基于石墨烯的电磁波损耗材料研究进展

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摘 要: 随着军事装备隐身伪装需求的迅速增长, 石墨烯基电磁波损耗材料成为科学研究的热点。本文总结了石墨烯基电磁波损耗材料的研究进展, 详细介绍了石墨烯与其它碳系材料、金属纳米材料、铁氧体材料、导电高聚物材料及非金属材料复合而成的二元、三元及以上多元石墨烯基电磁波损耗材料。简要阐述了电磁波损耗机理, 着重讨论了石墨烯基电磁波损耗材料的微观结构、组分数量及不同损耗机制对吸波性能的影响, 展望了石墨烯基电磁波损耗材料的研究重点和发展方向。

关 键 词: 石墨烯; 石墨烯复合吸波材料; 吸波性能; 综述

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Development of Microwave Absorbing Materials Based on Graphene

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Abstract: Nowadays, electromagnetic interference receives great attention for wireless communication and charging, electronic device, and modern weapons. Materials and the various novelty structures are required and designed to absorb the emitted electromagnetic wave energy and to minimize reflection of the electromagnetic wave in certain direction. Development of graphene-based electromagnetic absorption materials are reviewed, consisting of composition materials with other carbon materials, nano-metal materials, ferrite materials, polymer materials, and non-metallic materials. The electromagnetic absorption mechanisms is briefly described and the influences of microstructure, fraction and loss mechanism on the absorption properties are discussed. The future of graphene-based electromagnetic absorption materials is also prospected.

Key words: graphene; electromagnetic wave absorbing materials; absorption property; review

石墨烯作为二维单层碳原子材料, 是构成碳材料家族的最基本单元, 将石墨烯堆叠, 可得到六方石墨; 将其卷曲, 又可得到零维富勒烯或一维碳纳米管。科学工作者对石墨烯及其衍生物的研究最早可追溯到 1840 年, 但直到 Geim 和 Novoselov 首次制备石墨烯以来, 石墨烯才受到全世界科学家的广泛关注[1-3]。

1 石墨烯及其衍生物的基本性质

石墨烯轻质层薄, 理论厚度只有 0.35 nm[4]。表面无含氧基团, 呈化学反应惰性, 耐高温且不易氧

化。石墨烯具备优异的电学特性, 载流子迁移率超过商用硅片 10 倍。单层石墨烯是零带隙导体, 随着石墨烯层数的增加, 由多层石墨烯叠加形成的材料带隙约为 0.04 eV, 具备一定半导体特征[5-8]。

目前可基本实现低成本量产化石墨烯, 常用的合成方法有[9-10]: 机械剥离法、加热 SiC 法、外延生长法、化学气相沉积法、氧化石墨烯(rGO)还原法、有机合成法、碳纳米管切割法、低温膨化法和 PMMA 固相生成法等。其中, 氧化石墨烯还原法因目标产物——还原石墨烯(rGO)量大、效率高而被广泛采用[11-14]。

氧化石墨烯是石墨烯最重要的衍生物, 它保留了 2D 的碳骨架层, 并在边缘连接有羟基(–OH)、环氧基(C–O–C)、羰基(–C=O)和羧基(–COOH)等含氧官能团[15]。氧化石墨烯较石墨烯而言在水溶液或有机溶液中有非常好的分散性, 且易与其它物质发生化学反应[16], 通过与纳米金属粒子、铁氧体或导电聚合物等发生还原反应或引入缺陷, 可改变带隙结构, 进而提高电子、离子、分子或界面极化强度, 增强介电损耗或磁损耗, 从而实现材料对不同频率电磁波损耗。

2 电磁波损耗材料吸波机理

微波吸收材料是指能有效接收入射电磁波, 并使其转化成热能消耗或利用相干相消, 从而使目标回波强度显著减弱的一类电磁功能材料。吸波材料性能良好必须具备两个条件: (1)减少电磁波在材料表面的直接反射, 增加透射强度, 这就需要在设计材料时充分考虑电磁阻抗匹配特性; (2)电磁波一旦进入材料内部, 要实现最大限度衰减和损耗, 就需要考虑材料的损耗特性。根据损耗机制, 吸波材料可分为介电损耗型和磁损耗型, 介电损耗型吸波材料主要通过与电场的相互作用而实现电磁波损耗, 吸收率取决于电导损耗、介电弛豫损耗及谐振损耗; 而磁损耗型吸波材料对电磁波的衰减主要来自于畴壁共振和自然共振、磁滞损耗和后效损耗等磁极化机制。

目前, 常用的微波损耗材料有铁氧体、导电炭黑、石墨和碳纤维及碳化硅纤维等[17-18], 但这些材料存在密度较大、易氧化等固有缺陷。故新型微波吸收材料总是最大限度地追求"轻、薄、宽、强"特性。石墨烯的出现最大程度上满足了新型吸波材料的发展要求, 它轻质、层薄, 电磁波在石墨烯堆叠、自组装后经层间多次折/反射与表面起伏区/褶皱区散射协同耗散增大消耗, 从而提高纯石墨烯的吸波性能。同时利用氧化石墨烯优异的反应还原性, 与不同损耗机制(介电型损耗和磁损耗)材料进行多元复合, 实现对电磁波强损耗的发展要求。

本文针对不同类型石墨烯复合吸波材料的合成方法和结构性能进行综述, 并对其发展方向和应用前景进行展望。

3 石墨烯电磁波损耗材料研究进展

理想的准一维碳纳米管可以看作是由片层状石墨烯卷曲而来, 科学家对碳纳米管的微波损耗特性研究要早于石墨烯材料, 研究表明: 由于碳纳米管电容率较高, 磁导率较低, 故在微波频率下, 较高的磁导率实部与虚部以及与之相适应的电容率是构成宽频带吸波材料的基础。而碳纳米管的微波磁导率相对较低, 限制了其作为微波吸收材料性能的进一步提高, 因此碳纳米管的本征微波吸收性能较弱。对碳纳米管进行氟化活化处理可获得最大反射率为–69 dB 的氟化碳纳米管吸波材料[19], 且通过调控碳纳米管长径比、形貌结构或复合金属粒子、铁氧体、导电高聚物也可提升碳纳米管复合材料对电磁波的损耗[20-21]。所以, 功能化碳纳米管是获得强吸收、宽频带的碳纳米管微波损耗材料的热点研究方向。

