

缺陷介孔TiO₂的制备及其吸波性能研究

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摘要:目前,电子通信设备产生的电磁辐射问题日益突出。为了应对电磁污染,迫切需要开发一种厚度薄、重量轻、吸收频率宽和吸收能力强的微波吸收材料。TiO₂因具有密度低和稳定性高的特点,成为一种有潜力的微波吸收材料。然而,纯TiO₂材料因电磁响应性差、介电常数低及电磁波衰减能力不足,从而限制了其实际应用。为了提升TiO₂的微波吸收性能,采用无溶剂自组装策略,在不同温度下合成了介孔TiO₂,并通过N₂气氛还原处理引入缺陷,成功制备了富缺陷介孔TiO₂。通过X射线衍射(XRD)和透射电子显微镜(TEM)对试样的晶体结构和微观形貌进行表征,借助X射线光电子能谱(XPS)对介孔TiO₂还原前后元素价态的变化进行分析,利用N₂吸附-脱附等温曲线对试样的比表面积和孔结构特征进行探讨,并通过矢量网络分析仪测量试样的电磁参数。同时,系统地研究了合成温度和还原处理对试样电磁吸波性能的影响。结果表明:随着合成温度的提高,介孔TiO₂晶相从单一锐钛矿相转变为锐钛矿与金红石的混合相;尽管N₂气氛还原处理保持了介孔结构,但比表面积有所下降,并在表面生成大量氧空位缺陷;合成温度对试样的电磁参数影响较小,而还原处理显著提升了其介电常数。值得一提的是,在500℃下合成并还原处理的介孔TiO₂,其表现出优异的吸波性能,当厚度为5.05 mm时最小反射损耗值达到-30.5 dB、有效吸收带宽为2.32 GHz,该优异性能得益于介孔结构提供的大比表面积、第二相引入的界面极化损耗及缺陷诱导的偶极子极化。本研究为高性能TiO₂基微波吸波材料的制备提供了有效途径。(专精特新·电磁波吸收与屏蔽用新型材料的研究进展专辑十二之六)

关键词:介孔TiO₂;气氛还原;缺陷;介电损耗;阻抗匹配;衰减常数;微波吸收;RCS仿真

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0 引言

现代科技发展和电子设备普及给人们生活带来了巨大的便利。然而,随之而来的电磁辐射问题不仅会干扰电子元件的正常工作,还会对人类健康造成潜在威胁^[1-3]。电磁波吸收材料能够将电磁波转换为热能^[4],成为解决电磁污染的主要方法之一。因此,开发新型高性能电磁波吸收材料显得尤为迫切。理想的吸波材料必须具备重量轻、密度低、厚度薄和优异吸收能力等特性^[5-8]。目前,对电磁波吸收材料的研究主要集中在碳基材料^[9]、铁氧体^[10]、磁性金属^[11]等方面。然而,碳基材料因高导电性而导致阻抗匹配较差,而铁氧体和磁性金属则因高密度和低稳定性难以满足实际应用需求。二氧化钛

(TiO₂)作为一种典型的陶瓷材料,具有低密度、高稳定性、无毒性和低成本^[12-13]等特性,已在储能^[14]、催化剂^[15]和电磁波吸收^[16]等领域得到广泛应用。然而,纯TiO₂材料因电磁响应性差、介电常数小和衰减特性不足等缺点,表现出不令人满意的吸波带宽和吸波性能。因此,研究者提出了多种策略来提高TiO₂的微波吸收性能,如与磁性材料复合^[17]、与碳材料复合^[18]等。磁性材料的复合有助于引入磁损耗机制,从而提高TiO₂复合材料的微波吸收性能。Zhao等^[19]通过溶剂热法制备了Ni微球包覆TiO₂的Ni/TiO₂复合材料,该复合材料在频率8.4 GHz处最小反射损耗达到了一15.4 dB,优异的微波吸收性能归因于Ni带来的磁损耗与TiO₂本身

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介电损耗直接的互补。利用碳材料还可以提升TiO₂复合材料的介电损耗能力。Mo等^[20]通过调整氧化时间和温度,优化了碳纳米管(CNTs)和TiO₂组分的百分比,使所得材料的带宽为2.76 GHz,在频率10.35 GHz处最小反射损耗达到-31.8 GHz,优异的微波吸收性能归因于CNTs带来的高介电损耗和CNTs与TiO₂之间的界面极化效应。

尽管这些方法都能够提高TiO₂基复合材料的微波吸收能力,但TiO₂本身的介电常数并未改变。因此,人们通过各种方法对TiO₂进行本征改性,以增强其介电性能。Dong等^[21]的研究表明,氢化处理促进了TiO₂表面形成晶态-非晶异质结构,从而使其微波吸收能力进一步增强,在频率15.5 GHz下的最小反射损耗为-15.6 dB,但相应的带宽为1 GHz。Xu等^[22]采用密封转移还原法,在相对较低温度下通过氢化还原合成了黑色TiO₂纳米颗粒,当其填充率为50%(质量分数)时TiO₂的最小反射损耗为-40.8 dB,有效吸收带宽达到2 GHz,优异的微波吸收性能得益于黑色TiO₂的强介电损耗及良好的阻抗匹配性能。虽然有关TiO₂基复合材料的微波吸收能力研究取得了一些进展,但对TiO₂本身微波吸收性能的提升还不够显著。考虑到材料的孔结构对微波吸收性能也有一定的影响^[23],这为改善TiO₂本身的微波吸收性能提供了启示。因此,本文通过一种简单的无溶剂自组装策略,制备了具有良好孔隙率和较高结晶度的介孔TiO₂材料,并通过气氛还原处理引入缺陷,以期实现其介电常数的提升,为开发高性能TiO₂吸波材料开辟了一条新途径。

1 实验部分

1.1 实验原料

实验所用试剂均为分析纯试剂,其中钛酸四丁酯(TBOT)购自上海阿拉丁试剂有限公司,聚乙烯亚胺(PEI,平均分子量600)、乙酸(HOAc)、硼氢化钠(NaBH₄)和乙醇购自上海国药化学试剂有限公司,切片石蜡购自上海华灵康复器械厂。

1.2 制备方法及表征

本实验按照文献^[24]中的无溶剂自组装策略合成介孔TiO₂。将1.7 g的TBOT、0.45 g的PEI和1 mL的HOAc置于研钵中研磨5 min,随后将得到的凝胶混合物在不同温度(400、500和550 °C)下以2 °C·min⁻¹的升温速率在马弗炉中煅烧3 h,得到

