石墨烯作为前驱体制备了 Cu_2O /石墨烯复合材料并且表现出了良好的电化学特性，其制备过程如图4所示。中科院长春应用化学研究所的 Li 等^[120]利用尿素和盐酸一步法还原了 GO 和 $SnCl_2$ 的混合液制备出了具有良好电容性的石墨烯/ SnO_2 纳米复合材料。江苏大学的 Ji 等^[132]利用水合肼还原了 GO 和氯化镍的混合液制备了具有优异电化学性能的石墨烯/ NiO 纳米复合材料。

3.2.2 电化学沉积法

化学还原法中使用的还原剂和有机溶剂会降低石墨烯与纳米粒子结合界面的活性，从而降低复合材料的性能，直接在石墨烯基体电化学沉积无机纳米材料是制备石墨烯复合薄膜一种绿色环保且高效的方法。例如 Hu 等^[97]将纳米金粒子直接电化学沉

表 2 石墨烯无机纳米材料的制备方法和应用概况

Materials	Preparation methods	Applications	Ref.
Au/rGO	Sonolytic reduction		[94]
	Electrodeposition	Electrocatalysis	[96-97]
Au/GO	<i>In situ</i> reduction	Catalytic applications	[98]
Ru/rGO	Microwave assisted reduction	Catalysis	[110]
TiO ₂ /rGO	Self-assembly of TiO ₂ nanorods and rGO at two-phase interface	Photocatalysis	[112]
	Templated hydrolysis	Photocatalysis	[113]
	Hydrolysis starting with titanium butoxide	Dye-sensitized solar cells	[115]
	Hydrothermal starting with P25 and GO	Photocatalysis	[116]
TiO ₂ /GO	Non-covalent adhesion <i>via</i> solution mixing	Dye-sensitized solar cells	[114]
Ag/rGO	Solution-based chemical approach		[100]
	Redox reaction	Water purification	[101]
Ag/GO	Sol-Gel technique	Glucose detection	[102]
Pd/GO	Plasma reduction		[104]
Pt/rGO	Electrodeposition	Selected determination of Rutin	[105]
Ni/rGO	Electroless Ni/plating method		[107]
Cu/rGO	Electrodeposition	Non-enzymatic glucose sensor	[108-109]
Rh/rGO	Impregnation method		[111]
ZnO/rGO	Electrodeposition	Photovoltaics	[118]
SnO ₂ /FGS	Redox reaction	Li ion battery	[119]
MnO ₂ /GO	Chemical route in a water-isopropyl alcohol system	Supercapacitor	[121]
MnO ₂ /rGO	Redox reaction	Supercapacitor	[122]
Co ₃ O ₄ /rGO	Microwave assisted reaction	Supercapacitor	[124]
Fe ₃ O ₄ /rGO	Hydrolysis starting with FeCl ₃	Li ion battery	[127]
NiO/graphene	Sputtering	Nanocapacitor	[131]
NiO/rGO	Controlled hydrothermal method	Li ion battery	[133]
Cu ₂ O/rGO	Electrodeposition	Photovoltaics	[135]
RuO ₂ /rGO	Redox reaction	Supercapacitor	[137]
SiO ₂ /graphene	Redox reaction	Highly adsorption of Pb	[138]
PtNi/graphene	Electrodeposition	Nonezymatic amperometric glucose detection	[141]
N ₂ /graphene	Thermal solid-state reaction		[142-143]
	Microwave irradiation		[144]
Bi ₂ O ₃ /graphene	Simultaneous solvothermal reduction		[145]

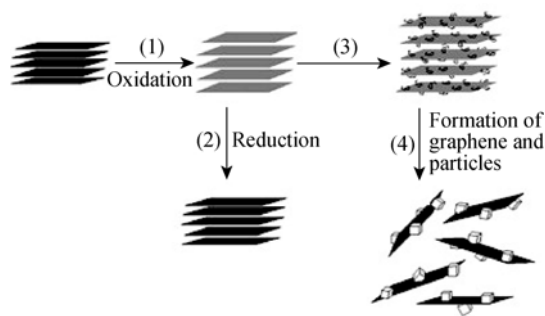


图 4 Cu₂O 石墨烯复合材料制备示意图^[136]
Fig. 4 A proposed scheme of the formation of graphene-Cu₂O composites^[136]

积到石墨烯表面制备出了具有极高催化活度的复合材料, 他们发现可通过控制沉积时间和 HAuCl₄ 前

驱体的含量调整纳米金粒子的形状和大小。最近, Yu 等^[105]将 Pt 电化学沉积到石墨烯修饰的玻璃碳电极表面从而制备了复合材料电极, 该电极可用于对芦丁的检测。而随着氧化石墨烯直接电化学沉积制备石墨烯工艺的出现, 人们发现可将 GO 和金属离子共沉积制备复合材料。例如湖南大学的 Liu 等^[96]将 GO 和 HAuCl₄ 电化学共沉积制备出了石墨烯金纳米粒子复合材料。然而该方法的局限性在于其无法控制沉积过程中石墨烯的厚度。