如图 1 所示, 石墨烯基电磁波损耗材料研究相对较晚[22], 经历了由二维结构到三维结构, 二元复合到多元复合的发展历程。通过调控微观结构和产物组分, 逐步提升复合材料阻抗匹配性, 对电磁波实现最大损耗。

3.1 二维结构石墨烯电磁波损耗材料

3.1.1 纯石墨烯材料

碳系吸波材料主要包括石墨、炭黑、碳纤维、碳纳米管和石墨烯等, 其中炭黑应用最广, 但作为吸收剂与石墨相似都有高温抗氧化性差的缺点。碳纤维和碳纳米管是近年来研究较多的吸波碳材料, 两者兼具结构与功能一体化等诸多优点, 但也存在表面化学反应惰性, 制备工艺难度大及掺杂改性后力学性能与吸波性能此消彼长的难题。

与传统的碳材料相比, 石墨烯不仅密度更低、比表面积更大, 而且具有更高的电导率和更好的热稳定性, 使其有可能取代传统碳材料而成为新型电磁波吸收材料[23-29]。图 2 展示了 rGO 的典型介电常数及其反射率曲线, 与其它碳材料类似, 单纯石墨烯主要以介电损耗为主, 优异的导电性使石墨烯阻抗
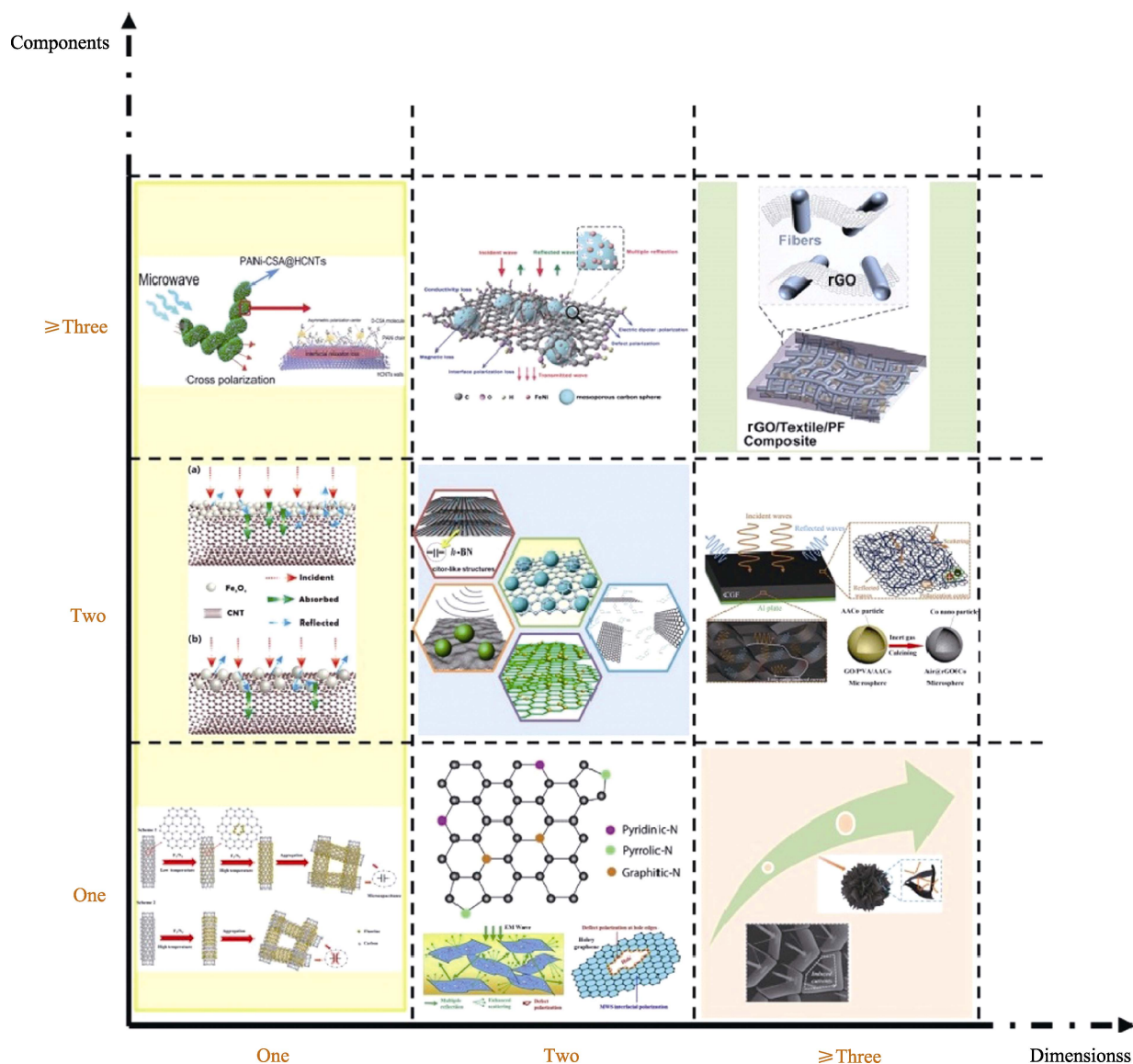
图 1　不同类型和结构的石墨烯基电磁波损耗材料示意图

Fig. 1　Schematic of electromagnetic loss materials based on different types and structures of grapheme

匹配性下降, 对电磁波形成反射, 吸波性能欠佳[30]。研究表明, 增大比表面积、引入缺陷或改变结构[31]可有效提高纯石墨烯材料阻抗匹配性, 增强电子从激发态向费米能级态的跃迁, 增加缺陷处极化驰豫/偶极子驰豫, 从而提高其吸波性能[30-34]。

　　如图 3 所示, 用导电聚合物替代石蜡作为基体与石墨烯复合, 可增强复合材料电磁波损耗能力[35-39]。这是由于导电聚合物链结构上的偶极子跃迁使其具有导电性, 电导率的大小取决于导电高分子的分子链长度及分子结构对偶极子的约束能力, 不同电导率的复合材料呈现不同的吸波性能。

