

花状Zn-MOF衍生碳@MoS₂复合材料制备及吸波性能

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摘要:采用Zn-MOF(MOF为金属有机骨架)制备纳米多孔碳材料,通过自组装法将多孔碳与花状MoS₂结合,制备出具有规整有序结构的花状Zn-MOF衍生碳@MoS₂复合吸波材料。基于Zn-MOF衍生纳米多孔碳的高孔隙率、大比表面积,MoS₂的花状结构引起的电磁波多次反射和散射,以及MoS₂和Zn-MOF衍生碳之间存在的强极化效应、良好的阻抗匹配和协同作用,Zn-MOF衍生碳@MoS₂在频率为9.28 GHz时的最佳反射损耗达到-49.68 dB,表现出优异的电磁波吸收性能。

关键词:电磁波吸收; Zn-MOF衍生碳; 花状MoS₂; 复合材料

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Preparation and wave-absorbing properties of flower-like Zn-MOF-derived carbon@MoS₂ composites

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Abstract: The polyhedral structure of Zn-MOF (MOF: metal-organic framework) was synthesized by the coordination of zinc nitrate hexahydrate and 2-methylimidazole. The Zn-MOF was calcined at high temperatures in a nitrogen atmosphere to prepare nanoporous carbon materials. In the process of preparation of flower-like MoS₂ by solvothermal reaction, the Zn-MOF-derived nanoporous carbon was introduced and combined with flower-like MoS₂ through self-assembly to prepare flower-like Zn-MOF-derived carbon@MoS₂ composite absorbing material with regular and ordered structure. A series of characterization and performance tests were carried out to study the physical properties and absorbing properties of the composites. The particle size of polyhedral Zn-MOF-derived nanoporous carbon was 80 nm and encased in 1 μm flower-like MoS₂. With the increase of the amount of Zn-MOF-derived carbon, the electromagnetic wave absorption performance of the flower-like Zn-MOF-derived carbon@MoS₂ composites firstly increased and then decreased. Based on the high porosity and large specific surface area of Zn-MOF-derived porous carbon and the flower-like structure of MoS₂, the electromagnetic wave was reflected and scattered many times, and there was a strong polarization effect, good impedance matching, and synergistic effect between MoS₂ and Zn-MOF-derived carbon. When the additional amount (mass fraction) of flower-like Zn-MOF-derived carbon@MoS₂ in paraffin was 25%, the frequency was 9.28 GHz, the matching thickness was 3 mm, and the effective absorption bandwidth was 3.04 GHz, the optimal reflection loss reached -49.68 dB, showing excellent electromagnetic wave absorption performance.

Keywords: electromagnetic wave absorption; Zn-MOF-derived carbon; flower MoS₂; composite materials

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随着信息技术革命新时代的到来,使用通信设备引起的电磁干扰不仅对军事应用产生不利影响,而且严重影响人体健康^[1-2]。因此,研究如何减少或避免这些问题是非常必要的,目前电磁吸波材料是解决上述电磁危害问题最有效的方法。在实际应用中,合格的电磁波吸收材料应具有电磁波吸收能力强、吸收带宽宽、吸收体匹配厚度薄、重量轻等特点^[3]。在设计过程中,适当的阻抗匹配和强大的衰减能力对于高性能吸收器很重要^[4]。尽管已经制备了一定数量的单组分电磁波吸收剂,例如碳材料、非磁性金属颗粒、磁性颗粒、导电聚合物和半导体材料^[5-9],但单组分吸波材料低衰减能力和固有阻抗不匹配限制了它们进一步应用^[10-11]。因此,构建多组分合理微观结构的电磁波吸收材料仍是主要研究方向。

金属有机骨架(MOF)是由金属离子和有机配体组装而成的一种高度规整多孔微纳米结构材料,对电磁波吸收效果显著。大量研究表明,微纳米结构的界面间隙可以作为极化中心,调节介电常数,多孔微结构可以诱导更多的自由空间和界面,促进入射电磁波的多重反射和散射行为,增强损耗能力,改善阻抗匹配^[12]。ZIF系列独特的类沸石结构材料更是被运用到各个领域^[13-17],尤其是ZIF基复合材料及其衍生物,在电磁波干涉、屏蔽和吸收领域都被广泛关注。Li等^[18]以ZIF-67为前驱体制备了Co/C多孔微球,该复合材料的多孔中空结构提高了其介电损耗能力,抑制了碳基体与入射电磁波之间的负相互作用,极大地提升了电磁波衰减性能。热解温度600 °C时,匹配厚度为1.53 mm,最佳反射损耗为-66.5 dB,有效吸收带宽为3.2 GHz。Wang等^[19]在800 °C直接热解MOF-74合成了Co/C核壳纳米复合材料,多孔碳骨架介电损耗、金属钴磁损耗以及核壳结构界面极化是其强电磁波吸收的原因。在频率为11.85 GHz时,其最佳反射损耗为-62.12 dB,匹配厚度为2.4 mm,对应的有效吸收带宽为4.6 GHz。

过渡金属硫化物二硫化钼(MoS₂)是一种新型二维半导体材料,由共价键S—Mo—S组成层状结构,由于其高导电性和极化效应,近年来被用作新型微波吸收材料^[20]。Liang等^[21]通过水热法合成的二维MoS₂纳米片具有优异的电磁波吸收性能,其高介电损耗和界面极化使MoS₂纳米片在频率为12 GHz时,最佳反射损耗达到-47.8 dB,匹配厚度为2.0 mm,有效吸收带宽为5 GHz。Zhou等^[22]发现花状MoS₂纳米颗粒比片状MoS₂纳米颗粒表现出更强的

电磁波吸收性能。在匹配厚度为2.4 mm时,具有最佳反射损耗-39.20 dB,有效吸收带宽为4.48 GHz。因此,将具有纳米结构的Zn-MOF衍生碳和花状MoS₂结合,实现对电磁波高效吸收,对开发新型吸波体有重要参考意义。