3.2.3 热蒸发法

热蒸发法是一种低成本、可规模化、不使用化学试剂并且形态可控的制备石墨烯基无机纳米复合材料的方法。如 Zhou 等^[99]利用热蒸发法在石墨烯表面沉积了金纳米粒子并且研究了石墨烯层数对纳

米金粒子粒径大小和密度的影响。他们发现随着石墨烯层数的增加,粒子密度降低而粒径尺寸增大,这是因为在不同表面沉积的金原子扩散系数不同,并且石墨烯表面的自由能与层数有关,而层数控制着石墨烯与热蒸发金原子的交互作用从而影响了石墨烯表面对金纳米粒子的吸收、解析和扩散。

3.2.4 水热法

水热法是一种可在高温固定体积下产生高压从而制备无机纳米复合材料的简单方法。例如 Wang 等^[145]利用水热法制备了 Bi_2O_3 /石墨烯纳米复合材料,该材料在 10 A/g 时比电容达到了 757 F/g。最近 Marlinda 等^[146]利用水热法处理含有 GO、 $\text{Zn}(\text{CH}_3\text{COO})_2$ 、NaOH 和氨水的混合液制备出了 ZnO 纳米棒/石墨烯复合材料,其可应用在气体传感器领域。

3.2.5 溶胶-凝胶法

溶胶-凝胶法是制备金属氧化物结构材料和薄膜涂层材料非常有效的一种方法,其以金属醇盐或金属氯化物作为前驱体进行一系列的水解和缩聚反应。此方法已成功制备石墨烯/ TiO_2 ^[113, 115]、 Fe_3O_4 ^[127]、 SiO_2 ^[119]纳米复合材料。最近, Lu 等^[102]结合超声和溶胶-凝胶技术首次制备出了没有 GO 功能化的 SiO_2 /GO 纳米薄片,随后将 Ag 纳米粒子沉积在复合基体上从而可应用于对 H_2O_2 和血糖的检测中。

3.2.6 其他方法

除了上述方法外,南京理工大学的张树鹏等^[147]利用有机合成技术及超分子自组装技术逐级合成了一种新颖的石墨烯基超分子杂化纳米材料。华南理工大学的袁文辉等^[148]采用氧化石墨和七水合硫酸锌作为初始反应物通过低温剥离法制备了高质量石墨烯/ZnO 纳米复合材料,通过荧光性能测试发现该材料发生了荧光淬灭现象,可应用在光电子领域。

3.3 块体石墨烯金属基复合材料

与传统的增强体材料相比,石墨烯具有优异力学、热学和电学性能,加之独特的单原子层结构特征,受到了复合材料领域研究者的关注,期望石墨烯能够带给复合材料新的性能。随着石墨烯量产工艺的逐步改进和完善,低成本石墨烯增强体使得石墨烯复合材料的实际工程化变为可能。目前这方面的研究以聚合物基复合材料居多^[149-151]。石墨烯增强体陶瓷材料也表现出了优异的力学和电学性能^[152-154]。

石墨烯的高强、高导电、导热性是区别已有增

强体材料如碳纳米管的重大优势特点,如果能将这些性能优势引入到块体金属基复合材料中,将为金属基复合材料的设计和性能提升带来巨大的影响。此外需要特别注意的是,石墨烯与金属基体的界面将是具有独特科学内涵的研究对象,一个或者几十个原子层厚度的石墨烯特征结构超出了我们对金属基复合材料界面研究的已有认知,石墨烯与金属基体之间的界面结合、界面热稳定性等问题亟待用实验来完整地描述。