3.1.2　复合/掺杂改性石墨烯材料

3.1.2.1　石墨烯基二元复合材料

　　① 石墨烯/纳米碳复合材料

　　碳纤维和石墨烯组合形成 1D-2D-1D 异质结构

复合材料, 吸波性能较纯石墨烯有较大提升, 最大反射损耗值为–16 dB[33]。而如果将石墨烯引入碳纤维织物内, 所得复合材料最大反射损耗达–27.78 dB[40]。不同电导率的碳纳米微球与石墨烯复合可制备吸波频率可调的复合材料。研究发现层厚为 1.5 mm 时, 复合材料的最大反射损耗为–28.1 dB[32]。

　　碳纳米管的中空结构增加了电磁波的耗散途径, 增强了界面极化效应, 但碳纳米管作为吸波剂与基体材料复合时易团聚, 从而减弱其对电磁波的耗散。引入石墨烯并以共价 C–C 键结合可以改善碳纳米管分散性, 降低表面接触电阻。石墨烯/碳纳米管多层结构增强复合材料极化效应, 增加介电损耗途径, 有效提高电磁波损耗能力。结构和形态差异导致碳纳米管/石墨烯复合材料吸波性能有所不同。煤焦油沥青基或冻结石油沥青基碳材料包覆的碳纳米
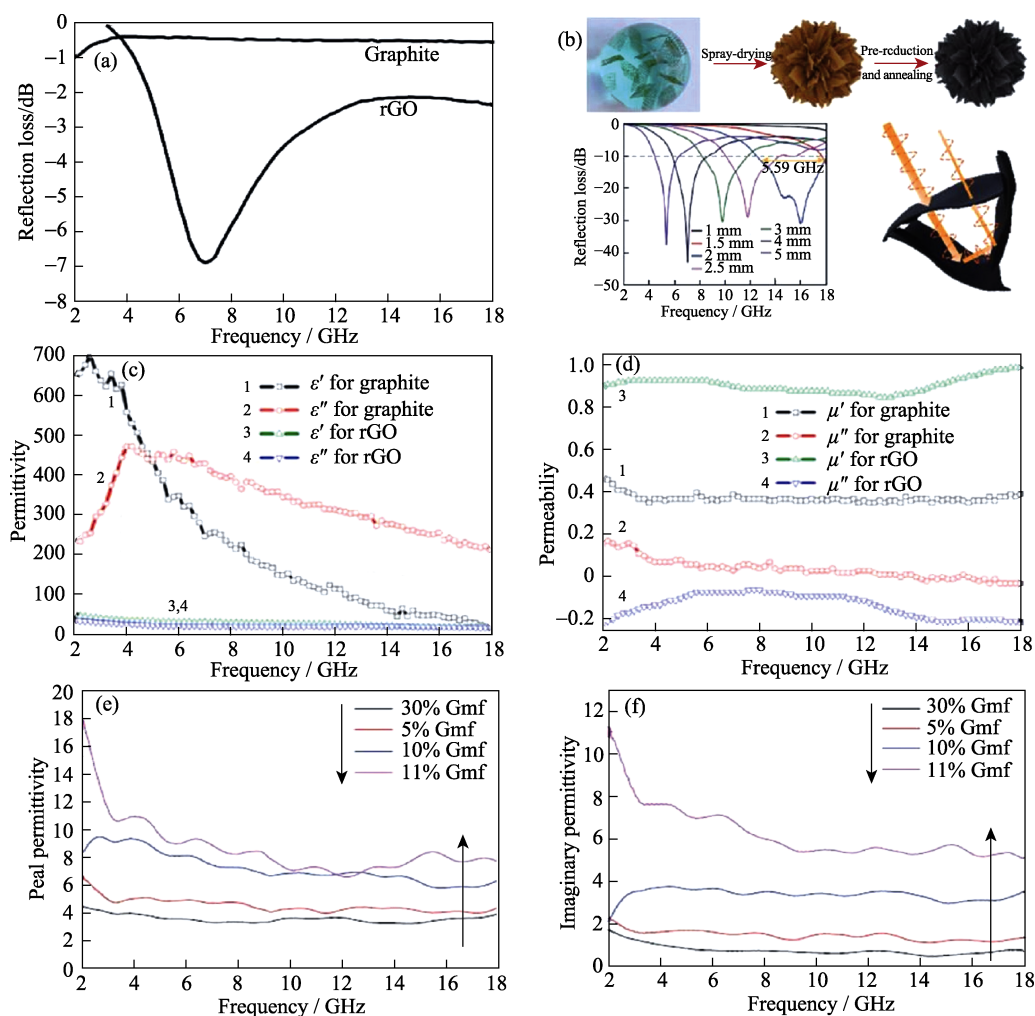
图 2 rGO 的介电常数与反射率曲线

Fig. 2 Complex permittivity and reflection loss curves of rGO

(a) Reflection loss curves of rGO[30]; (b) Schematic illustration of MA mechanism of Gmfs[31]; (c-d) Frequency dependence of relative complex permittivity real part (ε') (c) and imaginary part (ε'') (d) of graphite and rGO[30]; (e-f) Real parts (e) and imaginary parts (f) of permittivity of Gmfs/paraffin composites with different filler contents[31]
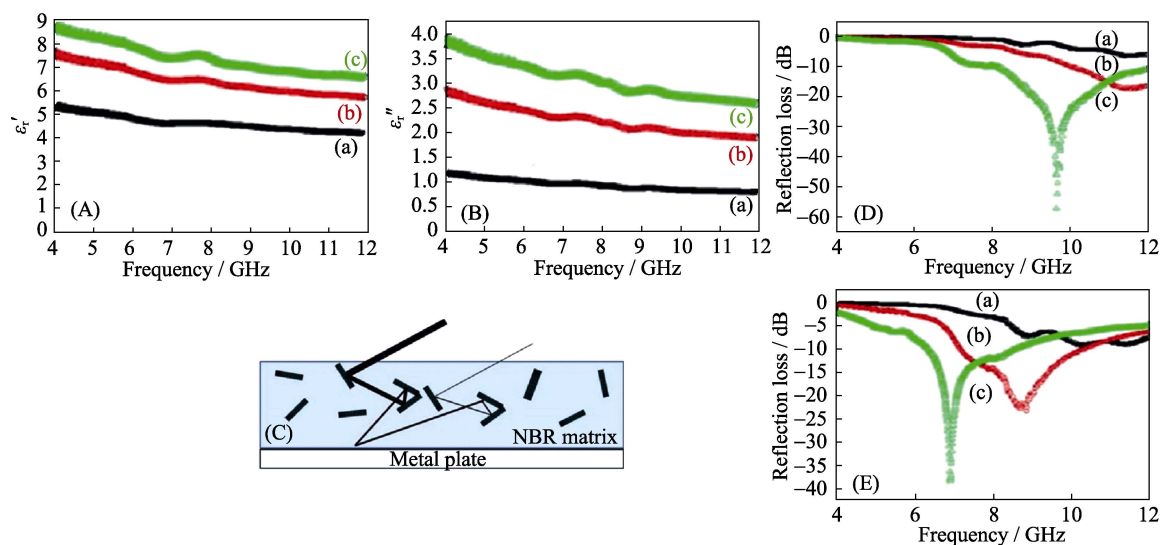