以Zn-MOF为前驱体,设计了一种新型Zn-MOF衍生碳@MoS₂复合材料。Zn-MOF衍生碳有利于电导损耗和极化弛豫,相互连接的孔和花状结构产生丰富的极化位点,促进了界面极化、电磁波反射和散射损失,这种组合在提高电磁波吸收性能方面发挥着关键作用。此外,由于Zn-MOF衍生碳基体与花状MoS₂之间的强协同作用,可以有效提高阻抗匹配和衰减能力。得益于这些特性,该复合材料获得了优异的电磁波吸收性能,为高性能电磁波的合理设计提供了新思路。

1 实验部分

1.1 实验材料

2-甲基咪唑(2-MeIM)、六水合硝酸锌(Zn(NO₃)₂·6H₂O)、甲醇、二水合钼酸钠(Na₂MoO₄·2H₂O)、硫脲(CH₄N₂S)、去离子水、切片石蜡均购自上海泰坦科技股份有限公司。

1.2 Zn-MOF衍生碳的制备

Zn-MOF衍生碳颗粒通过Zn-MOF的合成和碳化处理两步工艺制备^[23]。首先,通过简单的沉淀反应合成Zn-MOF。室温下,先将2.500 g Zn(NO₃)₂·6H₂O和3.382 g 2-MeIM分别溶于135 mL甲醇溶液中,剧烈搅拌。然后将含有Zn(NO₃)₂·6H₂O的甲醇溶液缓慢滴入含有Zn(NO₃)₂·6H₂O的甲醇溶液中,搅拌4 h,静置8 h,离心收集白色产物,用甲醇多次洗涤。最后,将得到的Zn-MOF白色固体在真空烘箱中60 °C干燥12 h。然后,将Zn-MOF白色固体研磨成粉末后,放入管式炉中在N₂气氛下以5 °C·min⁻¹的升温速率在800 °C下煅烧2 h,得到黑色Zn-MOF衍生碳(标记为ZC)颗粒。

1.3 Zn-MOF衍生碳@MoS₂复合材料的制备

将0.32 g ZC分散在60 mL去离子水中。将1.44 g Na₂MoO₄·2H₂O和1.71 g CH₄N₂S在磁力搅拌下溶解在上述悬浮液中,超声10 min,再搅拌1 h。随后,将得到的溶液转移到100 mL内衬为聚四氟乙烯的不锈钢高压釜中,并在200 °C下溶剂热反应24 h。反应结束后待高压反应釜自然冷却至室温,通过离心机分离沉淀物,并用乙醇和去离子水洗涤数

次以纯化样品,在60 °C真空烘箱中干燥12 h得到ZC、MoS₂质量比1:3的Zn-MOF衍生碳@MoS₂(标记为ZCM-1:3)。为探索不同ZC添加量对最终产物吸波性能的影响,以找到最佳质量比,另设置2组不同ZC、MoS₂质量比(1:4、1:2)的实验,所得产物分别记为ZCM-1:4、ZCM-1:2。

1.4 样品表征

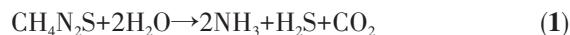
所制备材料的晶体结构通过荷兰Nalytical公司生产的X'pert Prow MPD型X射线衍射分析仪(XRD,Cu K α 辐射,波长0.154 nm,电压40 kV,电流40 mA,扫描范围5°~90°)确定。拉曼光谱由具有488 nm激光激发的拉曼光谱系统(HORIBA,型号HR-800)记录。通过场发射扫描电子显微镜(FESEM,JEOL,JSM-7001F型,电压10 kV)观察样品形态和结构。通过英国Kratos Axis公司生产的Ultra DLD型X射线光电子能谱仪(XPS)分析样品的元素及价态。电磁参数通过矢量网络分析仪(VNA,型号AV 3672B)在2~18 GHz范围内进行测试。

2 结果与讨论

2.1 ZCM复合材料形成机理分析

Zn²⁺与2-MeIM通过配位结合形成多面体结构

的Zn-MOF,在碳化过程中2-MeIM充当氮源和碳源。在MoS₂合成过程中引入ZC,Na₂MoO₄·2H₂O作为Mo源,CH₄N₂S作为S源同时充当反应的还原剂。当溶液中的温度和压力达到一定条件时,CH₄N₂S会分解生成H₂S和NH₃(式1),H₂S在溶液中进一步水解,以H⁺和S²⁻的形式存在(式2)。在S²⁻的作用下,Mo⁶⁺被还原为Mo⁴⁺,形成化学性质稳定的MoS₂核(式3)^[24]。由于静电相互作用和范德瓦尔斯力,MoS₂核吸附在ZC表面上,并原位生长成纳米片。然后,在表面能的驱动下,纳米片相互聚集自组装成花状MoS₂纳米球,而ZC颗粒被嵌入在MoS₂纳米片的间隔中^[25-27]。



2.2 结构和形貌分析

图1a为Zn-MOF、ZC、MoS₂以及ZCM-1:3的XRD图。Zn-MOF具有良好的结晶度和纯度^[28],ZCM-1:3在2θ=25°附近显示出一个石墨型碳片的典型(002)层间峰^[29],MoS₂分别在14.1°、33.4°、39.5°和59.0°处有4个衍射峰,分别归属于(002)、(101)、(103)和(110)晶面^[30],对于ZCM-1:3,除了具有对应ZC和MoS₂的特征峰外,没有观察到其他杂峰。该结果证

