

La³⁺掺杂 ZnFe₂O₄ 材料的制备及其气敏性能

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摘 要: 呼出气中挥发性有机物(VOCs)浓度低, 实现其精准检测至关重要。本工作采用静电纺丝法制备了 La³⁺掺杂 ZnFe₂O₄ 材料, 通过 X 射线衍射(XRD)、扫描电子显微镜(SEM)和 X 射线光电子能谱(XPS)对材料的晶体结构、表面形貌和元素价态进行分析。结果表明, 8%(质量分数) La³⁺掺杂的 ZnFe₂O₄ 材料在室温下对 0.1 g/L 丙酮的灵敏度为 21.3, 是纯 ZnFe₂O₄ 的 11.5 倍, 最低检测限为 0.000 01 g/L, 该复合材料制备的气体传感器能够在室温下检测低浓度丙酮气体, 对人体呼出气体中丙酮的检测具有良好应用前景。

关键词: 气体传感器; 室温传感; 丙酮; 铁酸锌

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呼气分析技术通过检测人体呼出气中挥发性有机化合物(VOCs)的浓度实现一些疾病的初步诊断^[1]。研究表明, 丙酮可作为辅助糖尿病诊断的生物标志物, 其中糖尿病患者呼气中丙酮浓度超过 0.001 8 g/L, 而健康人体呼气中丙酮浓度低于 0.000 9 g/L^[2]。因此, 研发具有低检测限与高选择性的丙酮气体传感器, 对实现糖尿病早筛查至关重要。

尖晶石型铁氧体作为一种重要的金属氧化物(MOS), 因其成本低和优异的稳定性而备受气体传感领域研究人员的关注^[3-4]。例如, 常见的尖晶石型铁氧体有 CuFe₂O₄ 和 ZnFe₂O₄^[5-6]。其中, ZnFe₂O₄ 可调控微观形貌改善材料表面活性位点数目, 从而对丙酮等 VOCs 表现出高灵敏度^[7-8]。Dong 等^[9]采用溶剂热法合成了单分散的 ZnFe₂O₄ 纳米球, 在 300 °C 对 0.001 g/L 和 0.100 g/L 甲苯的响应值分别为 1.41 和 9.98。Wen 等^[10]使用多重工艺制备了多孔 ZnFe₂O₄ 纳米片, 在 220 °C 条件下对 0.1 g/L 丙酮进行检测, 获得了较高的响应值($R_a/R_g=64.9$)。然而, 单一 ZnFe₂O₄ 气体传感器在实际检测中存在工作温度高、气敏选择性低等问题。

离子掺杂是一种通过诱导金属氧化物产生晶格畸变进而调控材料表面缺陷的改性方法。表面缺陷的产生能为气敏反应提供更多的活性中心, 促进氧分子在材料表面的吸附, 进而改善材料气敏性能^[11]。此外, 稀土元素(如 La³⁺)掺杂到 MOS 材料中, 能够提高其催化活性和增加电子迁移速率, 从而提高传感性能^[12-13]。Ma 等^[14]通过溶剂热法制备了 La³⁺掺杂 In₂O₃ 纳米球, 其形貌由不规则纳米花状变成相对均匀大纳米球, 对甲醛的灵敏度提高 16 倍, 最佳工作温度从 220 °C 降至 170 °C。Jansi 等^[15]通过滴铸法将 La³⁺掺杂到 ZnO 薄膜中, 材料形貌从球形颗粒变为片状颗粒, 增大了材料的比表面积, 提供了更多活性位点。室温下, 该材料对 NO₂ 灵敏度较纯 ZnO 提高了 15.6 倍。尽管 La³⁺在 In₂O₃、ZnO 等常见金属氧化物中展现显著的改性效果, 但在尖晶石型氧化物中的研究仍相对有限。

本工作通过静电纺丝法制备一系列 La³⁺掺杂 ZnFe₂O₄ 复合材料, 相较于水热法^[16]、共沉淀法^[17]、溶胶-凝胶法^[18]等传统合成方法, 静电纺丝法制备的材料具有可调控的形貌和更高的稳定性。气敏测

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试结果显示, 8%(质量分数) La^{3+} 掺杂 ZnFe_2O_4 在室温下对 0.1 g/L 丙酮响应值为 21.3, 最低检测限为 0.000 01 g/L。与纯 ZnFe_2O_4 相比, 不仅降低了工作温度还提高了响应值。

1 实验

1.1 试剂

试剂有分析纯的 $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (硝酸镧水合物, AR)、 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (六水合硝酸锌, AR)、 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (九水合硝酸铁, AR)、DMF(N, N-二甲基甲酰胺, AR)和 PVP(聚乙烯吡咯烷酮, AR), 无水乙醇(AR)和自制去离子水。

1.2 样品制备

使用静电纺丝法制备纯 ZnFe_2O_4 和不同质量比 La^{3+} 掺杂 ZnFe_2O_4 材料, 实验过程如下: 取 0.808 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 、0.297 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和不同质量比(0%、1%、4%、8%、12%)的 $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, 分别置于 5 个 10 mL 的烧杯中, 各加入 5 mL DMF 搅拌溶解。缓慢加入 0.85 g PVP, 继续搅拌 12 h 以上, 使 PVP 完全溶解, 观察到溶液中无明显气泡产生时, 即停止搅拌。

