

WS₂-CdSnO₃ 复合材料的制备及甲醛气敏性能

刘醒醒¹, 胡梦婷¹, 刘翠翠¹, 李佳豪¹, 储向峰¹, 梁士明²

(1. 安徽工业大学化学与化工学院, 安徽 马鞍山 243002; 2. 临沂大学材料科学与工程学院, 山东 临沂 276005)

摘 要: 实现甲醛气体的高效检测对人类健康和环境污染十分重要。采用共沉淀-煅烧法制备了 CdSnO₃, 并利用超声分散法制备了一系列不同质量比的 WS₂-CdSnO₃ 复合材料。用 X 射线衍射、扫描电子显微镜和 X 射线能谱等对 CdSnO₃ 和复合材料 WS₂-CdSnO₃ 的相结构、形貌和元素价态进行了表征, 研究了 WS₂ 对 CdSnO₃ 的气体传感性能的影响, 结果表明: 与适量的 WS₂ 复合可以提高 CdSnO₃ 的气敏性能。在工作温度 140 °C 条件下, 3.5%(质量分数)的 WS₂-CdSnO₃ 复合材料对 0.01% 甲醛气体的响应为 15.7, 是 CdSnO₃ 的 4.2 倍。

关键词: 二硫化钨; 偏锡酸镉; 甲醛; 气敏性能

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有机化合物甲醛(HCHO)是一种具有刺激性气味的室内有毒挥发性气体, 主要来源于建筑材料、家具和各种胶黏剂涂料^[1-3]。研究发现长期暴露于甲醛气体中, 会对人的健康造成一定的威胁。例如, 它会导致头痛、过敏、恶心, 甚至引起基因突变和白血病^[4-5]。因此, 亟需设计一种具有良好传感性能的气体传感器来实时检测甲醛。

近年来, ABO₃ 型钙钛矿金属氧化物(A 和 B 表示 2 种不同的金属元素), 在传感器应用中引起了广泛关注。Jia 等^[6]通过共沉淀法成功制备了 CdSnO₃ 纳米颗粒, 气敏性能研究结果表明: CdSnO₃ 纳米颗粒制备的气体传感器在 267 °C 工作温度下对 0.01% 乙醇气体的灵敏度为 11.2, 且检测限为 0.000 2%。Sun 等^[7]合成了多孔 CdSnO₃ 纳米材料, 在 220 °C 条件下对 0.005% 硫化氢的灵敏度为 317.0。上述传感器存在灵敏度较差、工作温度较高等局限。在二维过渡金属二卤代化合物(2D TMDs)材料中, WS₂ 因其具有较高的比表面积、良好的热稳定性和优异的电子迁移率而受到学者广泛关注^[8]。用 2D TMDs 材料对金属氧化物进行改性是提高气敏性能的有效策略之一, 例如, Sun 等^[9]利用退火超声分散法合成

了 WS₂ QDs@In₂O₃ 复合材料, 气敏实验结果表明: 在室温下 3%(质量分数)WS₂ QDs@In₂O₃ 对 0.01% NO₂ 的响应是 In₂O₃ 的 7.7 倍。Wang 等^[10]通过水热法合成了不同比例的 WS₂/CuGa₂O₄ 复合材料。结果表明, 3% WS₂/CuGa₂O₄ 对 0.01% 乙醇气体的灵敏度为 345.3, 大大提升了 CuGa₂O₄ 的气敏性能。

本工作通过共沉淀-退火法制备了 CdSnO₃, 并使用超声混合法制备了一系列不同质量比例的 WS₂-CdSnO₃ 复合材料。对不同比例的 WS₂-CdSnO₃ 复合材料进行了形貌、物相及元素价态结构进行了表征, 气敏性能测试结果表明, 当工作温度为 140 °C 时, 3.5% 的 WS₂-CdSnO₃ 对 0.01% 甲醛气体的响应值为 15.7, 响应/恢复时间为 51.0 s/71.0 s, 且最低检测限为 0.0001%。

1 实验

1.1 药品

Cd(NO₃)₂·4H₂O(分析纯)购置于上海萨恩化学技术有限公司; SnCl₄·5H₂O(AR)和 WS₂(99.9%)均购置于上海阿拉丁试剂有限公司; NaOH(分析纯)和无水乙醇(分析纯)由国药集团化学试剂有限公司提供;

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第一作者: 刘醒醒(1995—), 女, 硕士研究生。

通信作者: 储向峰(1966—), 男, 博士, 教授;

梁士明(1983—), 男, 博士, 副教授。

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First author: LIU Xingxing (1995—), female, Master candidate.