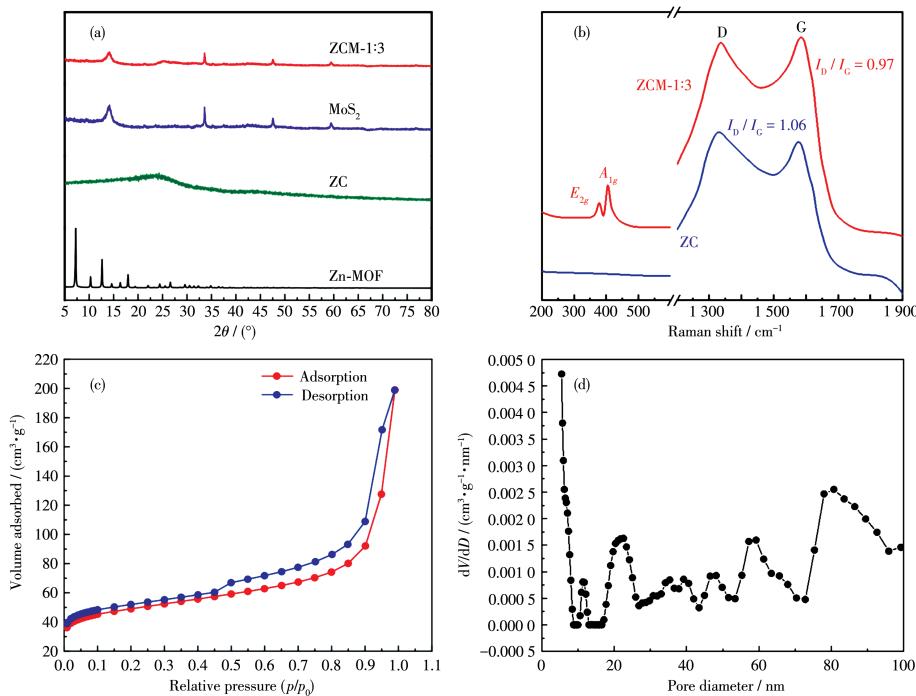


图1 (a) Zn-MOF、ZC、MoS₂以及ZCM-1:3的XRD图;(b) ZC和ZCM-1:3的拉曼谱图;ZCM-1:3的(c)氮气吸附-脱附等温线和(d)孔径分布曲线

Fig.1 XRD patterns of (a) Zn-MOF, ZC, MoS₂, and ZCM-1:3; (b) Raman spectra of ZC and ZCM-1:3; (c) Nitrogen adsorption-desorption isotherm and (d) pore size distribution curve of ZCM-1:3

实了ZC被成功引入花状MoS₂中。图1b是ZC和ZCM-1:3的拉曼光谱图,其强E_{2g}和A_{1g}峰位于376和404 cm⁻¹,这与2H-MoS₂拉曼谱图相对应。1 353和1 586 cm⁻¹处的峰分别属于ZC的D和G波段^[31]。D波段归因于结构缺陷无序石墨碳原子,G波段属于碳原子的面内振动。D和G波段的强度比(I_D/I_G)反映了碳材料的缺陷和变形程度。ZCM-1:3的I_D/I_G=0.97,ZC的I_D/I_G=1.06,证实了所制备的复合材料中存在缺陷碳和石墨碳^[32],而缺陷碳和石墨碳更加有利于导电损耗和极化弛豫。用N₂吸附-脱吸等温线

表征ZCM-1:3的孔隙特性。如图1c所示,在压力中部区域的IV型曲线表明存在中孔,随着压力升高迟滞回线愈发明显,表明同时存在大孔。图1d表明ZCM-1:3中存在大量的介孔、大孔,孔径集中在5.48 nm左右,其比表面积和孔容分别为212 m²·g⁻¹和0.24 cm³·g⁻¹。丰富纳米孔的存在有利于界面极化和多次散射反射以及降低材料的密度。

为了探究ZCM-1:3化学组成和元素状态,对其进行XPS测试。如图2a所示,ZCM-1:3中存在Mo、S、C、Zn、O和N元素。图2b中Zn2p谱图在1 021.4