将溶液注入 10 mL 注射器后固定于水平静电纺丝装置, 设置针头接正极(11~13 kV)、铝箔接收器接负极, 极间距 15 cm。控制环境湿度 30%~50%, 以 3 $\mu\text{L}/\text{min}$ 供液速率纺丝, 所得纤维经马弗炉程序升温至 600 $^{\circ}\text{C}$ 煅烧 2 h(升温速率为 1 $^{\circ}\text{C}/\text{min}$)。所得产物分别标记为 ZnFe_2O_4 、LZF-1 (1% La^{3+})、LZF-4 (4% La^{3+})、LZF-8 (8% La^{3+})、LZF-12 (12% La^{3+})。

1.3 样品表征

通过 X 射线衍射(XRD, Bruker D8 Advance, 40 kV, 40 mA, Cu 靶, $\text{K}\alpha$ 射线), 以扫描速率为

5($^{\circ}$)/min、扫描范围为(10 $^{\circ}$ ~80 $^{\circ}$)分析物相组成。采用 TESCAN MIRA LMS 型扫描电子显微镜(SEM)观测样品微观形貌(加速电压为 15 kV)。采用 Thermo ESCALAB 250X 型 X 射线光电子能谱仪(XPS, Al $\text{K}\alpha$, $h\nu=1486\text{ eV}$)分析材料的元素价态。

1.4 气敏元件的制作与性能测试

将样品放入研钵中, 滴入 1~2 滴松节油透醇, 研磨至形成均匀的浆状物, 后用小毛刷将浆状物均匀涂抹在氧化铝陶瓷管的表面, 接着将镍铬加热丝穿过陶瓷管, 并焊接到气敏元件底座上, 最后, 将气敏元件在 200 $^{\circ}\text{C}$ 老化 12 h, 即可进行气敏性能测试。

n 型材料气体传感器灵敏度 R 定义为: $R=R_a/R_g$ (式中: R_a 为空气的电阻值; R_g 为待测气体的电阻值)。除研究相对湿度对气敏材料性能影响试验外, 其他实验过程中所有测试环境的相对湿度均为 45%。

2 结果与讨论

2.1 材料表征

采用 XRD 表征了 ZnFe_2O_4 及 La^{3+} 不同掺杂比例的 ZnFe_2O_4 纳米纤维晶体结构。当 2θ 位于 30.02 $^{\circ}$, 35.36 $^{\circ}$, 42.97 $^{\circ}$, 53.30 $^{\circ}$, 56.82 $^{\circ}$, 62.39 $^{\circ}$ 时, 衍射峰分别对应于(220)、(311)、(400)、(422)、(511)、(440)的晶面, 与立方相尖晶石 ZnFe_2O_4 的标准衍射峰(PDF No.89-1009)一致。由图 1b 可见, 随着 La^{3+} 含量增加, 衍射峰向左偏移, 晶面主峰强度减弱。衍射峰的偏移是因为较大的 La^{3+} (1.061 $\text{\AA}$)取代了八面体位点较小的 Fe^{3+} (0.79 $\text{\AA}$), 引起材料晶格常数发生变化, 导致晶格畸变^[19-20]。根据谢乐(Scherrer)公式计算得出, 纯 ZnFe_2O_4 的平均晶粒尺寸为 20.34 nm, LZF-8 材料的平均晶粒尺寸为 9.22 nm。显然在 La^{3+} 掺杂后, ZnFe_2O_4 的平均晶粒尺寸明显降低。

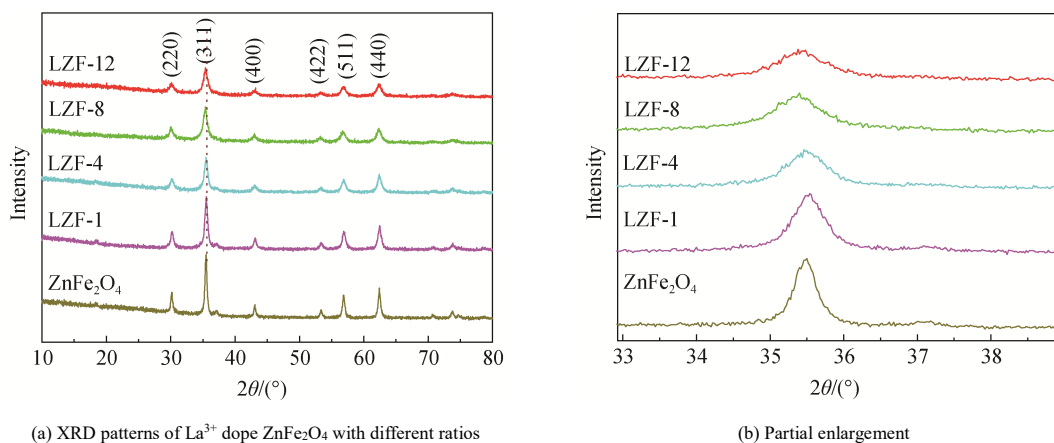


图 1 不同比例 La^{3+} 掺杂 ZnFe_2O_4 的 XRD 谱
Fig. 1 XRD patterns of La^{3+} dope ZnFe_2O_4 with different ratios