图 3 rGO/丁晴橡胶的介电常数与反射率曲线

Fig. 3 Complex permittivity and reflection loss curves of rGO/NBR composites

(A) Real part of permittivity (ε')[38]; (B) Imaginary part of permittivity (ε'')[38]; (C) A possible absorption mechanism; (D-E) Reflection loss characteristics with thickness: (D) 3 mm and (E) 4 mm for rGO/NBR composites[38]

(a) 2wt% rGO; (b) 4wt% rGO; (c) 10wt% rGO

管/石墨烯在层厚为 2 mm 时最大反射损耗为 –18.9 dB[41]。多壁碳纳米管由于缺陷多和导电性优良, 从而具有更好的吸波性能, 其与石墨烯复合最大反射损耗为–39.5 dB, 且在整个 C 波段(4~8 GHz)和 X 波段(8~12 GHz)的反射损耗均低于–22.5 dB[42]。

② 石墨烯/纳米金属(及其化合物)复合材料

纳米金属是良好的吸波材料, 具有宽频带和兼容性好等特点。根据能带理论, 减小颗粒尺寸易形成不连续能级, 分裂后的能级间隔处于微波能量范围内, 从而产生新的吸波通道增强吸波性能。磁性金属微粉是一类非常重要的纳米金属电磁波吸收剂, 但在使用中也存在易氧化、耐腐蚀能力差、密度较大和低频段吸收性能差等问题。因此, 减小粒径, 进行表面改性、掺杂或包覆是该类材料的主要发展方向。石墨烯的大比表面积有利于改善材料间的相互接触, 提供良好的电子传输通道, 其与金属纳米材料复合可增强界面极化强度, 从而提高高频介电损耗, 增强吸波效果。

通过掺杂 Fe[43]、Ni[44-47]、Co[48-49]等粒子能提高石墨烯基复合材料对电磁波的损耗能力[50]。改变反应条件, Ni、Co 粒子可以从密排六方晶体结构向面心立方晶体结构转变[46, 48], 研究发现, 密排六方结构 Co/石墨烯电磁波损耗能力优于立方面心晶体结构 Co/石墨稀。

纳米金属氧化物 (Co_3O_4[51-52]、ZnO[53-58]、$SrTiO_3$[59]、NiO[60-61] 和 MgO[62])、纳米金属粒子 (CoS_2[63]、$NiCO_2$[64]、MoS_2[65])、纳米金属片(层状 CuS[66]、层状 FeCoB[67])、层状羰基铁[68-69](FCI)和

金属有机框架化合物(MOF)[70]与石墨烯复合大大提升了对电磁波的损耗能力。通过调控反应条件可进一步提高产物对电磁波的损耗, 如 $Co(NO_3)_2 \cdot 6H_2O$ 与氧化石墨烯发生还原反应, 实现生成物由 Co_3O_4 向 Co 的转变[51, 71], 当产物为 Co_3O_4/Co/石墨烯时最大反射损耗达–52.8 dB; 优化反应物结构或石墨烯形貌[72]也能达到同样效果, 如四针状 ZnO[56]、星形 ZnO[57]或空心 ZnO 多孔微球[58]分别与石墨烯复合, 所得材料最大反射损耗值达–77.5 dB。图 4 为用于石墨烯复合的部分典型纳米金属化合物的结构形貌。

③ 石墨烯/铁氧体复合材料

铁氧体属于双复介电材料, 既有亚铁磁性又有介电特性。虽然铁氧体吸波材料具有吸收性能优异、成本低廉等优点, 但纯铁氧体由于密度较大、高温表现欠佳和吸收频带窄等缺点难以满足高性能吸波材料要求, 需将铁氧体粉末分散到非磁性微粒中制成复合铁氧体材料来改善产物吸波性能。将铁氧体与石墨烯复合可以发挥各自优点, 通过多种损耗途径吸收电磁波, 达到密度小且高效吸收的效果。

Luo 等[73]通过计算模拟预测石蜡基片状羰基铁粉/蜂窝状石墨烯的最大反射损耗可达–27.5 dB, 8~12 GHz 时全频段反射损耗低于–10 dB, 且蜂窝状石墨烯对电磁波的损耗起到非常重要的作用。由此可见, 改变基体材料种类、反应物结构及各组分间相互结合状态可以提高复合材料吸波性能, Fe_3O_4/石墨烯复合材料体系存在类似的情况。虽然 Fe_3O_4/石墨烯最大反射损耗仅为–22.7 dB[74-75], 但通过改善 Fe_3O_4 在石墨烯中的分散性[76-77], 改变 Fe_3O_4[78-80]