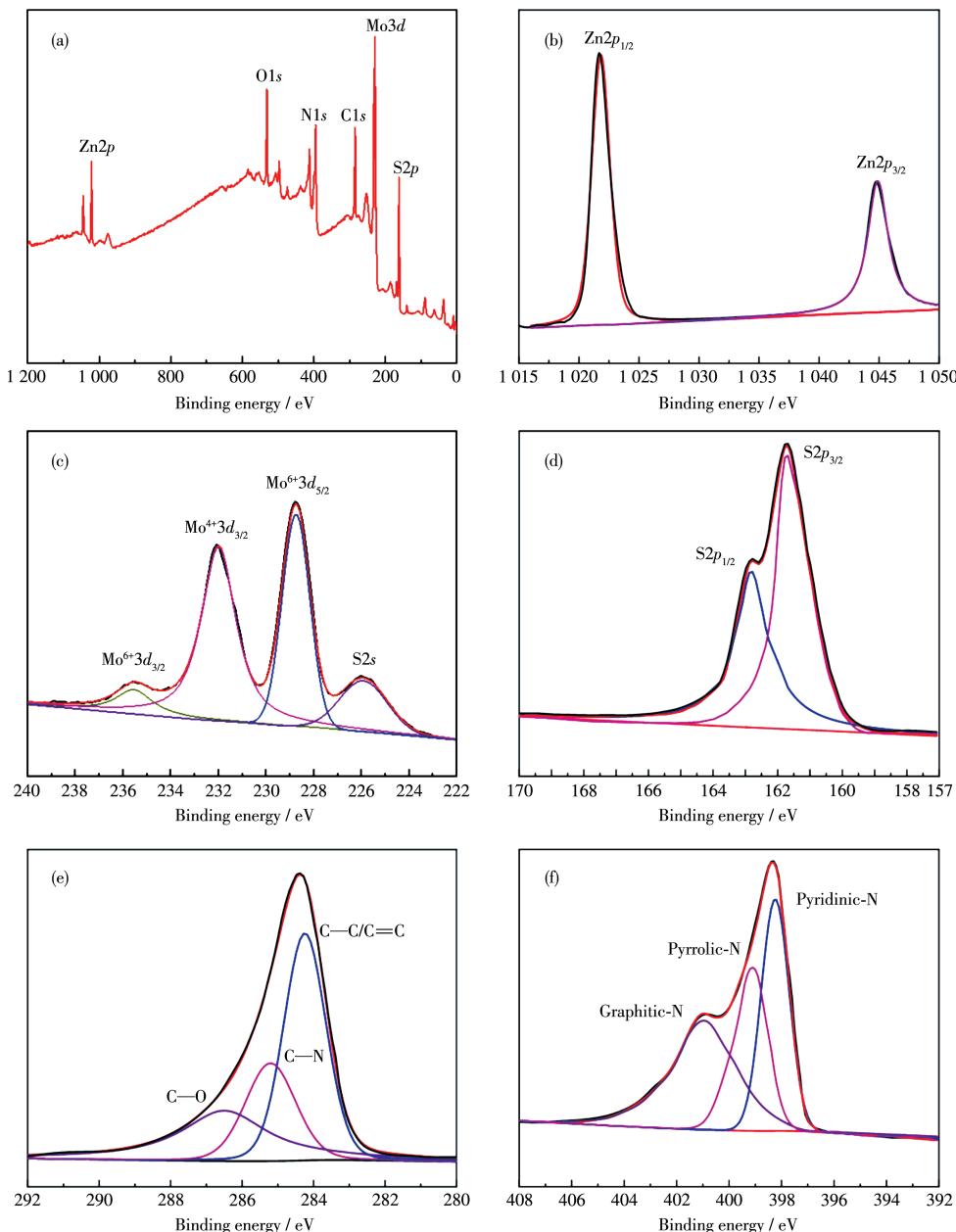


图2 ZCM-1:3的(a) XPS全谱图及(b) Zn2p、(c) Mo3d、(d) S2p、(e) C1s、(f) N1s XPS谱图

Fig.2 (a) XPS survey spectrum and XPS spectra of (b) Zn2p, (c) Mo3d, (d) S2p, (e) C1s, and (f) N1s of ZCM-1:3

和1 045.1 eV处的结合能分别为Zn $2p_{3/2}$ 和Zn $2p_{1/2}$ 的特征双峰。2个峰之间的结合能隙为23.7 eV,这说明在ZCM-1:3中有金属锌和氧化锌存在,而氧化锌的存在有利于改善介电损耗和阻抗匹配^[33],并且导电的金属锌可用于增加电导率。Mo3d谱图如图2c所示,Mo $^{4+}3d_{5/2}$ 和Mo $^{4+}3d_{3/2}$ 特征峰分别位于228.1和231.4 eV,234.8 eV处的小峰对应Mo $^{6+}3d_{3/2}$ 轨道的结合能,可能是由于MoO $^{2-}_4$ 的不完全还原。同时在225.2 eV处的特征峰对应于S2s轨道。S2p谱图如图2d所示,162.8和161.6 eV处分别对应S2p $_{1/2}$ 和S2p $_{3/2}$ 轨道,这证明了2H-MoS₂存在^[34]。C1s谱图(图2e)中284.6、285.4和286.7 eV附近的3个峰分别对应C=C—C、C—N和C—O^[35]。C—N键的存在证实了氮成功地掺杂到ZC中。图2f显示了N1s谱图,398.4、399.2和400.8 eV处的峰分别属于吡啶N、吡咯N和石墨N^[36]。综上分析,证明ZCM-1:3复合材料成功

合成。

如图3所示,通过SEM表征ZC、MoS₂和ZCM-1:3的微观形貌图。由图3a、3b可知,ZC颗粒的尺寸为约80 nm,很好地继承了Zn-MOF多面体结构。图3c表明花状结构MoS₂由大量自组装在一起的纳米片构成。反应过程中生成的MoS₂纳米片厚度约为25 nm,平均直径1 μm左右。图3d为ZCM-1:3的SEM图,MoS₂的表面呈现出均匀的层状结构,ZC颗粒被嵌在纳米片的间隔中,二者相互连通在一起,构成三维网状结构,这些连接结构有助于增加电磁波传播路径以增强衰减性能^[37]。图3f~3l为ZCM-1:3的元素分布图,结果表明,Mo、S、C、Zn、O和N元素均被检出,且均匀分散在ZCM-1:3表面,确保了良好的界面极化,增强了电磁波吸收^[38]。基于上述分析,该复合材料独特的结构和组成可以大大提高电磁波吸收性能。