E-mail: 1638708379@qq.com

Correspondent author: CHU Xiangfeng (1966—), male, Ph.D., Professor;

LIANG Shiming (1983—), male, Ph.D., Associate Professor.

E-mail: xfchu99@ahut.edu.cn; lsmwind@163.com

去离子水为实验室自制。使用药品均无需进一步提纯。

1.2 CdSnO₃ 材料的制备

准确称取 0.616 9 g Cd(NO₃)₂·4H₂O 和 0.701 2 g SnCl₄·5H₂O 置于烧杯中, 加入 20 mL 去离子水并搅拌 30 min 使其充分溶解, 用 1 mol/L NaOH 溶液调节溶液的 pH 值为 7, 随后将调节 pH 值后的溶液保持 80 °C 水浴搅拌 6 h。取出反应溶液, 待冷却到室温后, 用去离子水和无水乙醇交替洗涤, 所得白色沉淀物于 80 °C 条件下烘干 12 h。最后, 在马弗炉中以 2 °C/min 的升温速率达到 700 °C 保温 1 h, 冷却后研磨得到浅黄色 CdSnO₃。

1.3 WS₂-CdSnO₃ 复合材料的制备

分别称取 0.100 0 g CdSnO₃ 于 4 只烧杯中, 加入 20 mL 无水乙醇搅拌均匀, 随后称取不同质量的 WS₂(0.002 5、0.003 5、0.004 5、0.005 5 g) 分别置于上述烧杯中, 磁力搅拌 12 h 后超声处理 2 h, 将处理后的溶液离心 30 min 得到沉淀, 并在 80 °C 条件下将沉淀干燥 8 h, 所得样品即为 WS₂-CdSnO₃ 复合材料, 分别标记为样品 WSC-1(2.5% WS₂-CdSnO₃)、样品 WSC-2(3.5% WS₂-CdSnO₃)、样品 WSC-3(4.5% WS₂-CdSnO₃)、样品 WSC-4(5.5% WS₂-CdSnO₃)。

1.4 样品表征

采用日本 Rigaku SmartLab SE 型 X 射线衍射仪 (XRD) 分析材料的物相组成。用捷克 TESCAN MIRA LMS 型扫描电子显微镜 (SEM) 观察材料的表面形貌。用美国 Thermo Scientific K-Alpha 型 X 射线光电子能谱仪 (XPS) 分析材料的表面元素组成和价态。采用美国 Micromeritics ASAP 2460 型全自动比表面及孔隙度分析仪 (BET) 比表面和孔径分布测定仪测定了材料的孔径分布情况与比表面积。

将 WS₂-CdSnO₃ 复合材料置于研钵中, 加入松节油透醇 1~2 滴, 充分研磨至混合均匀。将该浆状物用小毛刷均匀地涂抹于氧化铝陶瓷管外壁, 然后将 Ni—Cr 加热丝穿入陶瓷管内, 并焊牢在六角基座上。工作温度高低通过调节加热丝 2 段所加功率大小来间接控制, 对于旁热式气体传感器, 其灵敏度被定义为:

$$S(\text{sensitivity}) = R_a/R_g \quad (1)$$

其中: R_a 为气敏材料在空气中的稳定电阻值; R_g 为气敏材料在被测气体中的稳定电阻值。在对复合材料进行气敏性能测试时, 均为 55% 的相对湿度条件。(除湿度测试外)。

2 结果与讨论

2.1 材料表征

图 1 为 CdSnO₃ 和样品 WSC-2 的物相结构。由图 1a 可见, CdSnO₃ 呈现出较均匀的微立方体状的形态, 并且微立方体的表面凹凸不平。由图 1b 可见, CdSnO₃ 微立方体团聚在层状结构的 WS₂ 表面上^[11], 证明了 WS₂ 与 CdSnO₃ 成功复合; 而这种结构为反应提供了较大的比表面积, 有利于提高气敏性能^[12]。由图 1c 可见, 样品 WSC-2 中含有 Cd、Sn、O、W、S 元素, 并且不含任何其他杂质, 进一步证实了 WS₂ 与 CdSnO₃ 成功复合。由图 1d 可见, CdSnO₃ 材料在 2θ 分别为 22.42°、30.68°、32.98°、45.62°、49.74°、57.36°、58.82° 时出现了明显特征峰, 分别与 CdSnO₃ (JCPDS NO.34-0758) 标准卡片中 (012) (104) (110) (024) (116) (214) (300) 晶面相吻合^[13]。此外, 样品 WS₂-CdSnO₃ 在 $2\theta = 14.64^\circ$ 处出现了 WS₂ 特征峰对应其 (JCPDS NO.08-0237) 标准卡片中的 (002) 晶面^[14], 并且随着 WS₂ 复合量的增多, 特征峰的强度也在逐渐增大, 进一步证明了 WS₂-CdSnO₃ 复合材料被成功制备。