图 2 为 ZnFe_2O_4 和样品 LZF-8 的物相结构。由图 2a 和图 2b 可见, 纯 ZnFe_2O_4 经 600°C 退火后, PVP 完全分解, 形成表面粗糙的纳米纤维。由图 2c 和图 2d 可见, LZF-8 材料则呈现显著差异, 其纳米纤维表面相对光滑且相互交联构成网状结构。结合 XRD 结果可知, LZF-8 表面光滑的特性与其晶粒尺

寸的减小相关。根据 EDS 能谱分析(图 2e)和元素分布图(图 2f), La、Zn、Fe 和 O 元素在 LZF-8 材料中均有分布, 证实了 La^{3+} 已掺杂到 ZnFe_2O_4 中。

图 3 为 LZF-8 材料的 XPS 能谱和 ZnFe_2O_4 的 O 1s 谱。由图 3a 和图 3b 可见, 在 1021.12 eV 和 1044.18 eV 附近 2 个拟合峰分别归属 $\text{Zn } 2\text{p}_{3/2}$ 和

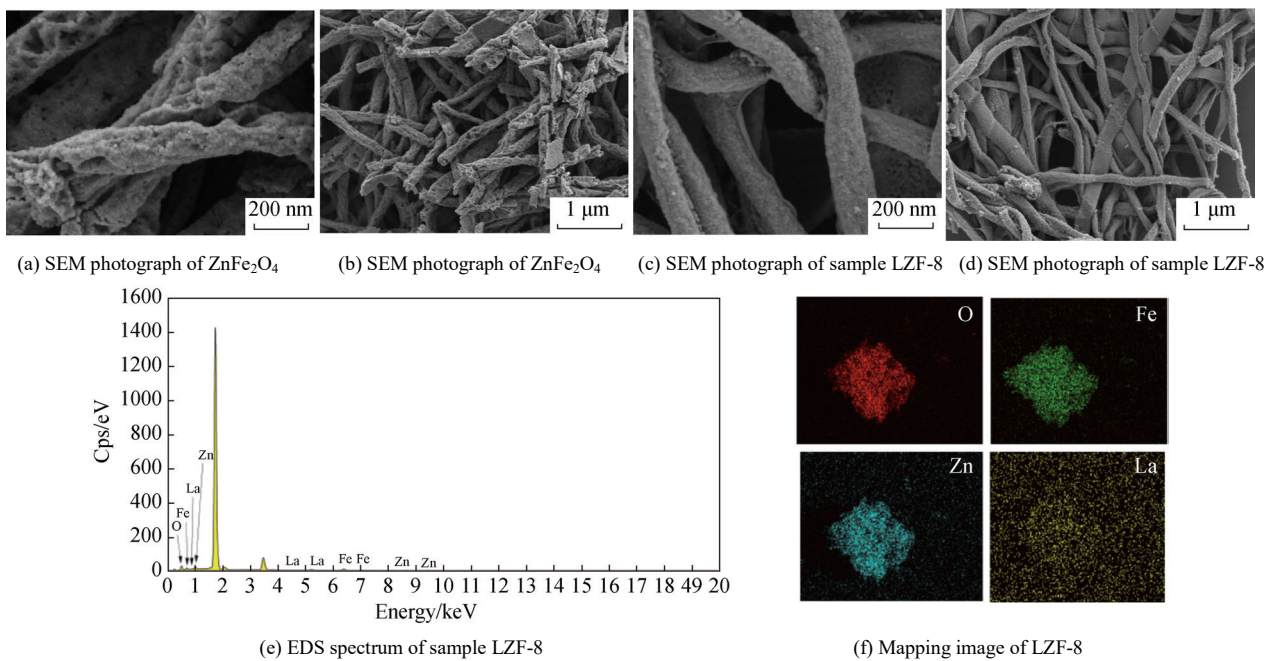


图 2 ZnFe_2O_4 和样品 LZF-8 的物相结构
Fig. 2 Phase Structure of samples ZnFe_2O_4 and LZF-8