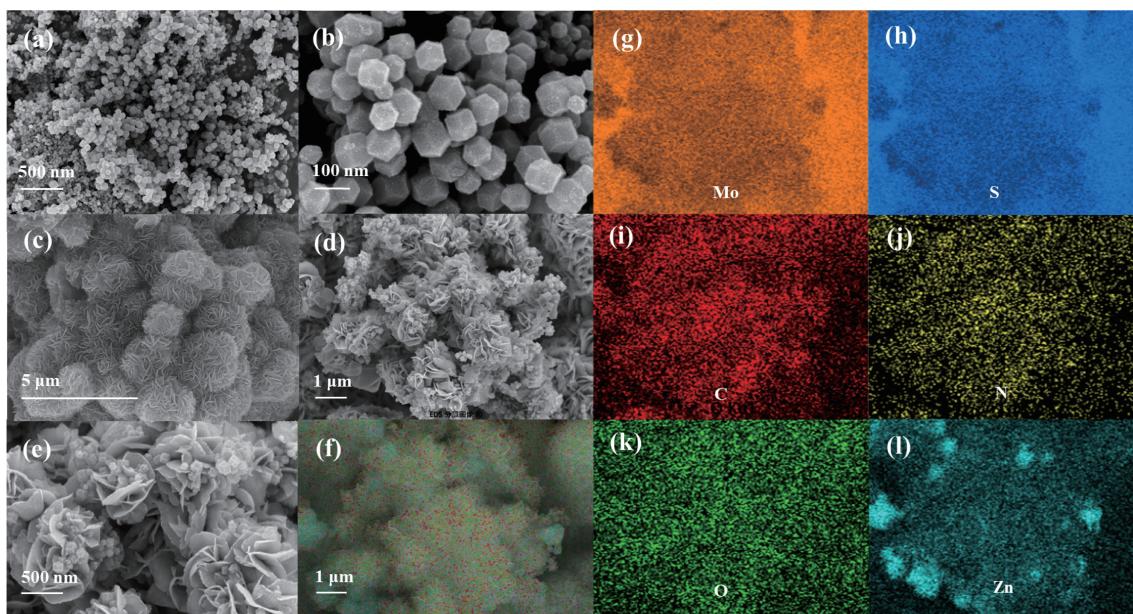


图3 (a,b) ZC、(c) MoS₂、(d,e) ZCM-1:3的SEM图;(f-l) ZCM-1:3的元素面扫图

Fig.3 SEM images of (a, b) ZC, (c) MoS₂, and (d, e) ZCM-1:3; (f-l) Element mappings of ZCM-1:3

2.3 吸波性能分析

为了分析ZCM复合材料吸波性能,将不同样品与石蜡混合(样品填充量为25%),利用压环模具压制外径7 mm、内径3.04 mm的同心环,利用矢量网络分析仪采用同轴法测量了不同样品的电磁参数,并分析了微观结构对吸波性能的影响。根据传输线理论可计算反射损耗(RL)^[39-40]:

$$RL = 20 \lg \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (4)$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left(j \frac{2\pi fd}{c} \sqrt{\mu_r \epsilon_r} \right) \quad (5)$$

其中,Z_{in}和Z₀是输入阻抗和自由空间阻抗,f、d、h、c分别代表自由空间电磁波的频率、样品的厚度、普朗克常数及电磁波在真空中的速度,ε_r为复数介电常数,μ_r为复磁导率。通常,RL值低于-10 dB表示90%以上电磁波被吸收^[41]。如图4a、4b所示,单纯MoS₂在频率为6.4 GHz时,对应匹配厚度为5.5 mm,有效吸收带宽为3.04 GHz,最佳反射损耗为-26.23

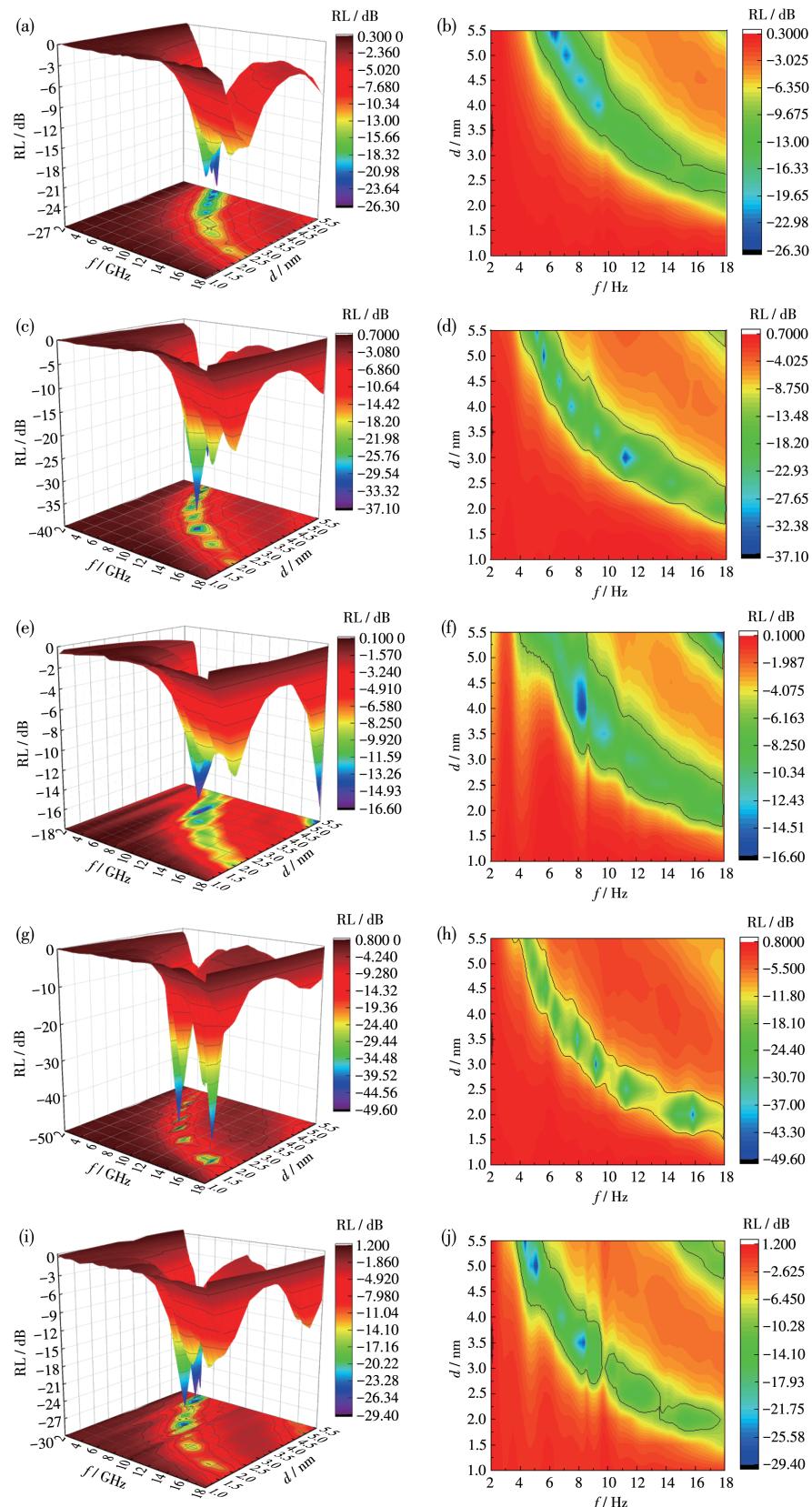


图4 (a,b) 单纯MoS₂、(c,d) 单纯ZC、(e,f) ZCM-1:4、(g,h) ZCM-1:3 和(i,j) ZCM-1:2的三维反射损耗图及等高线图