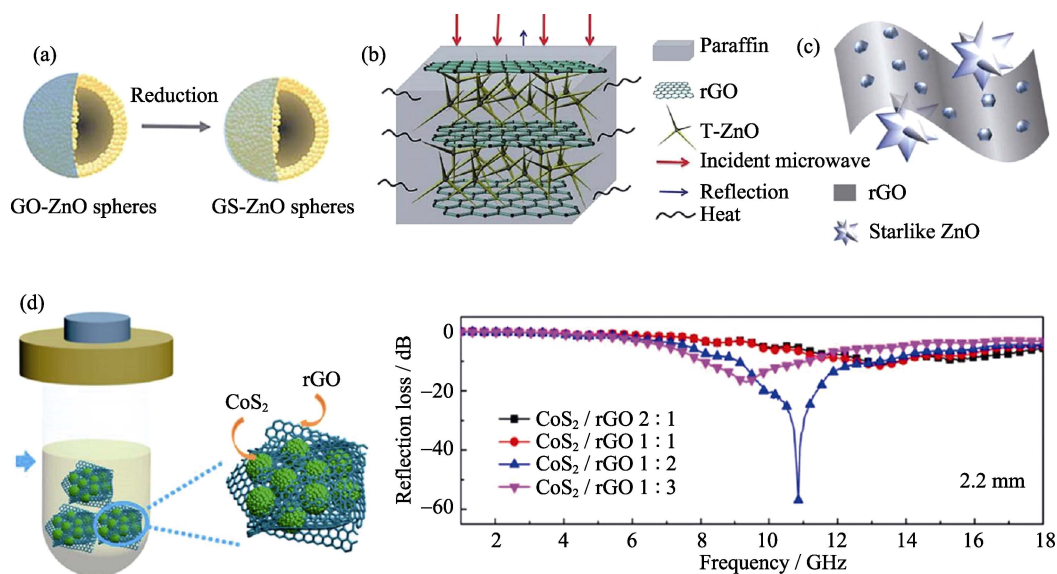图 4　用于石墨烯复合的部分典型纳米金属化合物的结构形貌

Fig. 4　Typical microstructures of metal nanomaterials for graphene composites

(a) ZnO spheres[55]; (b) T-ZnO[56]; (c) Starlike-ZnO[57]; (d) CoS_2 spheres and reflection loss curves[63]

(胶囊状 Fe_3O_4、团簇状 Fe_3O_4、亚微球状 Fe_3O_4 和碳包覆顺磁性 Fe_3O_4)或石墨烯形貌结构[81-82]可以增强材料对电磁波的损耗。调控反应条件(如提升反应温度)，会发生由 α-Fe_2O_3 向 γ-Fe_2O_3 再向 Fe_3O_4 晶体结构的转变过程[83]，晶体结构的改变对不同结构铁的氧化物/石墨烯复合材料电磁波损耗能力影响极大。枸杞状 α-Fe_2O_3/石墨烯[84]在 5.6 GHz 时最大反射损耗为–46.6 dB，经表面修饰的团簇状纳米胶体 γ-Fe_2O_3/石墨烯[85]最大反射损耗为−59.65 dB。对 α-Fe_2O_3 晶体结构进行修饰，可得空心纳米棒状 α-Fe_2O_3/石墨烯复合材料[86]，其最大反射损耗为−71.4 dB，在 Fe_2O_3/石墨烯复合材料中添加 TiO_2[87]、SnO_2[88]都能提升材料对电磁波的损耗能力。

$BiFeO_3$ 纳米线[89]、$MgFe_2O_4$ 纳米棒[90]、$MnFe_2O_4$[91]、$BaFe_{12}O_{19}$[92]、$CoFe_2O_4$[93-95]、$BaTiO_3$[96]、$Bi_2Fe_4O_9$[97]、$Ni_{0.5}Zn_{0.5}Fe_2O_4$[98]和 $NiFe_2O_4$[99-102]等与石墨烯复合都有良好的电磁波损耗效果，通过调控石墨烯形态及 $Bi_2Fe_4O_9$ 结构[97]，可以获得最大反射损耗为–71.88 dB 的多孔 $Bi_2Fe_4O_9$ 微球/石墨烯复合材料。用氢气/氨气混合气氛对 $CoFe_2O_4$/石墨烯还原得到 FeCo/石墨烯复合材料，8.9 GHz 时最大反射损耗为–40.2 dB[95]。

④ 石墨烯/导电聚合物复合材料

导电聚合物具有密度低、结构多样和环境适应性好等优点，经掺杂修饰后的导电聚合物复合材料的导电性具有在绝缘体、半导体和金属性范围内变化的特性，因此可通过控制导电聚合物电导率调节其电磁波损耗能力。利用石墨烯修饰导电聚合物，可以有效改善产物阻抗匹配性，降低层厚度，使电导率可调，从而达到最优吸波效果。

常见制备石墨烯–导电聚合物纳米复合材料的基体包括：聚吡咯、丙烯腈丁二烯、聚甲基丙烯酸甲酯、聚苯胺和环氧乙烷等。其中，聚环氧乙烷/石墨烯的最大反射损耗为–38.8 dB[39]，多孔丙烯腈丁二烯橡胶/氧化石墨烯的最大反射损耗为–57 dB[38]。6 层聚甲基丙烯酸甲酯/石墨烯在 30 GHz 左右电磁波损耗效果最佳[103]。

⑤ 石墨烯/非金属复合材料

由于硼、氮原子与碳原子结构相似，相互结合可形成 n-型或 p-型半导体，且通过调节硼、氮和碳原子组成比例可以获得一系列电磁参数可调的 B-C-N 吸波材料[104-105]。研究显示掺氮石墨烯中吡咯氮位可诱导材料磁损耗，在 12.7 GHz 时最大反射损耗为–11.3 dB[106]。掺杂碳纤维的 BCN 复合材料在 9.41 GHz 时最大反射损耗为–29.23 dB[107]。纳米 BNNC/石墨烯的最大反射损耗达–32.38 dB，且当层

厚为 1.5~5.0 mm 时，有效反射频宽为 3.49~17.28 GHz[105]。

本课题组利用硼酸、尿素及氨硼烷和氧化石墨烯反应制备 h-BN/石墨烯复合材料[108-109]，测量发现，面内掺杂的 BCN 材料最大反射损耗为–33.6 dB，层间掺杂的 BCN 材料最大反射损耗为–40.5 dB。