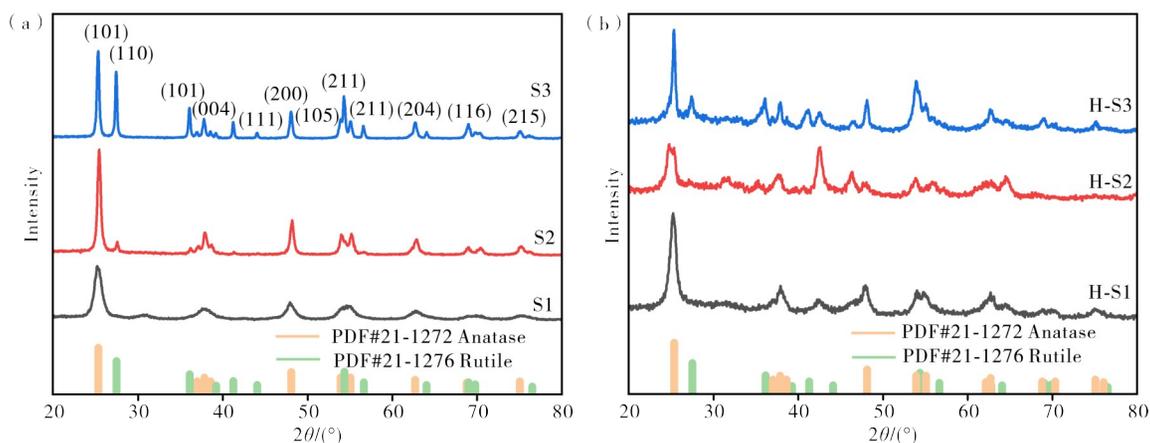
不同制备温度的介孔TiO₂,分别命名为S1、S2和S3。将3组试样与NaBH₄按照质量比4:2.5均匀混合,在N₂气氛下以10 °C·min⁻¹的加热速率在425 °C下保温2.5 h,待自然冷却至室温后用水和无水乙醇洗涤数次,经干燥得到试样,分别标记为H-S1、H-S2和H-S3。

使用X射线衍射仪(XRD, D-max2500PC)对试样进行结构表征,其中电压为40 kV、电流为200 mA、扫描角度范围为20°—80°。采用钨灯丝扫描电子显微镜(SEM, JSM-5610LV, 3 kV)和透射电子显微镜(TEM, JM-2100F),对试样的微观形貌进行表征。利用X射线光电子能谱仪(XPS, Thermofisher Nexsa, 12 kV, 6mA),检测试样表面官能团的变化。同时,使用Micromeritics ASAP 2460 Version 3.01,对试样进行比表面积测试。将试样与石蜡按质量比1:1均匀混合,制备出外径为7.05 mm、内径为3.04 mm的空心圆环。使用矢量网络分析仪(Anritsu MS46322B),测试圆环在频率2—18 GHz范围内的电磁参数,并利用CST STUDIO SUITE软件对试样的吸波性能进行模拟。

2 结果与讨论

2.1 缺陷介孔TiO₂的表征

图1为N₂气氛还原处理前后介孔TiO₂的XRD图。从图1(a)可见:试样在25.3°、37.8°、48.1°、53.9°、55.1°、62.7°、68.8°和75.0°处存在特征峰,通过与PDF 21-1272对比,可确定分别为锐钛矿相的(101)、(004)、(200)、(105)、(211)、(204)、(116)和(215)晶面;随着合成温度的升高,在27.5°、36.1°、41.2°和54.3°处存在特征峰,通过与PDF 21-1276对比可确定分别为第二相金红石相的(110)、(101)、(111)和(211)晶面。结果表明,采用无溶剂自组装策略可成功合成出具有较高结晶度的介孔TiO₂,并且在试样中未观察到其他杂相。另外,较高的合成温度有助于形成锐钛矿和金红石两种相结构,且温度越高金红石相的含量越多,金红石相的生成有利于增强界面极化效应,进一步提高电磁波的耗散能力。图1(b)为气氛还原后试样的XRD图。从图1(b)可以看出,经过N₂气氛还原后,试样的衍射峰强度降低,其中金红石相的衍射峰强度下降明显。表明,缺陷介孔TiO₂的结晶度降低。这是由于还原过程中形成了空位或缺陷,从而影响了晶体中原子的排布^[25-26]。



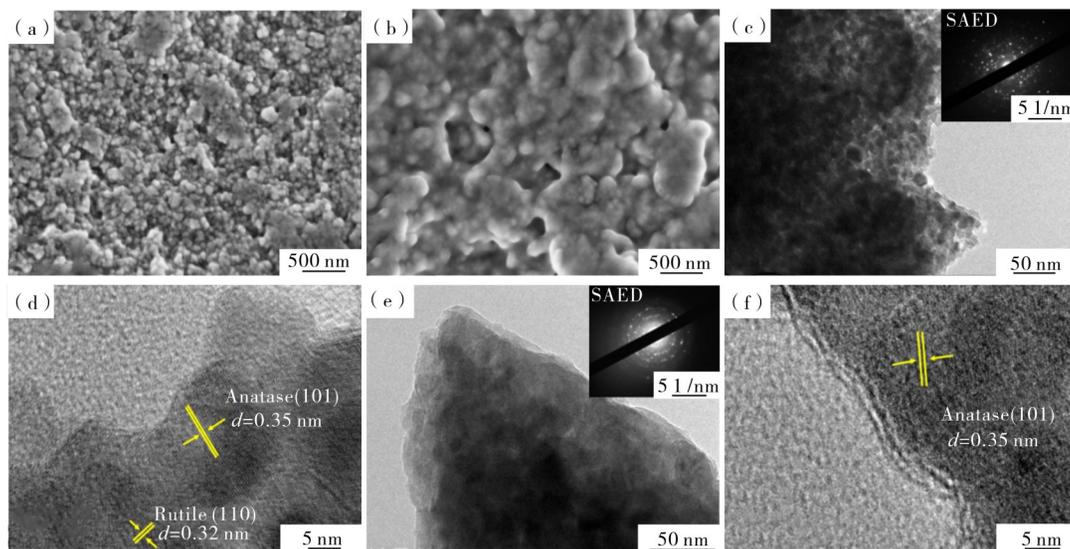
(a)—S1、S2、S3;(b)—H-S1、H-S2、H-S3。

图1 试样的X射线衍射图

Figure 1 X-ray diffraction patterns of the samples

考虑到较高温度不利于维持试样TiO₂的介孔结构^[24],因此选择S2和H-S2试样进行SEM和TEM观察,结果如图2所示。从图2(a)和(b)可以看出,S2试样的颗粒尺寸较小,经还原处理后颗粒的边缘出现明显的熔融连接现象,导致颗粒尺寸增大。图2(c—f)为N₂气氛还原前后试样的TEM图和HRTEM图。从图2(c)可见,试样S2具有介孔结构,从其SAED图(插图)中发现明显的衍射点。表明,通过无溶剂自组装策略可以成功合成介孔TiO₂,且具有良好的结晶性。从图2(d)可见,试样