Fig.4 Three-dimensional reflection loss figures and contour maps of (a, b) pure MoS₂, (c, d) pure ZC, (e, f) ZCM-1:4, (g, h) ZCM-1:3, and (i, j) ZCM-1:2

dB。单纯ZC在频率为11.2 GHz时,对应匹配厚度为3 mm,有效吸收带宽为5.28 GHz,最佳反射损耗为-35.50 dB(图4c、4d)。单纯MoS₂有一定的电磁波吸收能力,但匹配厚度较大,有效吸收带宽相对较小。单纯ZC有相对出色的电磁波吸收能力,较低的匹配厚度,良好的吸收带宽。但单组分吸波材料的电磁波吸波性能有一定的上限,于是将花状MoS₂与多面体ZC进行耦合,利用二者的特殊结构进一步提高电磁波吸收能力。图4e~4j表明ZCM-1:4、ZCM-1:3、ZCM-1:2在频率为8.32 GHz时,匹配厚度为4 mm,有效吸收带宽为2.12 GHz,最佳反射损耗为-16.5 dB;ZCM-1:3在频率为8.02、9.28、11.36、15.92 GHz时,对应匹配厚度分别为3.5、3、2.5、2 mm,有效吸收带宽分别为3.04、3.24、4.08、5.12 GHz,最佳反射损耗分别为-41.28、-49.68、-34.97、-45.09 dB;ZCM-1:2在频率为5.2 GHz时,匹配厚度为5 mm,有效吸收带宽为3.07 GHz,最佳反射损耗为-29.35 dB。由此可知,与单纯MoS₂、单纯ZC、ZCM-1:4、ZCM-1:2相比,ZCM-1:3表现出优异的电磁波吸收性能,且随着ZC添加量的增加复合物吸波能力显著增强,而ZCM-1:2的电磁吸波吸收性能并不理想,主要是当质量比为1:2时ZC添加量过高,导致阻抗不匹配,电磁波在材料表面反射增多。综上,多面体ZC与花状MoS₂特殊结构结合的协同效应可以有效地实现电磁波吸收,显著增强复合材料电磁波吸收性能的同时,也使复合材料获得了良好有效吸收宽度和较薄的匹配厚度。

2.4 损耗机制分析

电磁波吸收材料吸波性能在很大程度上取决于相对复介电常数($\varepsilon_r = \varepsilon' - j\varepsilon''$)和相对复磁导率($\mu_r = \mu' - j\mu''$)。由于MoS₂和ZC都不具有磁性,所以将更多关注复介电常数特性以及介电损耗机制。复介电常数实部(ε')和复磁导率实部(μ')代表材料对电磁波能量的储存能力,复介电常数虚部(ε'')和复磁导率虚部(μ'')代表材料对电磁波能量的耗散能力。图5a和5b是ZCM复合材料在频率2~18 GHz范围内 ε' 和 ε'' 与频率的关系图。不同质量比制备的ZCM复合材料的 ε' 和 ε'' 具有相似的波动趋势,都随频率增加而减小,ZCM-1:4的 ε' 从7.21降到5.2, ε'' 从1.7降到1.3。ZCM-1:3的 ε' 从12.6降到5.3, ε'' 从4.1降到2.5。ZCM-1:2的 ε' 从10.4降到5.3, ε'' 从3.7降到2.3。介电常数实部与虚部变化可能源于2种组分结合导致的空间电荷在异质界面分布不均匀,感应

电场对高频电场变化滞后导致的频散行为^[42]。当ZC含量增加, ε' 和 ε'' 显著增大,而ZCM-1:2的 ε' 和 ε'' 小于ZCM-1:3的 ε' 和 ε'' ,这是ZC颗粒团聚导致介电性能降低。上述结果表明ZC与MoS₂结合可以有效调节复合材料的介电参数,从而调节阻抗匹配。此外,介电损耗正切($\tan \delta_e = \varepsilon''/\varepsilon'$)是评价电磁波吸收材料介电损耗最直观而且有效的参数,该值越大对应的损耗能力越强。如图5c所示,在2~18 GHz的频率范围内,ZCM-1:3的 $\tan \delta_e$ 曲线呈现宽峰,且ZCM-1:3的 $\tan \delta_e$ 明显高于其他质量比的 $\tan \delta_e$,说明ZCM-1:3的损耗电磁波能力最强。同时 $\tan \delta_e$ 的波动变化也表明存在多种极化作用。为进一步分析介电损耗的各种极化作用,用德拜理论描述 ε' 和 ε'' 的关系^[43]:

$$\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2} \right)^2 \quad (6)$$

其中, ε_s 和 ε_∞ 分别是高频极限处的静态介电常数和光学介电常数, ε_0 是自由空间的介电常数。当 $\varepsilon' - \varepsilon''$ 曲线为一个半圆时,称为Cole-Cole圆,对应一个德拜弛豫过程。在图5d~5f中观察到3种不同质量比复合材料中都存在多个Cole-Cole半圆,而ZCM-1:3表现出更多的Cole-Cole圆,说明其具有更强的极化作用,这是因为多面体结构ZC与花状结构MoS₂的有效耦合,提供了丰富的异质界面,大量的空间电荷聚集在异质界面处,增强了极化效应。同时复合材料中的三维多孔结构产生多重散射行为,在三维网络结构中丰富的交联可以进一步延长电磁波传播路径,增强微波吸收^[44-45]。另外在Cole-Cole半圆尾部的直线说明不仅有极化损耗,还存在导电损耗^[46]。上述结果表明多面体结构ZC的引入有效提高了ZCM复合材料的介电损耗能力。