3.1.2.2 石墨烯基三元复合材料

相较石墨烯基二元复合材料，三元及以上多元组分复合可进一步改善产物阻抗匹配性，提升电磁波损耗能力。目前，三元复合材料主要以介电损耗和磁损耗协同消耗机理为主。其中，石墨烯较大的比表面积在复合材料中可以形成导电网络，载流子受电磁波激发在导电网络中取向运动从而产生介电损耗；加载磁性材料且通过调控负载的密度、形貌、结构和各组元含量，增加复合材料磁损耗；随着组元的增多，各组元材料在复介电常数上的差值导致的界面散射，加剧了材料对电磁波的损耗作用。故需将不同形貌和结构的铁氧体、纳米金属、导电聚合物及纳米碳材料与石墨烯结合，制备集吸波和承载于一体的具有优异化学、力学和电学性能的高效电磁波损耗材料[110-115]。

通过引入碳纳米管[116-120](沙棘状单壁碳纳米管[119]、多壁碳纳米管[120])、纳米棒状 ZnO[121]、片层 MoS_2[122]可以有效阻止 Fe_3O_4/石墨烯复合材料中各组分团聚，提高产物吸波性能。经磁性中空 $CoFe_2O_4$ 微粒修饰的多壁碳纳米管与石墨烯的复合材料的最大反射损耗达–46.8 dB，有效反射损耗频宽为 13.1 GHz[123]。Co_3O_4 和氧化石墨烯反应可制备经 Co 离子催化原位生成碳纳米管的 Co@碳纳米管/石墨烯复合材料[124]，通过调节反应温度，调控碳纳米管生长含量，实现对不同频率电磁波的损耗。当反应温度分别为 400 和 450℃时，最大反射损耗可达–65.6 和–58.1 dB。

用氰酸酯树脂[125]或聚(对亚苯基苯并二恶唑)(PBO)[126]修饰多壁碳纳米管/石墨烯不仅可以提升产物吸波性能，还可以提高其耐高温特性。用聚乙烯吡咯烷酮修饰的片状羰基铁/石墨烯[127]最大反射损耗为–27.59 dB，将片状羰基铁研磨成粉可大幅提升材料对电磁损耗能力[128]。用环氧树脂代替聚乙烯吡咯烷酮制备环氧树脂/片状羰基铁/石墨烯最大反射损耗值为–32.3 dB[129]。二元组分聚苯胺/石墨烯复合材料[130-132]的最大反射损耗为–45.1 dB。用 Cu_2O[133]、Co_3O_4[134]、$CoFe_2O_4$[135]、$NiFe_2O_4$[136]、$CuFe_{10}Al_2O_{19}$[137]或 CNT-Fe_3O_4[138]改性可有效提高材料层间阻抗匹配性，增强界面极化作用。其中，

CuFe$_{10}$Al$_2$O$_{19}$/石墨烯/聚苯胺电磁波损耗能力最优，最大反射损耗达到–63.6 dB。经棒状聚苯胺修饰的 Fe$_3$O$_4$/C/石墨烯复合材料[139]中棒状聚苯胺是否共价连接对其吸波性能影响极大，共价键合聚苯胺修饰的复合材料吸波性能远优于非共价修饰效果。经测试所得材料在层厚 3 mm、11.4 GHz 时，最大反射损耗为–44.2 dB。

3.2　三维结构石墨烯电磁波损耗材料

3.2.1　"核–壳"结构石墨烯基复合材料

"核–壳"结构复合材料是通过化学键或其它相互作用包覆形成的有序组装结构，其核心原子、外壳原子以及可能存在的中间层或空隙层之间的电子交换使整个材料性能发生质变，从而改善不同组分原有的缺陷，提高材料对电磁波的损耗能力。

石墨烯修饰的"核–壳"结构复合材料电磁波损耗能力优异，多孔碳纳米微球@FeNi /石墨烯最大反射损耗为–45.2 dB[140]，CoNi@SiO$_2$/石墨烯最大反射损耗达到–50.3 dB[141]。铁氧体/石墨烯复合材料 (中空结构 Fe$_3$O$_4$@Fe/石墨烯[142]、纳米棒状 SiO$_2$@Fe$_3$O$_4$/石墨烯[143]、多孔状 ZnO@p-Fe$_3$O$_4$/石墨烯[120]、FeCo@SiO$_2$/石墨烯[144]、ZnFe$_2$O$_4$@SiO$_2$/石墨烯[145]及 MoS$_2$@Fe$_3$O$_4$/石墨烯[122])不仅电磁波损耗能力优异，而且实现了材料轻量化要求。"核–壳"结构 Fe$_3$O$_4$@聚吡咯/石墨烯三元复合材料[146]最大反射损耗为–25.1 dB，通过调控聚吡咯形态，如树枝状聚吡咯/CoFe$_2$O$_4$/石墨烯[147]和聚吡咯纳米棒/石墨烯复合材料[148]可以具有更加优异的电磁波损耗能力。

"核–壳"结构 CoNi@SiO$_2$@石墨烯–聚苯胺四元复合材料的最大反射损耗达–43 dB[149]。掺杂"核–壳–壳"结构 Fe$_3$O$_4$@SiO$_2$@聚苯胺的石墨烯复合材料的最大反射损耗为–40.7 dB[150]，用聚苯胺替换 NiO，可以制备多层包覆结构的石墨烯@Fe$_3$O$_4$@SiO$_2$@NiO 复合材料[151]，当厚度为 1.8 mm、14.6 GHz 时，最大反射损耗–51.5 dB。Fe$_3$O$_4$@Fe/ZnO/石墨烯四元复合材料[152]在层厚为 2.5~5 mm 时，最大反射损耗均低于–30 dB，且反射损耗值低于–20 dB 的频宽为 7.3 GHz。

3.2.2　"三明治"结构石墨烯基复合材料

"三明治"结构 Ag/NiO/聚苯胺/石墨烯[153]和 Fe$_3$O$_4$/WO$_3$/聚苯胺/石墨烯[154]由于介电损耗和磁损耗的协同作用，电磁损耗能力优异。利用碳纳米管修饰的 BaFe$_{12}$O$_{19}$/三维石墨烯[155]最大反射损耗值为–18.35 dB。而掺杂 Ni 的石墨烯/C 在 1.6 mm、13.9 GHz 时，最大反射损耗为–34.2 dB[156]。掺杂 ZnO 的 CoO@C/石墨烯在层厚 2.6 mm, 11.3 GHz 时最