图 2 为样品 WSC-2 的 XPS 谱和 CdSnO₃ 的 O 1s 谱。由图 2a 可见, W、S、O、Cd、Sn 对应的衍射峰。在 Cd 谱中 (图 2b), 2 个分离峰分别在 404.74 eV 和 411.48 eV, 分别对应 Cd 3d_{5/2} 和 3d_{3/2} 能级, 表明镉以 Cd²⁺ 形式存在^[15]。由图 2c 可见, 486.17 eV 和 494.64 eV 处 2 个明显的峰分别对应 3d_{5/2} 和 3d_{3/2} 能级, 2 个峰位置的差值为 8.47 eV, 说明在复合材料中 Sn 元素是以 +4 价存在^[16]。在图 2d 中, 32.45 eV 和 34.65 eV 处的峰分别代表 W 4f_{7/2} 和 W 4f_{5/2}, 另外, 位于 37.94 eV 的峰则对应 W 5p, 代表 W⁴⁺ 存在于 WSC-2 复合材料中^[17]。S 2p 的 XPS 谱如图 2e 所示, 主峰分别为 162.05 eV 和 163.24 eV, 对应 S²⁻ 的 2p_{3/2}, 2p_{1/2} 能级^[18]。由图 2f 可见, 2 幅图中的 3 个峰分别对应的是晶格氧 (O_L)、空位氧 (O_V) 和化学吸附氧 (O_C)^[19] 及其相对含量。其中, 529.81、531.43 eV 和 532.86 eV 分别归属于样品 WSC-2 的 O_L、O_V 和 O_C, 而 CdSnO₃ 的 O_L、O_V 和 O_C 的 3 个峰的位置位于 529.68、530.94 eV 和 531.73 eV 处。通过对比 2 种样品的 3 种氧形态相对比例可知: 样品 WSC-2 的 O_V 和 O_C 相对含量比 CdSnO₃ 高, 而大量的 O_V 为氧吸附提供了更多的位点, 产生更多的 O_C, 使更多的目标气体参与了材料表面的反应, 改善了传感器的气敏性能^[20]。