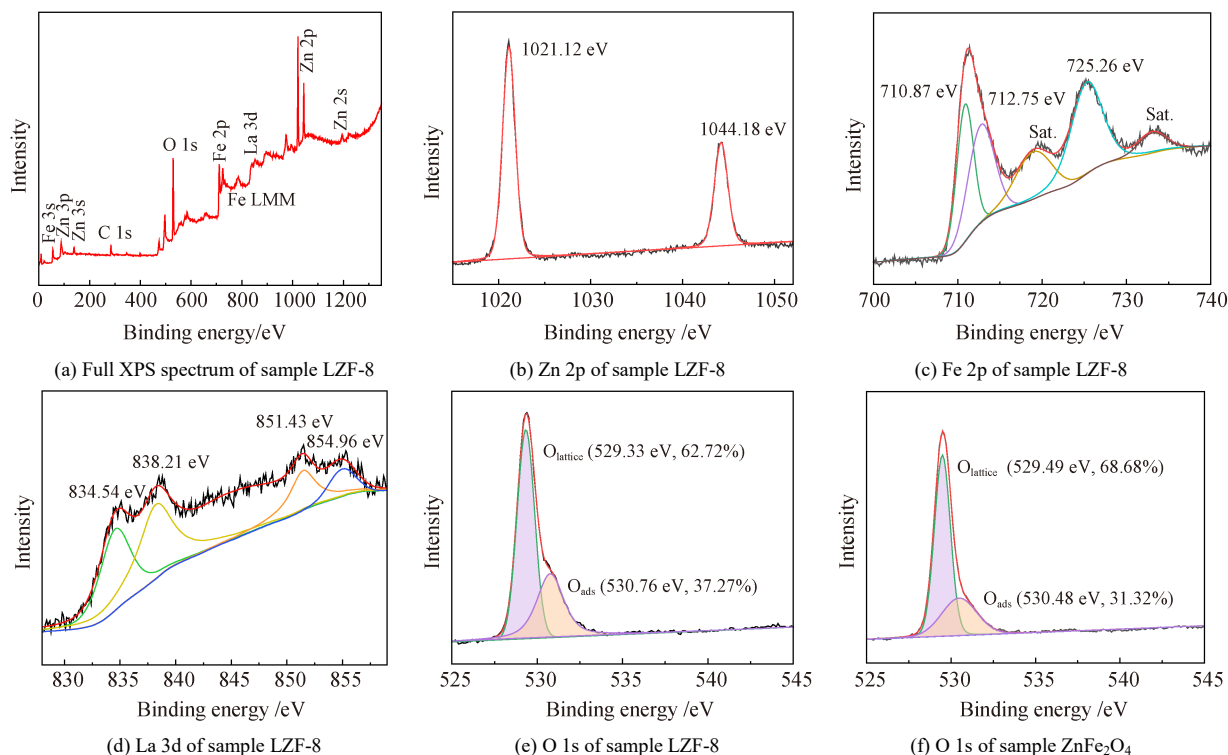


图 3 LZF-8 材料的 XPS 能谱和 ZnFe_2O_4 的 O 1s 谱
Fig. 3 XPS spectra of LZF-8 and O 1s of ZnFe_2O_4

$\text{Zn } 2p_{1/2}$ 。两峰之间的结合能差值约为 23 eV, 证明了 LZF-8 材料中 Zn 的氧化态为正二价^[21]。图 3c 中 $\text{Fe } 2p_{3/2}$ 的峰位于 710.87 eV 和 712.75 eV 处, 分别对应四面体和八面体位点; 结合能为 725.26 eV 的峰属于 $\text{Fe } 2p_{1/2}$ 。此外, $\text{Fe } 2p_{3/2}$ 和 $\text{Fe } 2p_{1/2}$ 的卫星峰分别位于 719.30 eV 和 733.30 eV, 表明 LZF-8 材料中的 Fe 以正三价形式存在。图 3d 为 La 3d 的 XPS 谱, 观察到 4 个拟合峰, 结合能为 834.54 eV 和 851.43 eV 的峰分别对应于 $\text{La } 3d_{5/2}$ 和 $\text{La } 3d_{3/2}$, 其自旋-轨道分裂能为 16.89 eV。La $3d_{5/2}$ 和 $\text{La } 3d_{3/2}$ 的主峰均伴随 1 个卫星峰, 分别位于 838.21 eV 和 854.96 eV。La $3d_{5/2}$ 与其卫星峰之间的结合能差值为 3.6 eV, 表明 La 元素形成了 $\text{La}(\text{OH})_3$ ^[19]。图 3e 和 3f 分别为 LZF-8 材料和纯 ZnFe_2O_4 的 O 1s 光电子谱, 两者的 O 1s 光谱均

被分为 2 个拟合峰, 结合能从高到低分别代表化学吸附氧(O_{ads})和晶格氧($\text{O}_{\text{lattice}}$)。当掺杂 8% La^{3+} 时, O_{ads} 的相对百分比达到 37.27%, 比纯 ZnFe_2O_4 高 5.95%。 La^{3+} 掺杂引起晶格畸变, 导致材料表面吸附氧增加, 在材料的表面吸附更多氧气, 提升了气敏性能^[20]。

图 4 为纯 ZnFe_2O_4 和 LZF-8 材料的紫外-可见吸收光谱及对应的禁带宽度。由图 4a 和图 4c 可以看出, 纯 ZnFe_2O_4 和 LZF-8 材料均在 200 nm 至 450 nm 范围内都具有一定的吸收, 而当波长大于 450 nm 时, 吸收峰的强度快速下降。由图 4b 和图 4d 可以看出, 纯 ZnFe_2O_4 和 LZF-8 材料的带隙能量(E_g)分别为 2.10 eV、2.12 eV, 较窄的带隙宽度表明电子跃迁所需的能量较低, 有利于电子的迁移, 从而缩短响应/恢复时间。