S2的晶格条纹清晰,其中锐钛矿的晶面间距为0.35 nm,金红石的晶面间距为0.32 nm。结果证明,合成试样中存在锐钛矿和金红石两种相结构,这与XRD的表征结果相一致。从图2(e)可以看出,经N₂气氛还原后试样H-S2的介孔结构发生了明显变化,同时SAED图(插图)中的衍射点模糊。这是由于高温导致的介孔结构坍塌,以及无序缺陷的增加^[27-28]。从图2(f)可以看出,试样H-S2的晶格条纹变得不清晰,仅检测到晶面间距为0.35 nm的锐钛矿相结构。该结果进一步表明,经过还原处理后金红石相结构逐渐消失。



(a)—S2的SEM图像;(b)—H-S2的SEM图像;(c)和(d)—S2的TEM图像;(e)和(f)—H-S2的TEM图像。
(a)—S2,SEM;(b)—H-S2,SEM;(c),(d)—S2,TEM;(e),(f)—H-S2,TEM。

图2 试样S2和H-S2的形貌图

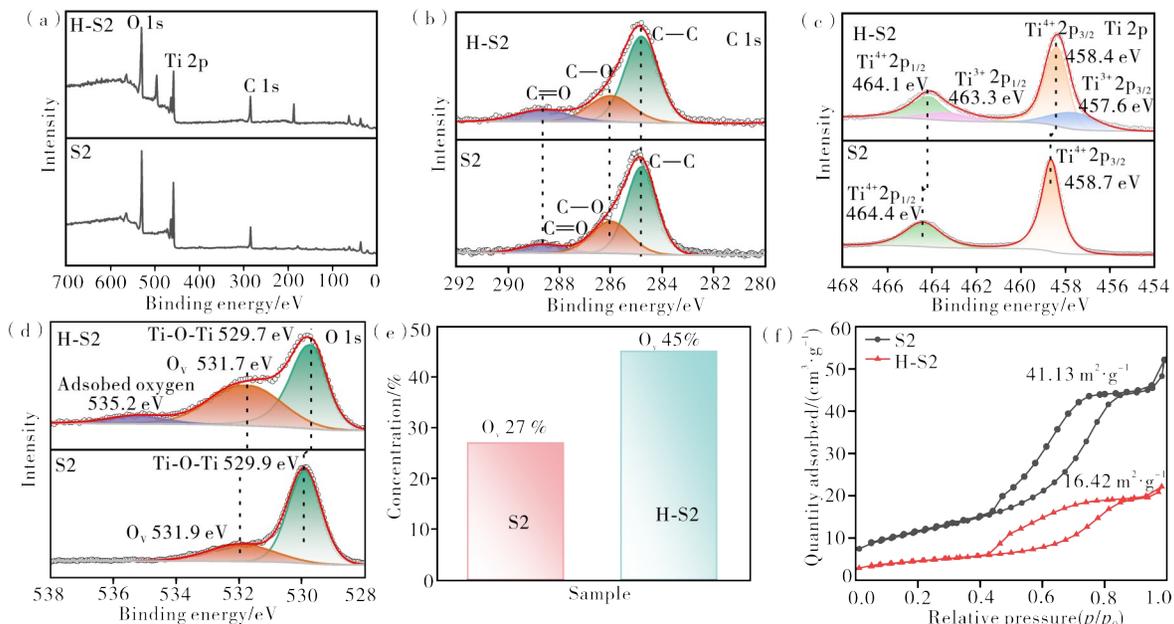
Figure 2 The morphologies of S2 and H-S2

采用XPS检测试样S2和H-S2的官能团的价态变化,结果如图3所示。从图3(a)可以看出,试样S2和H-S2中存在3种元素,分别为元素C、Ti和O。从图3(b)可见,在结合能为284.8、286.0和288.7 eV

附近存在特征谱峰,分别对应C 1s的C—C、C—O和C=O^[29]峰。从图3(c)可以看出,在结合能458.7和464.4 eV处存在特征峰,分别对应Ti⁴⁺ 2p_{1/2}和Ti⁴⁺ 2p_{3/2}轨道。值得注意的是,在试样S2表面没有

检测到Ti³⁺的信号,而经N₂气氛还原处理后的H-S2,由于缺陷的产生使其Ti⁴⁺的结合能向较低的结合能偏移^[30-31]。同时,在结合能为457.6和463.3 eV处出现两个拟合峰,分别对应Ti³⁺的Ti 2p_{3/2}和Ti 2p_{1/2}轨道^[32]。从图3(d)可见,在结合能为529.9和531.9 eV处出现特征峰,分别对应于晶格氧(Ti-O-Ti)和缺陷氧(O_v)^[33-34]。XPS分析结果表明,试样在还原处理过程中引入了大量的氧空位缺陷,导致试样H-S2中O 1s的结合能向低能量偏移,这一现象与文献[35]报道的情况类似。从图3(e)可见,缺陷氧含量从27%增加到45%。由于缺陷氧含量的增加,使试样能够吸附空气中的氧气,导致在结合能

535.2 eV处出现吸附氧的特征峰^[36]。大量氧空位的存在会打乱电荷平衡,增强电荷之间的转移^[37],进而促进电导损耗,提高对电磁波的耗散能力。从图3(f)可以看出,试样S2和H-S2均显示出IV型吸附曲线^[38],二者的比表面积分别为41.14和16.42 m²·g⁻¹。结果表明,试样S2和H-S2均为介孔结构,比表面积的降低进一步印证了高温导致介孔结构的坍塌,这与SEM/TEM的分析结果一致。说明,还原过程对材料比表面积的影响很大。介孔结构的成功保留有利于促进电磁波的多重反射和散射,从而提高电磁波的衰减能力。



(a)—S2和H-S2的全谱;(b)—S2和H-S2的C 1s谱图;(c)—S2和H-S2的Ti 2p谱图;(d)—S2和H-S2的O 1s谱图;(e)—S2和H-S2的O_v含量;(f)—S2和H-S2的N₂吸脱附曲线。

(a)—the full spectra of S2 and H-S2; (b)—C 1s spectra of S2 and H-S2; (c)—Ti 2p spectra of S2 and H-S2; (d)—O 1s spectra of S2 and H-S2; (e)—O_v content of S2 and H-S2; (f)—N₂ adsorption-desorption curves of S2 and H-S2.