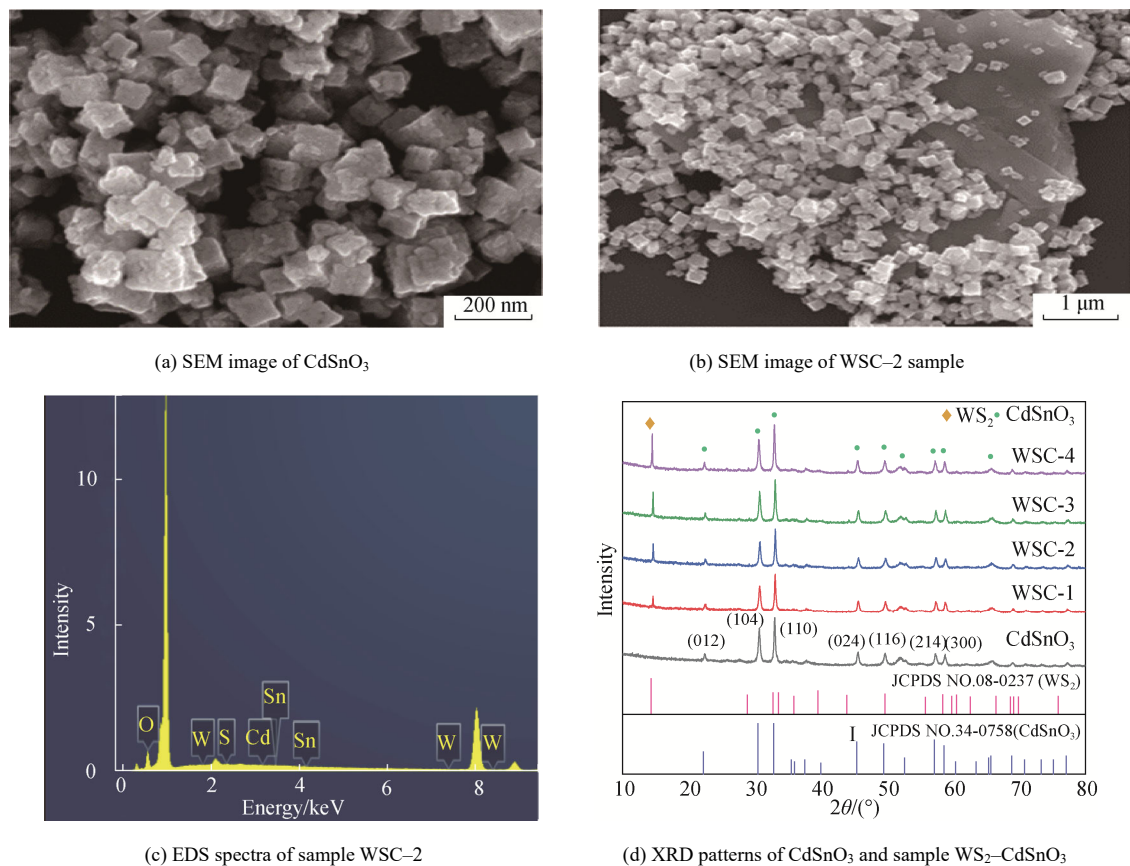
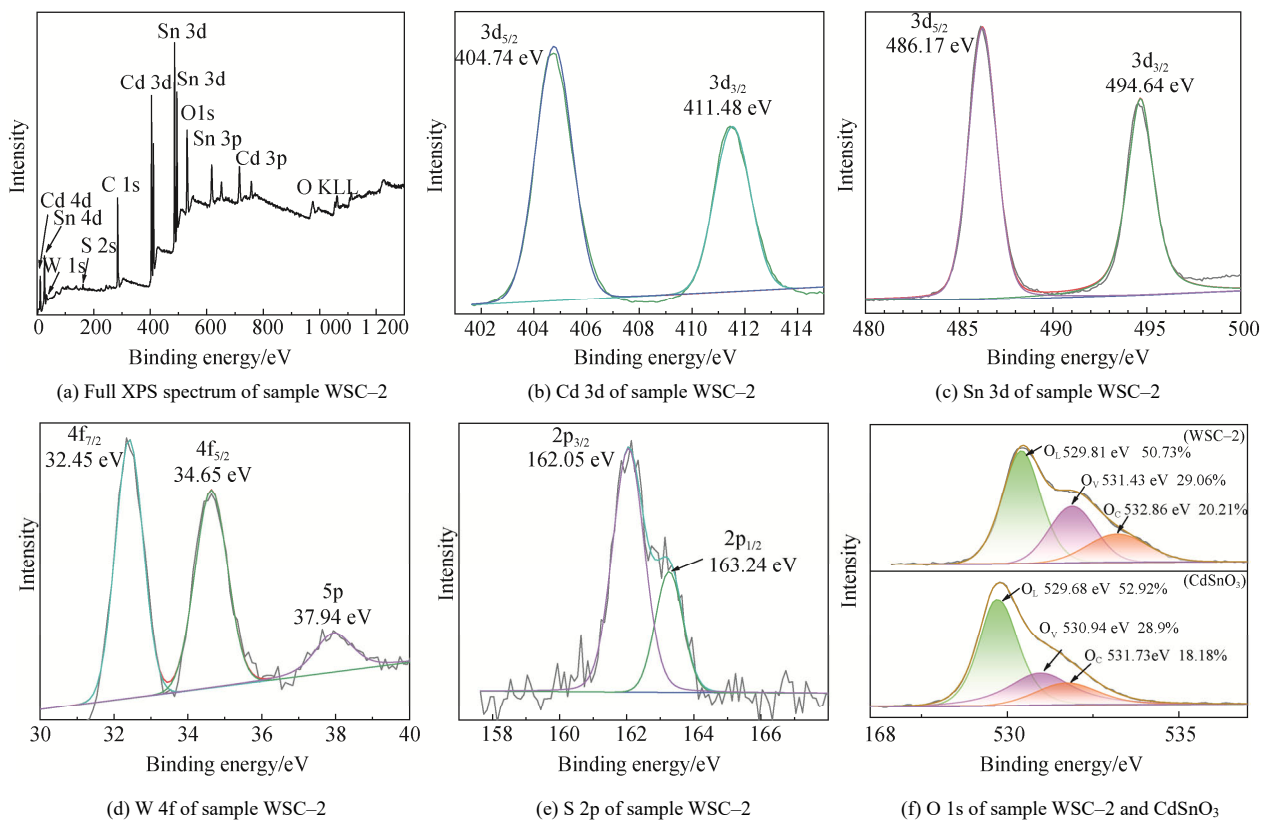
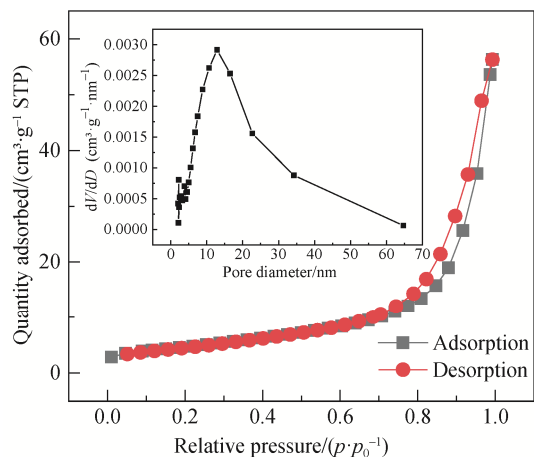
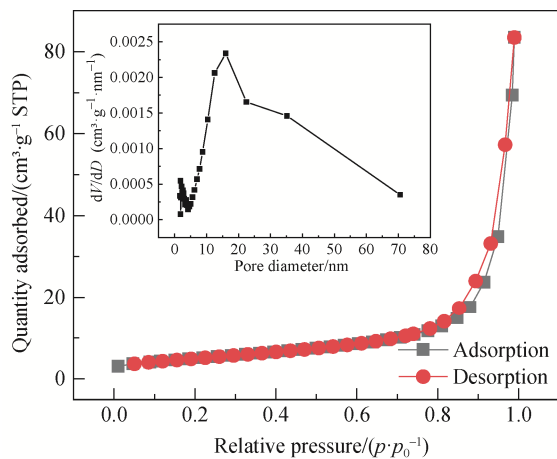
图 1 CdSnO_3 和样品 WSC-2 的物相结构Fig. 1 Phase Structure of samples CdSnO_3 and WSC-2图 2 样品 WSC-2 的 XPS 谱和 CdSnO_3 的 O 1s 谱Fig. 2 XPS spectra of sample WSC-2 and O 1s of CdSnO_3