大反射损耗达–51.1 dB, 有效反射频宽为 4.7 GHz[157]。

3.2.3　"多孔泡沫"结构石墨烯基复合材料

微观结构的变化可以显著改善材料吸波性能，宏观结构的影响则更为显著[158-169]。轻质多孔石墨烯泡沫在 2~110 GHz 范围内吸波效果良好，且可通过简单物理压缩对电磁波损耗实现调控。研究发现经不同浓度反应溶液和处理温度制备的石墨烯泡沫吸波性能与微结构中的碳/氧比例和共轭碳畴尺寸密切相关。

掺杂 Ni 粒子的多孔石墨烯发泡材料最大反射损耗达–59.7 dB[170]；一维纳米金属线(ZnO 纳米线[171]、Si$_3$N$_4$ 纳米线、SiC 纳米线[172-173])/石墨烯复合材料吸波性能优异且高温条件下材料结构保持长久稳定 (质量损失低于 10%)；掺杂 TiO$_2$[174]、Mn$_3$O$_4$[175]和 Fe$_3$O$_4$[176]的石墨烯气凝胶具有轻质和反射耗散强等特点；Al$_2$O$_3$[177]、SiCN[178]与石墨烯烧结可合成具有优良力学性能及良好电磁波损耗特性的陶瓷材料，这为新材料在军事装备上的应用奠定了良好的基础。

4　吸波性能的影响因素

纯石墨烯材料多采用化学氧化还原法制备，大量存在的缺陷及残留的含氧基团不仅可以改善石墨烯的阻抗匹配性，还可以有效提高其吸波性能。通过水/溶剂热法、共沉淀法、溶胶–凝胶法、原位聚合溶液共混法、熔融共混法及冷冻干燥法可以制备功能化的石墨烯基复合材料，制备过程要求尽可能减小晶体颗粒尺寸，提高不同组分之间的分散性，使得反应过程容易控制，从而通过掺杂/改性达到增强石墨烯基复合材料电磁波损耗能力的作用[179-187]。

目前，基于石墨烯的吸波材料：在制备方法上，二元复合材料多采用一步法，三元复合材料多采用两步法；在结构上，三维多孔结构逐渐受到人们的重视；在复合基材上，趋向于选用多元的不同吸波机理的吸波基材。下面分别从损耗机制、组分数量及微观结构三个方面对石墨烯基电磁波损耗材料吸波性能的影响因素进行分析。图 5 为典型石墨烯基电磁波损耗材料最大反射率值与厚度的关系。

4.1　损耗机制影响因素

纯石墨烯是介电损耗型吸波材料，引入吡咯位氮原子可诱发产生磁损耗，而将铁氧体材料、金属粒子或金属化合物与石墨烯通过单一或与多元组分搭配复合可进一步提升产物电磁波损耗能力(如图5所示)。这主要得益于多元组分间良好的阻抗匹配性及介电损耗和磁损耗的协同消耗机理。例如，Yuan 等[47]
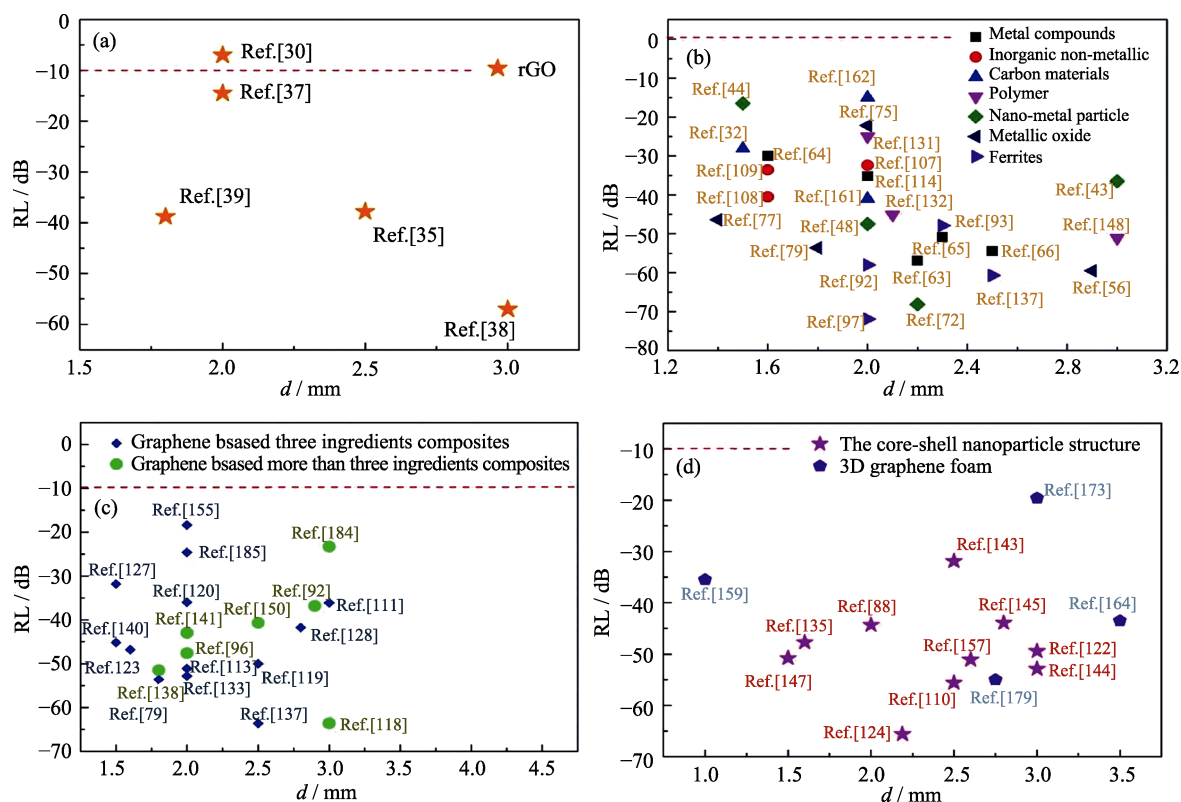
图 5　石墨烯基电磁波损耗材料最大反射率值与厚度的关系

Fig. 5　Schematic of relationship between maximum reflectivity and thickness of graphene based electromagnetic wave loss material