图3 S2和H-S2试样的XPS谱图及N₂吸脱附曲线图

Figure 3 XPS spectra of S2 and H-S2 samples and N₂ absorption and desorption curves

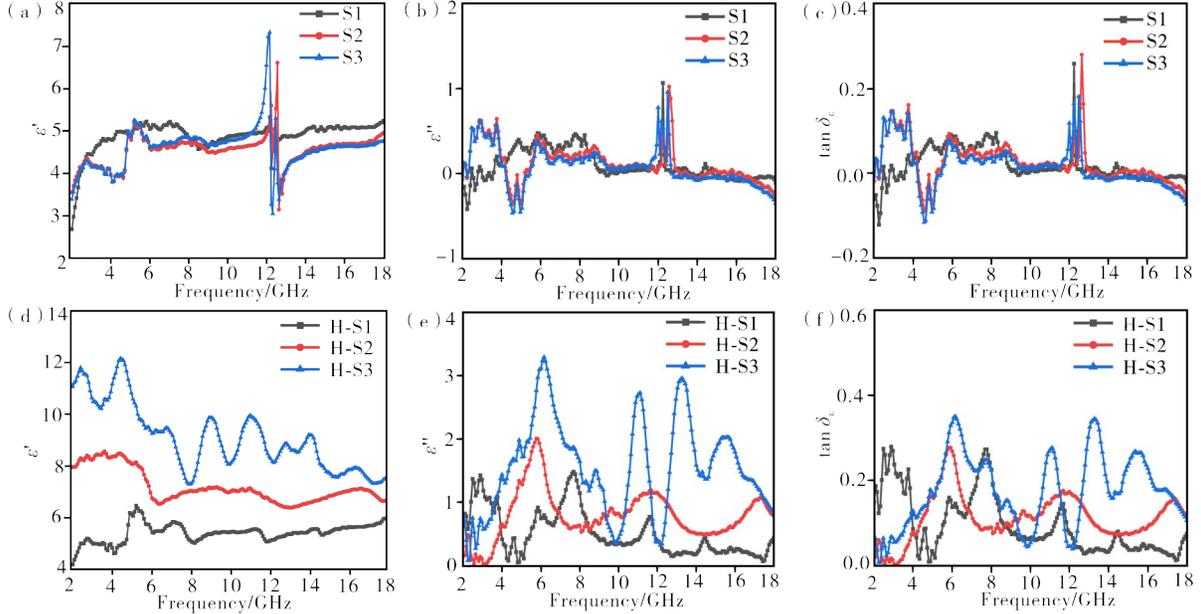
2.2 缺陷介孔TiO₂的电磁吸波性能研究

为了比较合成温度和还原处理对介孔TiO₂吸波性能的影响规律,对合成试样的相对复介电常数($\epsilon_r = \epsilon' - j\epsilon''$)进行了测试(见图4),测试频率范围为2—18 GHz。介电常数的实部(ϵ')和虚部(ϵ'')分别与材料对电磁波的储存和耗散能力有关,介电损耗因子($\tan\delta_\epsilon = \epsilon''/\epsilon'$)用于衡量材料的介电损耗能力。从图4(a—c)可见,不同热处理温度下试样S1—S3在频率2—18 GHz范围内,实部和虚部的变化均不大,实部平均值保持在4.5—4.8之间波动,虚部平均值保持在0.1—0.2范围内波动。说明,合成温度对介孔TiO₂介电常数的影响不大,主要是TiO₂自身介电常数偏小和介电损耗偏弱所致。从图4(d—e)

可以看出:经N₂气氛还原后,试样H-S1—H-S3的介电常数值随着频率的增加而减小。其中,试样H-S2的 ϵ' 值从7.95降至6.69,并在频率6.16、11.12、13.28和15.52 GHz下依次出现明显的极化峰。随着制备温度的升高,试样H-S1—H-S3的 ϵ' 值和 ϵ'' 值均显著增加, ϵ' 值平均从5.37增加至7.20后再增加到9.27,而 ϵ'' 值则由0.53增加至0.78后再增加到1.58,均超过了N₂气氛处理前的值。此外,介电常数值的大小顺序为H-S3>H-S2>H-S1,究其原因:一方面,试样H-S3的介电常数明显增大归因于内部存在两种相结构,且随着制备温度的升高第二相的出现增强了界面极化,而试样H-S1中只有一种相,试样H-S2中虽然有两种相,但第二相的强度较弱;

另一方面,还原过程中引入的缺陷诱导了缺陷偶极子极化,同时氧空位的引入增强了电荷之间的转移,促进了电导损耗能力。从图4(f)可见,试样H-S1—H-S3的介电损耗值($\tan\delta_e$)也表现出与介电常数类

似的变化,试样H-S2展现出较好的介电损耗能力。这主要是由于制备温度的升高促进了第二相金红石的生成,导致界面极化损耗的增大,同时缺陷的引入也增强了对电磁波的衰减能力。



(a)—S1, S2和S3的实部;(b)—S1, S2和S3的虚部;(c)—S1, S2和S3的介电损耗角正切值;(d)—H-S1, H-S2和H-S3的实部;(e)—H-S1, H-S2和H-S3的虚部;(f)—H-S1, H-S2和H-S3的介电损耗角正切值。
(a)—the real parts of S1, S2 and S3; (b)—the imaginary parts of S1, S2 and S3; (c)—tangent values of dielectric loss angles of S1, S2 and S3; (d)—the real parts of H-S1, H-S2 and H-S3; (e)—the imaginary parts of H-S1, H-S2 and H-S3; (f)—dielectric loss tangent of H-S1, H-S2 and H-S3.

图4 试样的复介电常数和介电损耗图

Figure 4 Structure characterization diagram complex dielectric constant and dielectric loss diagram of the sample

此外,通过德拜弛豫理论进一步分析试样的损耗机制, ϵ' 和 ϵ'' 之间的关系可以由以下方程描述。

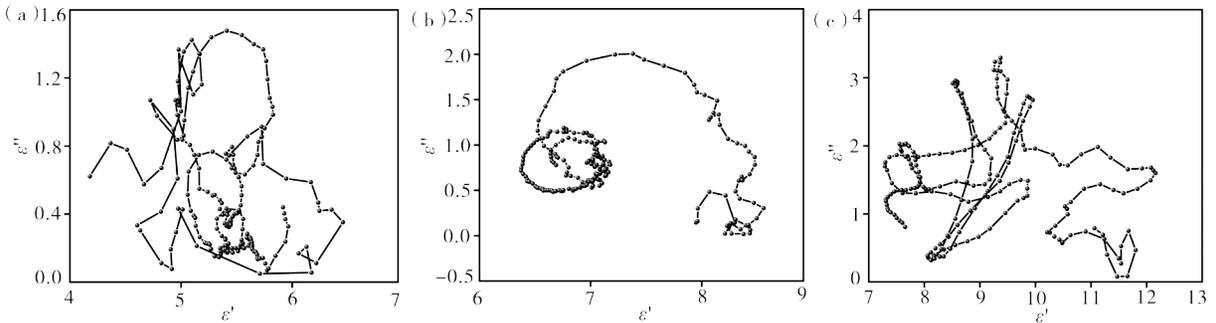
$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (2\pi f)^2 \tau^2} \quad (1)$$

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1 + (2\pi f)^2 \tau^2} + \frac{\sigma}{\omega \epsilon_0} = \epsilon_p'' + \epsilon_c'' \quad (2)$$

$$\left(\epsilon' - \frac{\epsilon_s + \epsilon_\infty}{2} \right)^2 + (\epsilon'')^2 = \left(\frac{\epsilon_s - \epsilon_\infty}{2} \right)^2 \quad (3)$$