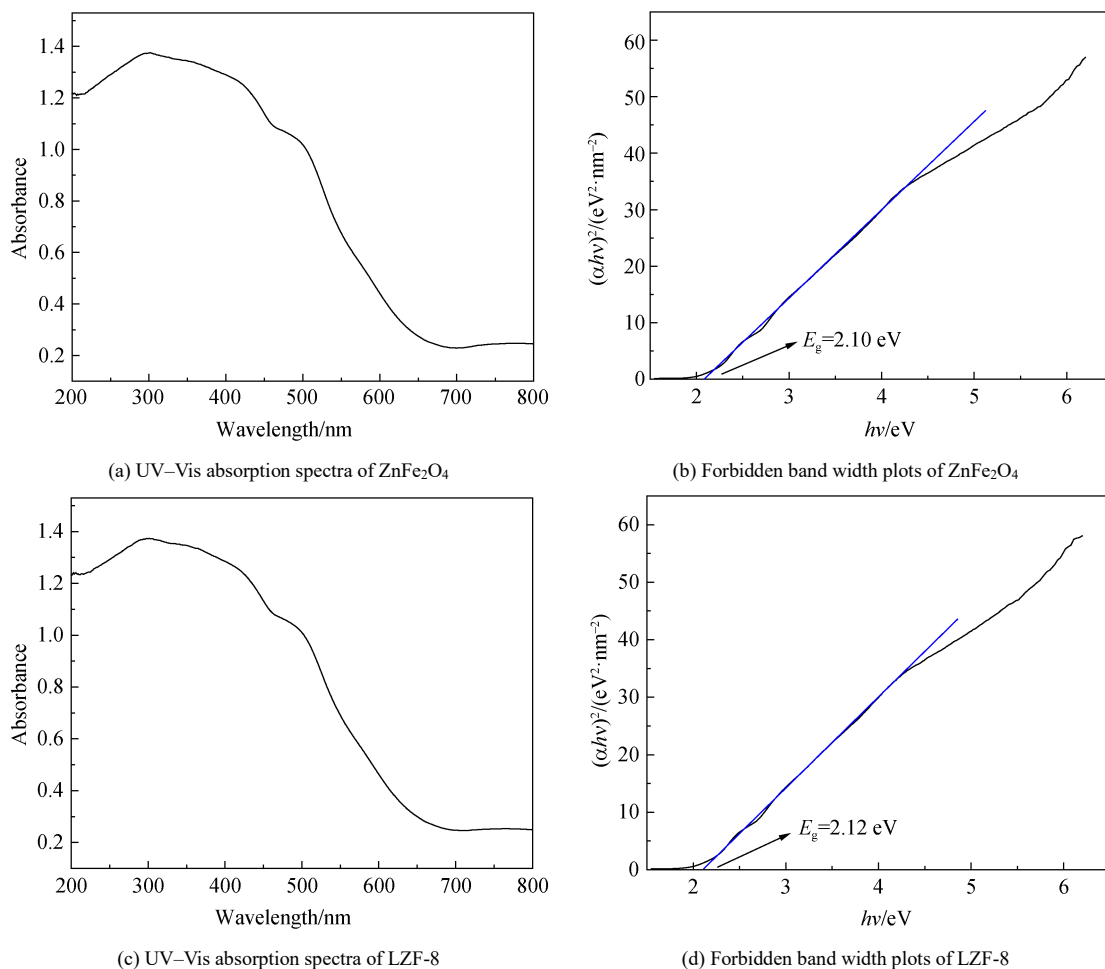


图 4 ZnFe_2O_4 和 LZF-8 材料的紫外-可见吸收光谱与禁带宽度

Fig. 4 UV-Vis absorption spectra and forbidden band width plots of ZnFe_2O_4 and LZF-8 material

2.2 气敏性能

图 5 为材料气敏性能测试结果。由图 5a 可见, 室温(25 $^{\circ}\text{C}$)条件下, 样品材料对 0.1 g/L 丙酮的响应

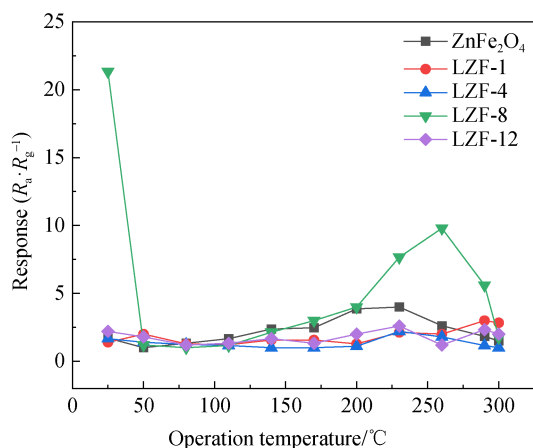
值随 La^{3+} 掺杂量的增加呈现“先增大后减小”的趋势, 其中, LZF-8 响应值最大($R_a/R_g=21.3$)。LZF-8 在室温下的响应值, 显著高于其他温度下的响应值,

这是因为 La^{3+} 的掺杂改变了晶格中原子的排列顺序, 降低了晶界的能垒高度, 从而提升了载流子的扩散和传输速率^[22]。此外, 纯 ZnFe_2O_4 在 230°C 对 0.1 g/L 丙酮的响应值为 4.0 , 低于 LZF-8 室温下对丙酮的响应值。因此, 掺入 $8\%\text{ La}^{3+}$ 不仅提高了对丙酮气体的响应, 还降低了工作温度。