衰减常数和阻抗匹配是鉴定吸波材料对电磁波吸收与损耗的2个必要条件。理想的阻抗匹配要求 $Z=1$,以实现电磁波在空气-吸波材料界面的完全吸收,衰减常数越大电磁波吸收材料的损耗能力越强^[47]。为了确定不同质量比的ZCM复合材料的电磁波阻抗匹配和衰减能力的差异,根据以下公式计算了不同质量比制备的ZCM的衰减常数(α)和阻抗匹配(Z)^[48]:

$$\alpha = \frac{\sqrt{2} \pi f}{c} \sqrt{(\mu'' \varepsilon'' - \mu' \varepsilon') + \sqrt{(\mu'' \varepsilon'' - \mu' \varepsilon')^2 + (\mu' \varepsilon'' + \mu'' \varepsilon')^2}} \quad (7)$$

$$Z = Z_{in}/Z_0 = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left(j \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right) \quad (8)$$

由图6a可知,ZCM-1:3的衰减常数显然高于

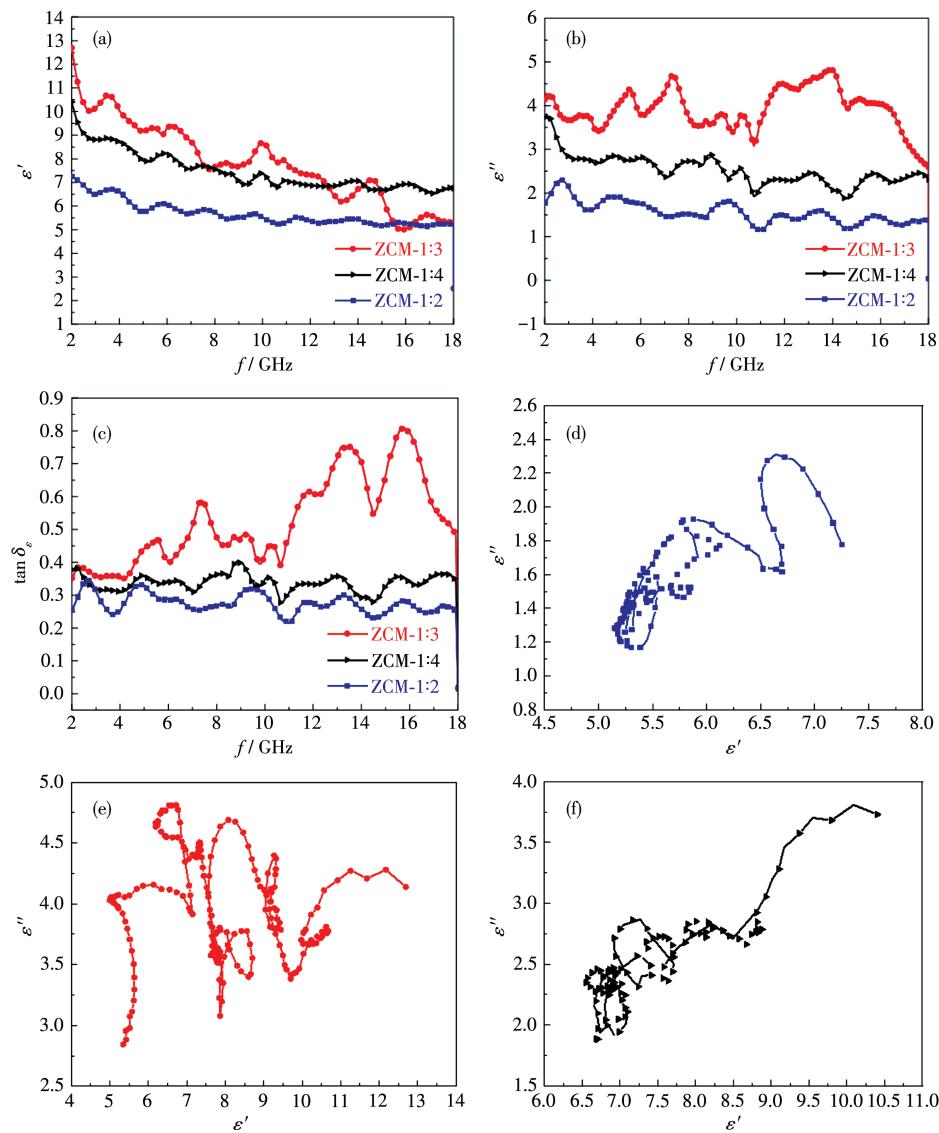


图5 ZCM的(a) ϵ' 、(b) ϵ'' 和(c) $\tan \delta_\epsilon$ 与频率的关系图;(d) ZCM-1:4、(e) ZCM-1:3、(f) ZCM-1:2的 $\epsilon'-\epsilon''$ 曲线

Fig.5 Relationship between (a) ϵ' , (b) ϵ'' , (c) $\tan \delta_\epsilon$ and frequency of ZCM; $\epsilon'-\epsilon''$ curves of (d) ZCM-1:4, (e) ZCM-1:3, and (f) ZCM-1:2