式中, $\omega(2\pi f)$ 和 τ 分别表示角频率和极化弛豫时间,

ϵ_s 为静态介电常数, ϵ_∞ 为高频下的介电常数, σ 为电导率, ϵ_0 为真空中的介电常数($\epsilon_0 = 8.85 \times 10^{-12} F/m$), ϵ_p'' 对应极化损耗的虚部, ϵ_c'' 对应电导损耗的虚部。由 ϵ' 和 ϵ'' 绘制的曲线称为Cole-Cole曲线(见图5)。从图5可以看出,试样H-S1和H-S3的Cole-Cole曲线均偏离标准的半圆弧形。表明,试样内部存在多种极化种类。这是由于随着制备温度的升高促进了第二相的生成,增强了界面极化效应,同时引入的氧空位缺陷也会诱导强的极化损耗。



(a)—H-S1;(b)—H-S2;(c)—H-S3。

图5 试样的Cole-Cole曲线

Figure 5 Cole-Cole curve of the sample

反射损耗RL值是衡量吸波材料对电磁波吸收能力的最直观指标。一般来说,当吸波材料的反射损耗RL值小于-10 dB时,对应90%的入射电磁波被吸收^[39]。根据试样的复介电常数测量结果,可以利用传输线理论计算试样的反射损耗RL值。根据线性传输理论及电磁波反射损耗公式(见式(4)和式(5)),对试样的电磁波反射损耗进行了模拟计算。

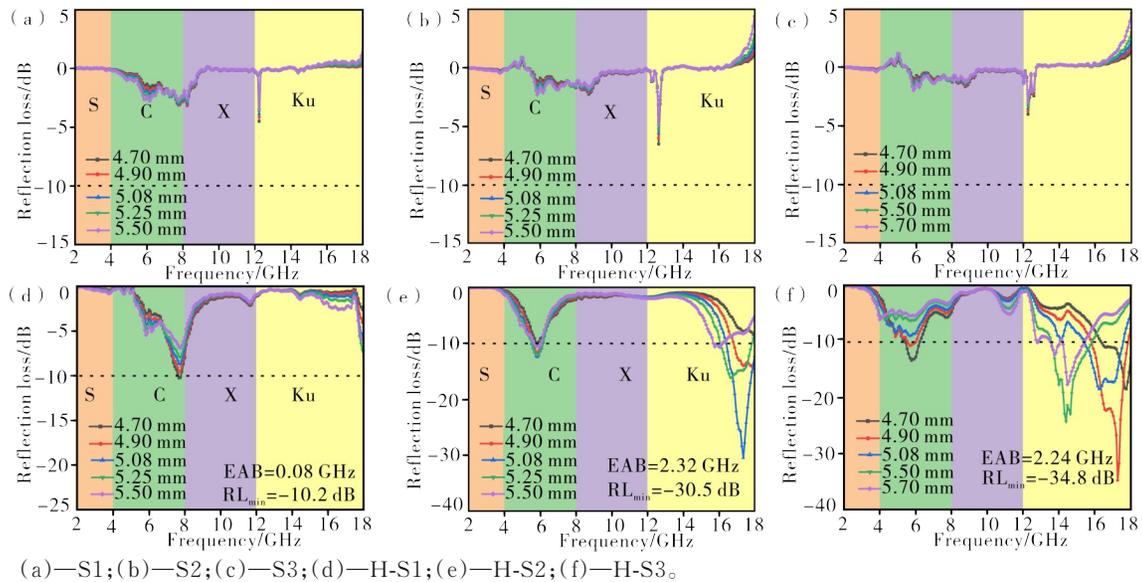
$$RL = 20 \lg \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right| \quad (4)$$

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

式中, Z_0 为空气阻抗(常量), Z_{in} 为材料的阻抗, ϵ_r 为复介电常数, μ_r 为复磁导率, f 为电磁波的频率, d 为材料的厚度, c 为光速, j 为虚数单位。

图6为不同模拟厚度下试样经N₂气氛处理前后的反射损耗曲线。从图6可见:未经N₂气氛处理试

样S1、S2和S3的吸波性能较差,最小反射损耗均未达到-10 dB以下;经N₂气氛还原处理后,试样H-S1、H-S2、H-S3的吸波性能显著提升;H-S1试样在模拟厚度为4.7 mm时,其最大有效吸收带宽仅为0.08 GHz、最小反射损耗RL值为-10.2 dB;试样H-S3在模拟厚度为5.08 mm时,其最小反射损耗RL值为-30.5 dB、最大有效吸收带宽为2.32 GHz;而试样H-S3在模拟厚度为5.50 mm时,其最大有效吸收带宽达到2.24 GHz、最小反射损耗RL值为-34.8 dB。通过反射损耗及有效吸收带宽的结果可知,经过N₂气氛还原处理后,试样H-S2的吸波性能显著提升,具有较宽的有效吸收带宽,表明其在频率2—18 GHz范围内具备较强的电磁波损耗能力。从图6还可以看出,随着模拟厚度的增加,试样的最小反射损耗对应的峰值向低频方向移动。该结果与 $\lambda/4$ 波长理论^[40]相吻合。



(a)—S1;(b)—S2;(c)—S3;(d)—H-S1;(e)—H-S2;(f)—H-S3。

图6 不同模拟厚度下试样的反射损耗图

Figure 6 Reflection loss diagram of sample at different simulated thicknesses

阻抗匹配(Z)和衰减常数(α)是影响材料吸波性能的两个重要参数,可用公式6和7表示。一般而

$$Z = \frac{Z_{in}}{Z_0} = \frac{\sqrt{(\mu''^2 + \mu'^2)}}{\sqrt{(\epsilon''^2 + \epsilon'^2)}} \quad (6)$$