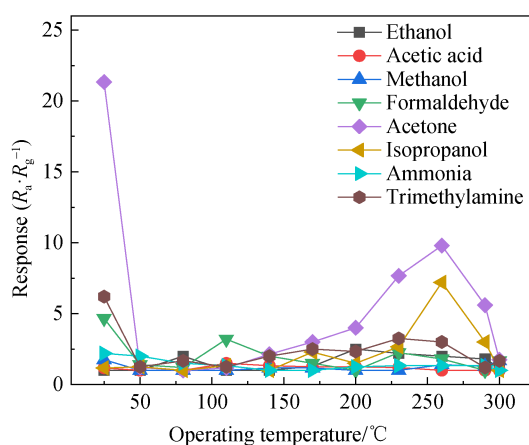
图 5b 为 LZF-8 材料在不同温度下对 0.1 g/L 的 8 种气体的响应折线图。对于 0.1 g/L 的丙酮, LZF-8 在室温和 260°C 下的响应值分别为 21.3 和 9.8 , 其室温下的响应值较 260°C 提升了 2.17 倍。该材料在室温下对其余 7 种气体的响应值均小于 6.2 , 说明 LZF-8 材料在室温下对丙酮有较好的气体选择性; 而 260°C 时异丙醇响应值为 7.2 与丙酮相近, 说明在 260°C 对丙酮气体的选择性较差。因此, LZF-8 的最佳工作温度是室温。

图 5c 为纯 ZnFe_2O_4 和 LZF-8 材料在室温条件下对 0.1 g/L 的 8 种气体的响应值。LZF-8 材料在室温下对 0.1 g/L 丙酮的响应值($R_a/R_g=21.3$)显著高于三甲胺的响应值($R_a/R_g=6.2$), 其选择性系数 $S(0.1\text{ g/L 丙酮})/S(0.1\text{ g/L 三甲胺})=3.4$ 。而纯 ZnFe_2O_4 的选择性系数 $S(0.1\text{ g/L 三甲胺})/S(0.1\text{ g/L 乙醇})=1.1$ 。实验表明, La^{3+} 掺入可提高 ZnFe_2O_4 的气敏选择性。

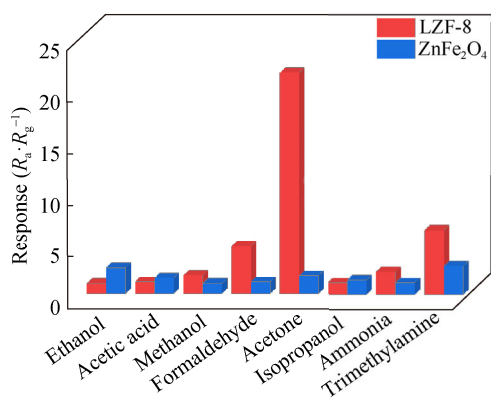
图 5d 为样品 LZF-8 在室温环境下对不同浓度丙酮气体的响应-恢复曲线。室温下, LZF-8 对丙酮的响应值随丙酮浓度的降低而减小。样品 LZF-8 不同浓度丙酮的响应值分别为 $21.3(0.1\text{ g/L})$ 、 $15.7(0.08\text{ g/L})$ 、 $10.6(0.05\text{ g/L})$ 、 $7.0(0.03\text{ g/L})$ 、 $5.5(0.01\text{ g/L})$ 、 $3.3(0.001\text{ g/L})$ 、 $1.7(0.00001\text{ g/L})$ 。因此, LZF-8 材料可检测到的最低丙酮浓度为 0.00001 g/L , 计算得到响应-恢复时间分别为 $3.0\text{ s}/3.7\text{ s}$ 。



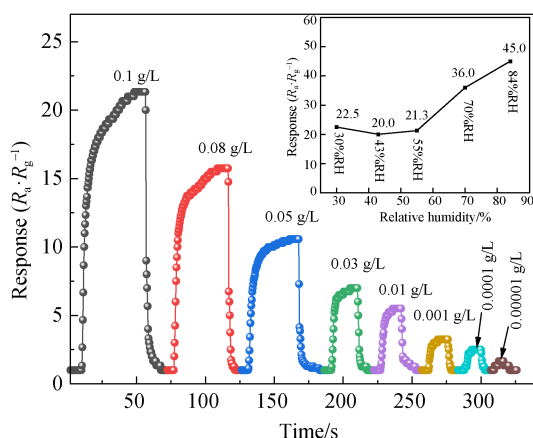
(a) Response of La^{3+} dope ZnFe_2O_4 composites with different ratios to 0.1 g/L acetone under different temperature



(b) Response of LZF-8 to 8 kinds of gases of 0.1 g/L under different temperature



(c) Response comparison under room temperature of ZnFe_2O_4 and LZF-8



(d) Response-recovery curve of LZF-8 for different acetone concentrations at room temperature

Inset in Fig.5d showing that response of LZF-8 to 0.1 g/L acetone under different humidity conditions.

图 5 材料气敏性能测试结果
Fig. 5 Results of gas response tests for the samples

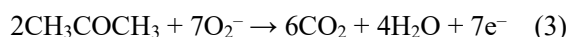
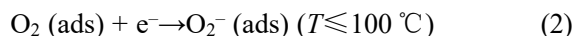
实际上,湿度也会影响材料的灵敏度。图 5d 插图显示,当相对湿度小于 55% 时, LZF-8 材料在室温下对 0.1 g/L 丙酮的响应值轻微波动;当相对湿度超过 55% 时,响应值随湿度的增加而显著增大;当相对湿度达到 84% 时,响应值高达 45.0。此时,高湿度对 LZF-8 材料的响应产生了促进作用,归因于双因素协同作用: 1) 在高湿度环境下,更多水分子与复合材料表面电子反应,释放出更多电子进入材料导带,导致电阻进一步降低,传感器响应升高^[23]; 2) 材料表面吸附水分子增多导致溶解丙酮浓度升高,传感器电信号强度显著提升,从而增强气体响应特性^[24]。