(a) rGO; (b) Two ingredients; (c) Three or more ingredients; (d) Three-dimensional structure

制备的 Ni 粒子掺杂的 N-石墨烯复合材料, 在 2~18 GHz 频率范围内, 介电损耗角正切值($\tan\delta_e$)均大于 0.4, 说明介电损耗发生在所有频率范围内, 同时磁损耗角正切值($\tan\delta_m$)均小于 0.4, 表明磁损耗小于介电损耗, 即所合成复合材料主要依赖于介电损耗。再如, Zhou 等[141]合成的 $CoNi@SiO_2@RGO$ 复合材料, 在石墨烯中加入 $CoNi@SiO_2$ 后电导率降低, 使得介电常数的实部和虚部值降低, 介电损耗减小, 但增强了复合材料阻抗匹配性。在 2~18 GHz 频率范围内, 介电损耗角正切值($\tan\delta_e$)均小于 0.4, 但在约 17 GHz 左右时出现最高峰。同时磁损耗角正切值($\tan\delta_m$)在 0~16 GHz 均大于 0, 说明磁损耗发生在所有频率范围内, 在约 9 GHz 时出现最高峰且大于同频率下的介电损耗角正切值, 表明 $CoNi@SiO_2@RGO$ 复合材料在介电损耗和磁损耗协同作用下增加了对电磁波的损耗。

4.2　组分数量影响因素

由图 5 可知, 二维结构石墨烯复合材料中, 三元/多元石墨烯基电磁波损耗材料的电磁波损耗能力整体优于二元复合材料, 这是由于多层材料各组分间良好的阻抗匹配性、增强的界面/层间极化效应、介电损耗和磁损耗相互协同效应及粒子间的空隙对电

磁波的折/反射效应叠加所致。但组分过多会造成材料密度增大、反应过程难以精确控制、基材分散不均匀、界面相容性差等问题。因此石墨烯基电磁波损耗材料应以不多于三组分组合为主。

4.3　结构影响因素

无论是改变反应条件, 还是各组分结合状态, 都会促使产物形貌及微观结构发生变化。研究发现, 形貌和结构的差异对复合材料电磁波损耗能力影响很大。通过调控产物形貌及结构, 改变阻抗匹配性, 增加界面及层间极化作用, 可以提高复合材料吸波性能。如 Chen 等[31]通过对微结构的设计制备了一种 "花朵" 结构的多孔石墨烯材料, 通过利用 3D 多孔褶皱石墨烯结构构建 3D 导电网络, 对微波实现多重反射, 从而大幅提升材料对电磁波的损耗能力, 使最大反射损耗达到−42.9 dB。Zhang 等[158]将石墨烯发泡制备多孔石墨烯泡沫, 所得材料在全波段都具有非常优异的吸波性能。最近研究发现 3D 石墨烯结构对 THz 频段也具有良好的损耗作用[188]。

综上所述, 三维结构石墨烯基复合材料较二维结构而言对电磁波有更大的损耗途径及折/反射空间, 且兼具轻质和耐高温等特性, 从而成为石墨烯基电磁波损耗材料的重要发展方向。

表 1　典型石墨烯基电磁波损耗材料性能统计表
Table 1　Comparison of EMW absorption properties of the materials based on graphene

Filler	Matrix	Reflection Loss/dB	Optimum thickness/mm	Effective bandwidth in 2–18 GHz/GHz	Ref.
rGO	Paraffin	−7.0	2.0	–	[30]
rGO	PEO	−38.8	1.8	4.10	[39]
Pitch carbon coating grapheme/carbon nanotubes	Paraffin	−18.9	2.0	~4.0	[41]
rGO/ polyaniline	Paraffin	−25.0	2.0	4.0	[131]
rGO-BN	Paraffin	−40.5	1.6	5.0	[108]
α-cubic Co/GN	Paraffin	−47.5	2.0	5.3	[48]
Fe_3O_4/N-graphene	Paraffin	−53.6	1.8	5.0	[79]
Tetrapod-like ZnO/ rGO	Paraffin	−59.5	2.9	6.9	[56]
MCl/rGO/PVP	Paraffin	−41.7	2.8	12.52	[128]
rGO/$CoFe_2O_4$/MWCNT	Paraffin	−46.8	1.6	3.44	[123]
Gr/Ti@CNT/Fe_3O_4/PANI	TPU	−63.57	3.0	4.20	[118]
Yolk-shell CoO@Co NPs/ZnO NPs/graphene	Paraffin	−51.1	2.6	4.70	[157]
rGO foams	–	−33.2	1.0	~14.00	[158]
3D-rGO/silica textile/PF	–	−36.0	3.3	4.20	[160]
Porous graphene microflowers	Paraffin	−42.8	2.0	5.59	[31]

5　结束语

本文系统地总结了近几年来在石墨烯基电磁波损耗复合材料方面的工作, 其中典型石墨烯基电磁波损耗复合材料吸波性能如表 1 所示。目前的研究已经证明石墨烯以其独特的物理结构、优异的力学和电学性能, 在改善复合材料不同组分间的阻抗匹配性, 提高材料电磁波损耗能力等方面有着巨大的应用潜力。但纯石墨烯材料作为介电损耗型吸波剂, 对电磁波损耗效果欠佳, 需要对其结构进行优化, 同时与其它物质复合, 从而可以制备轻质、高效且力学性能优异的电磁波损耗材料。总之, 石墨烯基电磁波损耗材料得到了科学界的广泛关注, 作为新型吸波材料已成为未来应用的研究重点, 但其在以下几个研究方向仍存在一些挑战, 值得进一步深入研究:

1) 多组分石墨烯基电磁波损耗材料吸波机理研究;

2) 三维复合结构石墨烯基电磁波损耗材料研究;

3) 石墨烯基电磁波损耗材料功能与结构一体化设计研究。

为了进一步提升石墨烯基电磁波损耗材料的吸波性能, 尽快在相关领域开展应用。必须开发规模化、量产化的石墨烯制备技术和复合工艺, 提高石墨烯质量。在减重和增效基础上实现功能与结构一体化设计目标, 这不仅会推动军事隐形材料的发展, 还会在防护电磁波辐射等民用方面发挥重要作用。

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