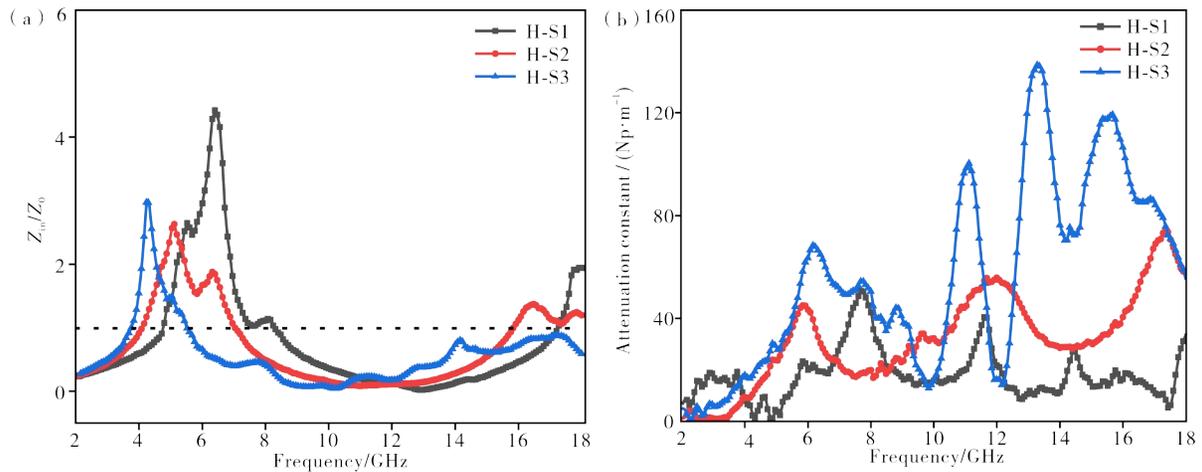
$$\alpha = \frac{\sqrt{2} \pi f}{c} \times \sqrt{(\mu''\epsilon'' - \mu'\epsilon')^2 + \sqrt{(\mu''\epsilon'' - \mu'\epsilon')^2 + (\mu'\epsilon'' + \mu''\epsilon')^2}} \quad (7)$$

式中, μ' 、 μ'' 分别代表磁导率的实部和虚部值,由于TiO₂不是磁性材料,因此其磁损耗可忽略不计,实部默认为1,虚部默认为0。

图7为试样的阻抗匹配、衰减常数图。从图7(a)可以看出,经过N₂气氛还原处理后,试样H-S2的 $|Z_{in}/Z_0|$ 值更接近于1。说明,H-S2具有相对较好的阻抗匹配性能。从图7(b)N₂气氛还原处理后试

言,当 $|Z_{in}/Z_0|$ 值接近于1时,材料呈现出较好的阻抗匹配性能。

样的衰减常数(α)变化曲线可以看出,随着制备温度的升高,试样的衰减常数 α 也随之增加。表明,试样对入射电磁波的衰减能力显著提升,这主要是由于高温还原处理提高了材料的介电损耗能力。值得注意的是,尽管试样H-S2的衰减常数并不是最大的,但其相较于其他试样展现出优异的阻抗匹配性能。



(a)—阻抗匹配;(b)—衰减常数。

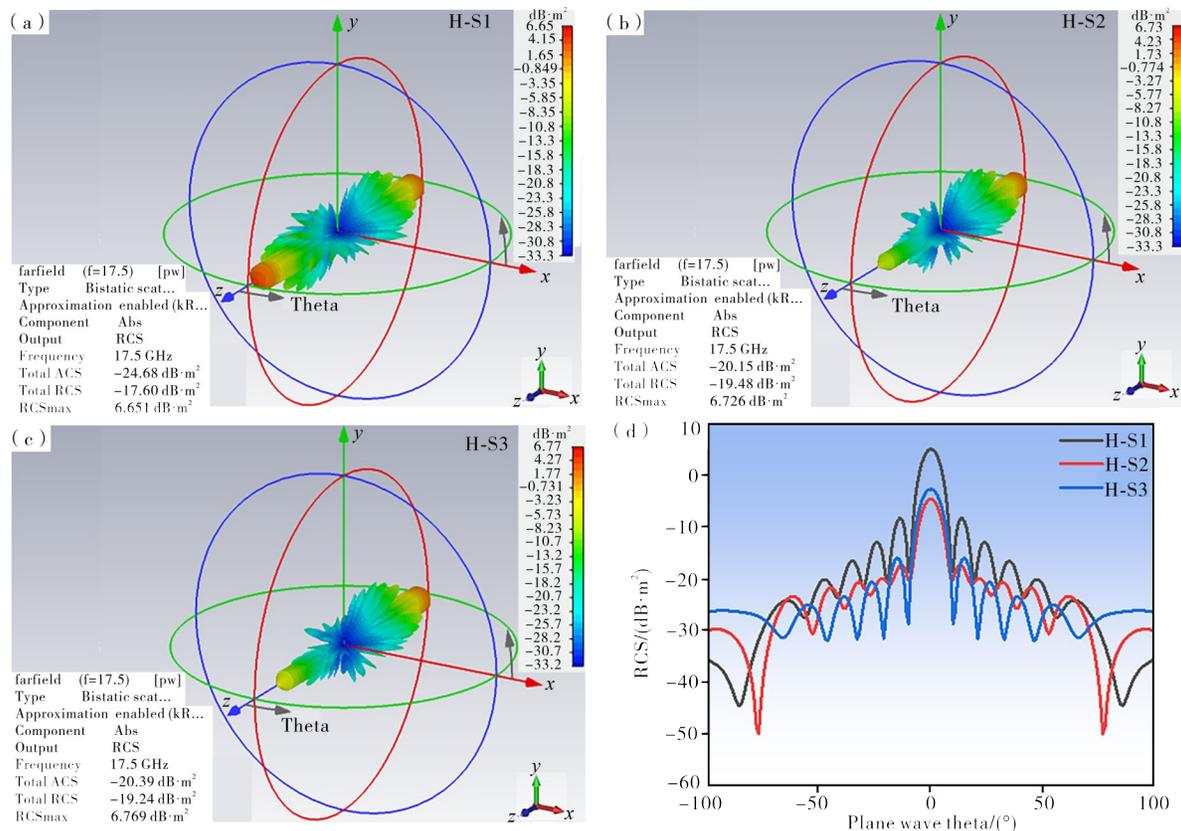
(a)—impedance matching;(b)—attenuation constant.

图7 试样H-S1、H-S2和H-S3的阻抗匹配、衰减常数图

Figure 7 Impedance matching and attenuation constant of the sample

雷达散射界面(RCS)是雷达隐身技术中评估电磁波吸收特性的重要参数,可以通过CST STUDIO SUITE软件仿真得出实际远场条件下电磁波吸收特性。仿真模型是假定在理想导体(PEC)表面分别涂覆H-S1、H-S2和H-S3吸波材料。其中,试样厚度为5.05 mm、频率为17.5 GHz、电磁波

水平入射。对纯PEC线及涂有H-S1、H-S2和H-S3薄膜的PEC板的反射信号强度进行了全方位检测,结果如图8所示。从图8(a—d)可见,试样H-S2的水平反射强度明显低于其他试样。表明,H-S2能够消耗更多的电磁波能量。从图8(d)H-S1、H-S2和H-S3在X-Y平面中的RCS分布的2D投影可见,试



(a—c)—试样H-S1、H-S2、H-S3三维雷达波散射信号;(d)—试样H-S1、H-S2、H-S3的RCS仿真曲线图。

(a—c)—three-dimensional radar wave scattering signals of H-S1, H-S2 and H-S3 samples;(d)—RCS simulation curves of samples H-S1, H-S2 and H-S3.