相比于石墨烯聚合物复合材料和石墨烯基无机纳米复合材料而言,近年来关于石墨烯作为增强体的块体金属基复合材料方面的研究较少。石墨烯密度小、分散性能差以及熔体制备过程中的界面反应问题是制约该类复合材料发展的重要原因。采用传统熔炼冶金方法获得块体石墨烯金属基复合材料较为困难,因此阻碍了该领域内一些原创性研究工作的进展。尽管如此,还是有少数研究者利用不同的方法制备出了块体金属基石墨烯增强体复合材料。例如哈尔滨工业大学的杨帅^[155]使用高速球磨机和高剪切均质机制备出了少层石墨烯和纳米铜粉的复合粉体,随后采用电火花烧结工艺制备出了少层石墨烯增强的铜基复合材料,复合材料的压缩性能测试表明其屈服强度达到了 476 MPa,高于同样条件制备的碳纳米管增强铜基复合材料。Chen 等^[156]运用两步法制备了石墨烯增强的 ZnO 复合材料,其含量为 6.7wt%,他们发现石墨烯在 ZnO 基体中部分重叠形成三维网状结构,与纯 ZnO 相比,复合材料的比电容提高了 128%。最近, Wang 等^[157]首次利用片状粉末冶金技术制备了含有 0.3wt% 石墨烯增强体的 Al 基复合材料,其抗拉强度达到了 249 MPa,比纯 Al 提高了 62%。Goyal 等^[158]利用石墨烯优异的热学性能制备了含有 5vol% 石墨烯增强体的金属微纳米复合材料,温度在 300~400 K 之间时该材料的热导率提高了 5 倍,而复合材料热导率的提高主要归结于石墨烯自身良好的导热性以及其与基体材料的耦合作用。与上述传统制备方法不同,李晓春课题组^[159]利用液态超声结合固态搅拌的方法制备出了块体石墨烯纳米颗粒增强镁基复合材料,该材料表现出了极高的力学性能和完美的增强效果,并且该方法为块体石墨烯金属基复合材料的制备提供了新的思路。对上述块体石墨烯增强金属基复合材料优异的力学性能进行总结后可以发现石墨烯增强体主要通过晶粒细化、位错强化以及应力转移三方面作用导致复合材料应力的增加。首先纳米尺寸的石墨烯薄片可以细化金属晶粒;而塑性变形过程中石

石墨烯也可以钉扎位错阻止其运动;而受压力载荷时石墨烯可以承受很大一部分机械载荷,因此石墨烯的引入对块体复合材料的力学性能有巨大的提高。目前关于石墨烯与金属基体界面的相关研究还很少,Xu 等^[160]对石墨烯与金属基体之间的界面结构和力学特性做了开创性的研究。他根据密度泛函理论的计算结果研究了石墨烯-金属界面的结构和相互作用,其研究的金属基体为 Cu(111)和 Ni(111),他发现石墨烯与金属基体间的内聚能、强度和电子结构都与基体金属的原子结构有关,由于开放 D 轨道之间强烈的耦合作用,石墨烯-Ni 基界面间的内聚能更强。

本课题组提出了一种块体石墨烯金属基复合材料的电沉积制备方法。该方法的主要特点是采用低温液相电沉积的手段实现液相中石墨烯粒子与金属粒子的共沉积,获得石墨烯均匀分布在金属基体中的块体复合材料。低温液相电沉积避免了石墨烯在熔体中的界面反应,可以保持其自身的特征结构尺寸不发生损坏或缺失,同时通过后续的热处理实现复合材料从冷态到热态的逐渐过渡,有利于研究复合材料热状态下的界面组织结构演变,进而实现复合材料界面性能的有效控制。此外也可选用水相分散性好的氧化石墨烯通过电沉积过程中的阴极还原作用,使氧化石墨烯参与电极反应还原为石墨烯,同时与金属离子共沉积在基体材料中。尽管采用电沉积方法可选择的基体材料相对具有一定的局限性,仅限易于从溶液中沉积出来的金属或者合金,但从块体石墨烯金属基复合材料的制备角度来说,该方法不失为一种有效、低成本、便捷的工艺方法。目前我们组利用氧化石墨烯和金属镍粒子的共沉积制备出了石墨烯含量为 0.12wt% 的镍基块体复合材料,其表征如图 5 所示。从 SEM 和 TEM 照片可以看到复合材料中片状石墨烯的特征结构。对复合材料的性能研究发现其硬度与纯镍相比提高了 4 倍、热导率提高了 15%、电导率提高了 33%。复合材料性能的提高与增强体石墨烯的优异性能有关。

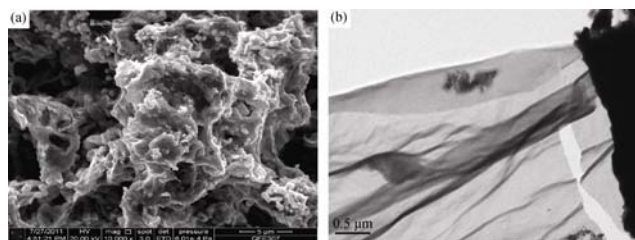


图 5 镍基石墨烯复合材料的 SEM(a)和 TEM(b)照片
Fig. 5 (a) SEM and (b) TEM images of Ni-graphene composites

4 结束语

石墨烯因其优异的性能刚一出现即成为研究热点,其制备工艺从最早的机械剥离法逐渐发展出如:化学气相沉积法、氧化还原法、液相剥离法、晶体外延生长法等多种制备方法,但制备大量、低成本高质量石墨烯仍是未来石墨烯制备研究的一个重点。目前石墨烯复合材料的研究主要集中在石墨烯聚合物材料以及石墨烯表面负载无机纳米粒子及其催化、生物传感器、光谱学等领域的应用研究上,而块体石墨烯金属基复合材料的研究相对较少,石墨烯优异的增强效果及其与金属基体独特的界面作用将使该类复合材料成为未来石墨烯复合材料的研究热点。

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