2.3 气敏机制

ZnFe_2O_4 作为 n 型半导体,通过表面吸附的氧离子与气体分子间相互作用,引起载流子浓度变化,从而导致气体传感器电阻发生改变^[25]。通过对丙酮的气敏性能测试,8% La^{3+} 掺杂 ZnFe_2O_4 材料表现为 n 型半导体传感行为。

图 6 为 LZF-8 材料在空气和丙酮气体中的气敏机理和相应的能带图。由图 6 可见,当 LZF-8 材料在室温下置于空气中时,氧气分子首先在材料表面转化为化学吸附氧,并捕获 LZF-8 材料导带中的自由电子,形成 O_2^- , 反应过程如式(1)和式(2)所示。

此时,载流子浓度降低,电阻(R_a)增大,空气和电子之间形成势垒,在材料界面处形成具有一定宽度的电子耗尽层(EDL)^[14]。当 LZF-8 材料暴露于丙酮气体中时,表面吸附的丙酮与 O_2^- 反应,生成 CO_2 和 H_2O ,并向材料导带中释放出 e^- ,如式(3)所示,这一过程导致 EDL 厚度减小,电阻(R_g)降低。因此,当丙酮与 O_2 结合时,会注入额外的电子,电阻(R_g)比纯 ZnFe_2O_4 减少得更多,与纯 ZnFe_2O_4 相比, La^{3+} 掺杂的 ZnFe_2O_4 具有更高的丙酮敏感性。



La^{3+} 掺杂 ZnFe_2O_4 气敏传感性能提升的原因: 首先,根据 XRD 显示晶粒的尺寸明显减小,气敏性能提升,表明 La^{3+} 的掺杂抑制了结晶过程,阻碍了晶体生长。晶粒尺寸减小,导致传感的比表面积增加,为材料的表面提供更多的丙酮活性位点^[26]; 其次, La^{3+} 掺杂会取代半径较小的 Fe^{3+} ,导致晶格畸变,XPS 结果表明, LZF-8 比纯 ZnFe_2O_4 的吸附氧含量更高,吸附氧的含量越高,越容易诱导氧空位缺陷的产生,有利于从 ZnFe_2O_4 的导带中捕获更多的电子,增加电子耗尽层的厚度,提升气敏性能^[27]; 最后, La^{3+} 的掺杂优化了带隙宽度,有利于进行电子转移^[28]。

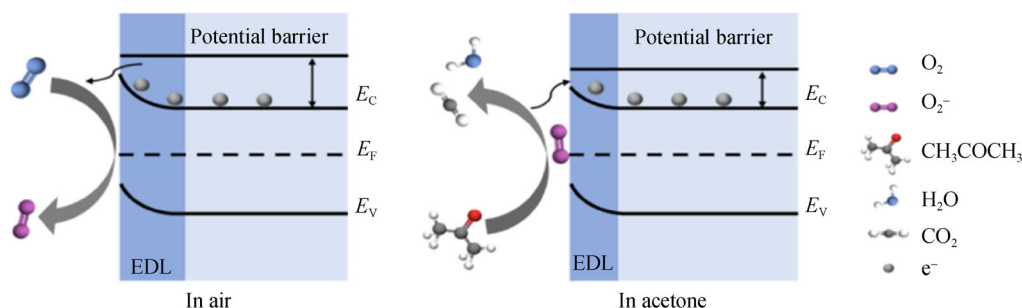


图 6 LZF-8 在空气和丙酮中的传感机理图及相应的能带图

Fig. 6 Sensing mechanism diagram of LZF-8 and corresponding energy band diagrams in air and acetone

3 结论

采用静电纺丝法制备不同比例 La^{3+} 掺杂的 ZnFe_2O_4 复合材料,结合 XRD、SEM、XPS 分析,证实了 La^{3+} 成功掺杂至 ZnFe_2O_4 晶格中。

当掺入 8% 的 La^{3+} 时,室温下对 0.1 g/L 丙酮的响应值($R_a/R_g=21.3$)较纯 ZnFe_2O_4 ($R_a/R_g=1.7$)提升约 11.5 倍,响应/恢复时间为 27.0 s/10.7 s,且丙酮浓度最低检测限为 0.000 01 g/L。该复合材料气体传感器在室温条件下展现出高效检测丙酮气体的巨大潜力。

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Gas-Sensing Properties of La^{3+} Doped ZnFe_2O_4 Materials

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Extended Abstract

Introduction Exhaled breath analysis technology enables the preliminary diagnosis of certain diseases *via* detecting the concentration of volatile organic compounds (VOCs) in human breath. Some studies indicate that acetone can serve as a biomarker to assist in the diagnosis of diabetes. Developing acetone gas sensors with low detection limits and high selectivity is thus crucial for achieving early screening of diabetes. In recent years, spinel ferrites, as an important class of metal oxides, have attracted much

attention in the gas sensing field due to their low cost and excellent stability. Among them, ZnFe_2O_4 can improve the number of active sites on the material surface *via* tailoring its microstructure, thereby exhibiting a high sensitivity to VOCs like acetone. However, single-component ZnFe_2O_4 gas sensors suffer from issues such as high operating temperatures and low gas-sensing selectivity in practical detection. The existing research shows that ion doping is a modification method that induces lattice distortion in metal oxides, thereby regulating surface defects on the material. The generation of surface defects can provide more active centers for gas-sensing reactions and promote the adsorption of oxygen molecules on the material surface, thus improving its gas-sensing properties. Furthermore, doping rare-earth elements into MOS materials can enhance their catalytic activity and increase electron migration rates, leading to an improved sensing performance. This study was to prepare a series of La^{3+} -doped ZnFe_2O_4 composites *via* electrospinning. Their morphology, surface chemical composition, and elemental valence states were characterized, and the gas-sensing properties of the composites were analyzed.