图8 试样的三维雷达波散射信号和RCS仿真曲线图

Figure 8 3D radar scattering signal and RCS simulation curve of the sample

样H-S2在角度 -100° — 100° 范围内表现出优越的微波吸收性能。CST模拟结果与前面讨论的电磁波吸收特性结果相一致。

基于上述实验和模拟分析,揭示了试样H-S2的主要电磁波吸收机理。首先,介孔结构提供的大比表面积促进了电磁波的多重散射和反射能力,从而提升了其吸收性能。其次,第二相金红石的引入增强了界面极化损耗,同时试样中存在的大量缺陷诱导了缺陷偶极子的产生,增强了偶极极化。次之,大量氧空位提升了电荷迁移能力,改善了电导损耗能力。界面极化、偶极子极化和传导损耗之间的良好协同作用,显著提高了试样H-S2对电磁波的高效吸收能力。

3 结论

本文采用无溶剂自组装策略并结合N₂气氛还原处理,成功制备了富缺陷介孔TiO₂,探讨了不同合成温度和还原处理对合成介孔TiO₂的晶体结构、微观形貌、比表面积及电磁吸波性能的影响。研究表明,经过N₂气氛还原处理后,试样的颗粒尺寸增大、结晶度降低。同时,氧空位的含量从27%增加至45%,说明试样通过N₂气氛还原处理引入了大量缺陷。经还原处理后试样H-S2的比面积从41.14 m²·g⁻¹减小至16.42 m²·g⁻¹,说明了介孔结构的坍塌。此外,经过N₂气氛处理后的试样介电常数显著提升。当制备温度为500℃时,经过N₂气氛还原处理后,H-S2试样在模拟厚度为5.08 mm的条件下,最小反射损耗为-30.5 dB,最大有效吸收带宽达到2.32 GHz。实验和仿真结果表明,试样H-S2具有良好的阻抗匹配和衰减能力,同时展现出优异的微波吸收性能。本研究为扩展TiO₂在吸波材料中的应用提供了一条可行的途径。

参考文献:

- [1] WANG L, HUANG M, QIAN X, et al. Confined magnetic-dielectric balance boosted electromagnetic wave absorption [J]. *Small*, 2021, 17(30): 2100970.
- [2] ZHI D, LI T, LI J, et al. A review of three-dimensional graphene-based aerogels: Synthesis, structure and application for microwave absorption [J]. *Composites Part B: Engineering*, 2021, 211: 108642.
- [3] WU Z, YAO X, XING Y. A review of nitrogen-doped graphene aerogel in electromagnetic wave absorption [J]. *Micromachines*, 2023, 14(9): 1762.
- [4] ZHANG Z, TAN J, GU W, et al. Cellulose-chitosan framework/polyaniline hybrid aerogel toward thermal insulation and microwave absorbing application [J]. *Chemical Engineering Journal*, 2020, 395: 125190.
- [5] CHOI J, JUNG H T. A new triple-layered composite for high-performance broadband microwave absorption [J]. *Composite Structures*, 2015, 122: 166-171.
- [6] XIA S, YAO B, CHEN Q, et al. Composites with Koch fractal activated carbon fiber felt screens for strong microwave absorption [J]. *Composites Part B: Engineering*, 2016, 105: 1-7.
- [7] DONG S, ZHANG W, ZHANG X, et al. Designable synthesis of core-shell SiCW@C heterostructures with thickness-dependent electromagnetic wave absorption between the whole X-band and ku-band [J]. *Chemical Engineering Journal*, 2018, 354: 767-76.
- [8] SULTANOV F, DAULBAYEV C, BAKBOLAT B, et al. Advances of 3D graphene and its composites in the field of microwave absorption [J]. *Advances in Colloid Interface Science*, 2020, 285: 102281.
- [9] SONG Q, YE F, KONG L, et al. Graphene and MXene nanomaterials: toward high-performance electromagnetic wave absorption in gigahertz band range [J]. *Advanced Functional Materials*, 2020, 30(31): 2000475.
- [10] 钟国媛,董季玲,石小雪,等. Fe-MOFs衍生碳基吸波材料研究进展[J]. *电子元件与材料*, 2024, 43(2): 127-136.
- [11] LIU Q, XU X, XIA W, et al. Dependency of magnetic microwave absorption on surface architecture of Co₂₀Ni₈₀ hierarchical structures studied by electron holography [J]. *Nanoscale*, 2015, 7(5): 1736-1743.
- [12] 项建乐. 氢化TiO₂及其复合物的可控制备、微波吸收性能与机理研究[D]. 武汉: 武汉大学, 2019.
- [13] FEI Y, JIAO W, WU Z, et al. Recent progress in TiO₂-based microwave absorption materials [J]. *Nanoscale*, 2023, 15(29): 12193-12211.
- [14] ZHANG M, YIN K, HOOD Z D, et al. In situ TEM observation of the electrochemical lithiation of N-doped anatase TiO₂ nanotubes as anodes for lithium-ion batteries [J]. *Journal of Materials Chemistry A*, 2017, 5(39): 20651-20657.
- [15] NIU L, ZHAO X, TANG Z, et al. Difference in performance and mechanism for methylene blue when TiO₂ nanoparticles are converted to nanotubes [J]. *Journal of Cleaner Production*, 2021, 297: 126498.
- [16] XIA T, ZHANG C, OYLER N A, et al. Hydrogenated TiO₂ nanocrystals: a novel microwave absorbing material [J]. *Advanced Materials*, 2013, 25(47): 6905-6910.
- [17] TUICHAJ W, DANWITTAYAKUL S, CHANLEK N, et al. High-performance giant-dielectric properties of rutile TiO₂ co-doped with acceptor-Sc³⁺ and donor-Nb⁵⁺ ions [J]. *Journal of*