ZCM-1:4和ZCM-1:2,说明其损耗能力更强。由图6b、6d可知,ZCM-1:4和ZCM-1:2较低的复介电常数导致阻抗匹配大于1.0,表示阻抗失配,这将导致大多数入射电磁波在材料表面强烈反射,对电磁波吸收性能不利。而ZCM-1:3适当的复介电常数产生大约1.0的阻抗匹配(图6c),表明其具有良好的阻抗匹配。由此说明将ZC适当地引入到花状MoS₂中,可以获得良好的阻抗匹配,同时由于优异的极化作用,复合材料的衰减电磁波能力提高,使花状ZCM-1:3获得优异的电磁波吸收性能。

综上分析,ZCM-1:3多面体和花状MoS₂结合,可以有效改善阻抗匹配,电磁波很容易进入复合材

料内部。复合材料内部的复杂孔道结构延长了电磁波传播路径,提高了电磁波多次反射、散射,并改善了衰减机制。当电磁波进入多面体ZC和花状MoS₂之间界面时,大量的异质界面和缺陷导致电荷逐渐积累产生界面极化和偶极极化,同时,由于花状ZCM-1:3具有较高电磁波衰减能力,大量电磁波进入复合材料后,并没有被反射出去,而是在多次反射和散射中损耗。因此,ZCM-1:3的特殊结构、优异的阻抗匹配和强大的衰减性能可以有效吸收、损耗入射电磁波。与类似微波吸收材料对比可知,本工作中制备的ZCM-1:3具有较好的吸波性能(表1),RL_{min}为电磁波吸收最小反射损耗。

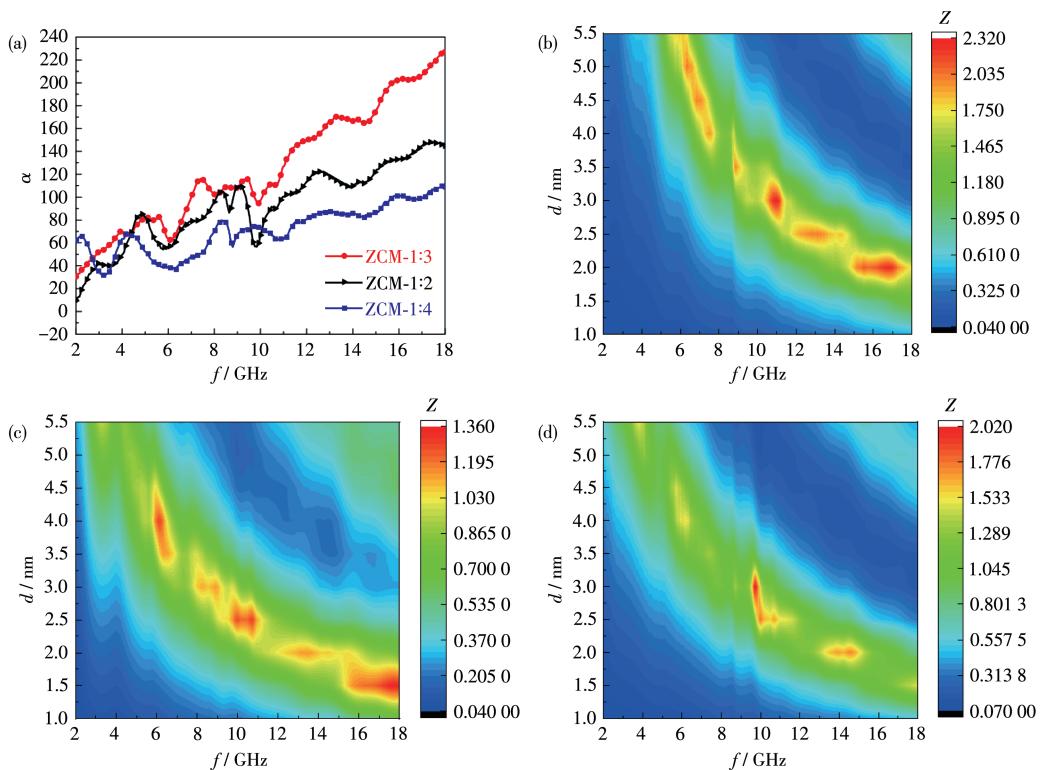


图6 (a) 样品的微波衰减常数; (b) ZCM-1:4、(c) ZCM-1:3 和(d) ZCM-1:2 的频率相关阻抗匹配Z值的二维等高线图

Fig.6 (a) Microwave attenuation constants of samples; Frequency-dependent impedance matching two-dimensional contour plots of Z -values for (b) ZCM-1:4, (c) ZCM-1:3, and (d) ZCM-1:2

表1 类似微波吸收材料之间的性能对比

Table 1 Performance comparison between similar microwave absorbing materials

Sample	RL_{min} / dB	Matching thickness / mm	Effective absorption bandwidth / GHz	Ref.
MoS ₂ /C	-44.67	1.44	3.32	[49]
PPy@MoS ₂	-49	5	6.41	[50]
3D-MoS ₂	-26.1	3	5.1	[51]
Fe@MoS ₂	-35.5	2	4.2	[52]
Co _x S _y /C@MoS ₂	-41.32	2.7	2.36	[53]
RGO/MoS ₂	-31.6	2.5	5.9	[54]
ZCM-1:3	-49.68	3	3.24	This work

3 结 论

通过碳化和溶剂热法制备的ZCM复合材料表现出出色的吸波性能。通过改变ZC和MoS₂质量比,可以调节复合材料电磁参数以获得最佳的微波吸收衰减能力。ZCM-1:3在频率为9.28 GHz时,匹配厚度为3 mm,有效吸收带宽为3.24 GHz,最佳反射损耗为-49.68 dB。得益于其独特的微观结构下的极化效应、传导损耗、多次反射、散射及协同效应,ZCM-1:3表现出优异的电磁波吸收能力,为电磁波吸收材料的制备提供了一种新途径。

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