Methods 0.808 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, Sinopharm Chemical Reagent Co., Ltd., China), 0.297 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, Sinopharm Chemical Reagent Co., Ltd., China), and varying mass ratios of $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (AR, Sinopharm Chemical Reagent Co., Ltd., China) were accurately weighed. Each mixture was put into respective 10 mL beakers, add 5 mL of DMF (AR, Sinopharm Chemical Reagent Co., Ltd., China), and stir to dissolve. 0.85 g of PVP (AR, Shanghai Aladdin Biochemical Technology Co., Ltd., China) was added slowly to each solution and continue stirring for over 12 h until complete dissolution of PVP. After stirring no visible bubbles remained in the solution. The solutions were transferred into 10 mL syringes and mounted onto a horizontal electrospinning apparatus. The needle tip was set as an anode (11–13 kV) and the aluminum foil collector as a cathode, with an electrode distance of 15 cm. The ambient humidity was maintained at 30%–50% and the solution was fed at a rate of 3 $\mu\text{L}/\text{min}$. The electrospun fibers collected were calcined in a muffle furnace at 600 $^{\circ}\text{C}$ for 2 h (at a heating rate of 1 $^{\circ}\text{C}/\text{min}$). The phase composition was analyzed by X-ray diffraction (XRD, Bruker D8 Advance, 40 kV, 40 mA, $\text{Cu-K}\alpha$, 5 $^{\circ}/\text{min}$, 10 $^{\circ}$ –80 $^{\circ}$). The microstructure of the samples was determined by scanning electron microscope (SEM) with an accelerating voltage of 15 kV. The elemental valence states of the materials were analyzed by a X-ray photoelectron spectroscopy (XPS, $\text{Al K}\alpha$, $h\nu=1486\text{ eV}$).

For the determination of the gas-sensitive properties of La doping ZnFe_2O_4 composite material, the sample was placed in a mortar, and 1–2 drops of turpentine penetration alcohol were added. The mixture was ground until a uniform paste was formed. The paste was then evenly applied onto the surface of an alumina ceramic tube using a small brush. Afterwards, a nickel-chromium heating wire was passed through the ceramic tube and welded to the base of the gas sensor. Finally, the gas sensor was aged at 200 $^{\circ}\text{C}$ for 12 h before conducting gas-sensing performance tests.

Results and Discussion The XRD patterns show that the grain size is significantly reduced and the gas-sensing performance is improved, indicating that La^{3+} doping inhibits the crystallization process and hinders crystal growth. A reduction in grain size leads to an increase in the specific surface area of the sensor, providing more acetone active sites on the surface of the material. The SEM images show that the surface of La^{3+} -doped ZnFe_2O_4 nanomaterials is relatively smooth and cross-linked to form a network structure. The EDS results indicate that the composite material is composed of elements La, Zn, Fe, and O. According to the XPS analysis, La^{3+} doping causes a lattice distortion, resulting in an increase in adsorbed oxygen on the material surface. The more oxygen is adsorbed on the surface of the material, which in turn improves the gas-sensing performance. Based on the analysis of UV-visible absorption spectroscopy and the corresponding band gap, the sample LZF-8 has a narrower band gap, indicating that the energy required for electron transition is lower, which is beneficial to electron migration, thereby shortening the response/recovery time. The response value of sample LZF-8 to 0.1 g/L acetone at room temperature is 21.3, which is 11.5 times greater than that of pure ZnFe_2O_4 . Meanwhile, the selectivity and sensitivity of the material to different gases at room temperature are investigated. The results show that the sample LZF-8 has good selectivity and detection limit for acetone, with the minimum detection limit of 0.00001 g/L, proving that the prepared sensor LZF-8 has a great application potential.

Conclusions ZnFe_2O_4 composites doped with different proportions of La^{3+} were prepared *via* electrospinning. Based on the analysis of the XRD patterns, SEM images, and XPS spectra, La^{3+} was successfully doped into ZnFe_2O_4 . The results of gas-sensing test showed that as 8% La^{3+} was doped, the response value (*i.e.*, $R_a/R_g = 21.3$) to 0.1 g/L acetone at room temperature was approximately 11.5 times greater than that of pure ZnFe_2O_4 ($R_a/R_g = 1.7$), with the response/recovery time of 27.0 s/10.7 s, and the minimum detection limit of acetone concentration of 0.00001 g/L. This composite gas sensor could have a great potential for efficient detection of acetone gas under room temperature conditions.

Keywords gas sensor; room temperature detection; acetone; zinc ferrite