- Alloys Compounds, 2017, 703: 139-147.
- [18] KANG S, QIAO S, CAO Y, et al. Hyper-cross-linked polymers-derived porous tubular carbon nanofibers@TiO₂ toward a wide-band and lightweight microwave absorbent at a low loading content [J]. ACS Applied Materials Interfaces, 2020, 12(41): 46455-46465.
- [19] ZHAO B, SHAO G, FAN B, et al. Effect of the TiO₂ amounts on microwave absorption properties of Ni/TiO₂ heterostructure composites [J]. Physica B: Condensed Matter, 2014, 454: 120-125.
- [20] MO Z, YANG R, LU D, et al. Lightweight, three-dimensional carbon nanotube@TiO₂ sponge with enhanced microwave absorption performance [J]. Carbon, 2019, 144: 433-439.
- [21] DONG J, ULLAL R, HAN J, et al. Partially crystallized TiO₂ for microwave absorption [J]. Journal of Materials Chemistry A, 2015, 3(10): 5285-5288.
- [22] XU J, QI X, LUO C, et al. Synthesis and enhanced microwave absorption properties: A strongly hydrogenated TiO₂ nanomaterial [J]. Nanotechnology, 2017, 28(42): 425701.
- [23] CAO K, YANG X, ZHANG Y, et al. Preparation of magnetic three-dimensional porous Co-rGO aerogel for enhanced microwave absorption [J]. Carbon, 2023, 208: 111-122.
- [24] XIONG H, ZHOU H, SUN G, et al. Solvent-free self-assembly for scalable preparation of highly crystalline mesoporous metal oxides [J]. Angewandte Chemie International Edition, 2020, 59(27): 11053-11060.
- [25] GUI Y, CHEN P, LIU D, et al. TiO₂ nanotube/rGO modified separator as an effective polysulfide-barrier for high electrochemical performance Li-S batteries [J]. Journal of Alloys Compounds, 2022, 895: 162495.
- [26] KUMAR N, DWIVEDI S K, TIWARI D C, et al. Study of rGO-CNF/Ce-TiO₂ based heterojunction for optoelectronic devices [J]. Materials Letters, 2022, 315: 131945.
- [27] PANG S Y, IO W F, HAO J. Facile atomic-level tuning of reactive metal-support interactions in the Pt QDs@HF-free MXene heterostructure for accelerating pH-universal hydrogen evolution reaction [J]. Advanced Science, 2021, 8(22): 2102207.
- [28] PANG S Y, IO W F, WONG L W, et al. Direct and in situ growth of 1T' MoS₂ and 1T MoSe₂ on electrochemically synthesized MXene as an electrocatalyst for hydrogen generation [J]. Nano Energy, 2022, 103: 107835.
- [29] HAO Z, LYU J, TIAN M, et al. Unraveling the synergistic effects of oxygen vacancy and amorphous structure on TiO₂ for high-performance lithium storage [J]. Small Structures, 2024, 5(4): 2300442.
- [30] CUI H, ZHAO W, YANG C, et al. Black TiO₂ nanotube arrays for high-efficiency photoelectrochemical water-splitting [J]. Journal of Materials Chemistry A, 2014, 2(23): 8612-8616.
- [31] BILLO T, FU F Y, RAGHUNATH P, et al. Ni-nanocluster modified black TiO₂ with dual active sites for selective photocatalytic CO₂ reduction [J]. Small, 2018, 14(2): 1702928.
- [32] ZHANG D, CONG T, XIA L, et al. Growth of black TiO₂ nanowire/carbon fiber composites with dendritic structure for efficient visible-light-driven photocatalytic degradation of methylene blue [J]. Journal of Materials Science, 2019, 54(10): 7576-7588.
- [33] LEI B, CUI W, SHENG J, et al. Synergistic effects of crystal structure and oxygen vacancy on Bi₂O₃ polymorphs: Intermediates activation, photocatalytic reaction efficiency, and conversion pathway [J]. Science Bulletin, 2020, 65(6): 467-476.
- [34] TIAN Q, YI S, LI C, et al. Design of charge transfer channels: Defective TiO₂/MoP supported on carbon cloth for solar-light-driven hydrogen generation [J]. Inorganic Chemistry Frontiers, 2021, 8(8): 2017-2026.
- [35] WU Z, YANG P, LI Q, et al. Microwave synthesis of Pt clusters on black TiO₂ with abundant oxygen vacancies for efficient acidic electrocatalytic hydrogen evolution [J]. Angewandte Chemie International Edition, 2023, 62(14): e202300406.
- [36] WU T, ZHAO H, ZHU X, et al. Identifying the origin of Ti³⁺ activity toward enhanced electrocatalytic N₂ reduction over TiO₂ nanoparticles modulated by mixed-valent copper [J]. Advanced Materials, 2020, 32(30): 2000299.
- [37] ZHANG L, LU C, YE F, et al. Selenic acid etching assisted vacancy engineering for designing highly active electrocatalysts toward the oxygen evolution reaction [J]. Advanced Materials, 2021, 33(14): 2007523.
- [38] KANG J, MIN J, KIM S I, et al. Three-level micro-meso-macroporous three-dimensional graphene for highly fast capacitive deionization [J]. Materials Today Energy, 2020, 18: 100502.
- [39] 邓云飞, 张海燕, 韩聪爱, 等. 三维蜂窝状碳包纳米铁颗粒复合材料的制备及吸波性能的研究[J]. 材料研究与应用, 2020, 14(3): 171-178.
- [40] WEN G, ZHAO X, LIU Y, et al. Electromagnetic wave absorption performance and electrochemical

properties of multifunctional materials;
Air@Co@Co₃-Sn₂@SnO₂ hollow sphere/reduced

graphene oxide composites [J]. Chemical Engineering
Journal, 2021, 420: 130479.

Study on the Preparation of Defective Mesoporous TiO₂ and Its Absorbing Properties

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Abstract: The issue of electromagnetic radiation from electronic communication devices has become increasingly critical. To tackle electromagnetic pollution, there is an urgent demand for microwave-absorbing materials that are thin, lightweight, possess a broad absorption frequency range, and demonstrate strong absorption capacity. TiO₂ has emerged as a promising candidate due to its low density and high stability. However, the application of pure TiO₂ is hindered by poor electromagnetic response, low dielectric constant, and insufficient attenuation characteristics. To enhance the microwave absorption performance of TiO₂, mesoporous TiO₂ was synthesized using a solvent-free self-assembly method at various temperatures, followed by reduction treatment to introduce defects, resulting in defect-rich mesoporous TiO₂. The crystal structure and morphology of the materials were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM), while X-ray photoelectron spectroscopy (XPS) was employed to analyze changes in elemental valence before and after the reduction of. The specific surface area and pore structure characteristics were evaluated through nitrogen adsorption-desorption isotherms, and the electromagnetic parameters were measured with a vector network analyzer. The study systematically explored the effects of synthesis temperature and reduction treatment on the electromagnetic absorption of mesoporous TiO₂. Results show that as synthesis temperature increase, mesoporous TiO₂ transitions from a pure anatase phase to a mixture of anatase and rutile phase. After reduction treatment, the mesoporous structure remains intact, although specific surface area decreases, and a significant number of oxygen vacancies are introduced. While synthesis temperature has a minor effect on electromagnetic parameters, the dielectric constant improves significantly after reduction treatment. Mesoporous TiO₂ synthesized at 500 °C and subjected to reduction treatment exhibited excellent wave absorption properties, with a minimum reflection loss of -30.5 dB at a simulated thickness of 5.05 mm and an effective absorption bandwidth of 2.32 GHz. This excellent microwave absorption performance is attributed to the large specific surface area provided by the mesoporous structure, enhanced interfacial polarization loss from the secondary phase, and defect-induced dipole polarization. This study provides a viable approach for the development of high performance TiO₂-based microwave absorbing materials.

Keywords: mesoporous TiO₂; atmosphere reduction; defect; dielectric loss; impedance matching; attenuation constant; microwave absorption; RCS simulation

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