图 3 为 CdSnO_3 和样品 WSC-2 的 N_2 吸附-脱附等温线和孔径分布曲线。由图 3 可以看出, 2 种材料的等温线均属于具有 H3 型滞后环的 III 型等温线, 表明材料中存在介孔结构^[21–22], CdSnO_3 和样品 WSC-2 的平均孔径分别分布在 17.44 nm 和 27.22 nm 处。对 CdSnO_3 和样品 WSC-2 进行氮吸附-解吸实验, 估算了 CdSnO_3 和样品 WSC-2 的比表面积。发现 CdSnO_3 和样品 WSC-2 的比表面积分别为 $16.91 \text{ m}^2/\text{g}$ 和 $18.08 \text{ m}^2/\text{g}$, WS_2 的引入增大了样品 WSC-2 的比表面积, 较大的比表面积使材料具有更多的气体吸附活性位点, 进而改善了其气敏特性^[23]。

(a) CdSnO_3 

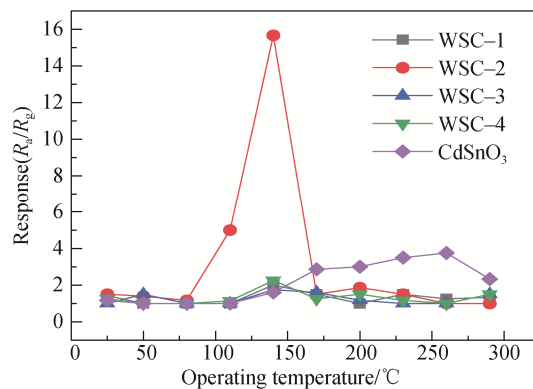
(b) Sample WSC-2

图 3 CdSnO_3 和样品 WSC-2 的氮吸附脱附等温线和孔径分布曲线

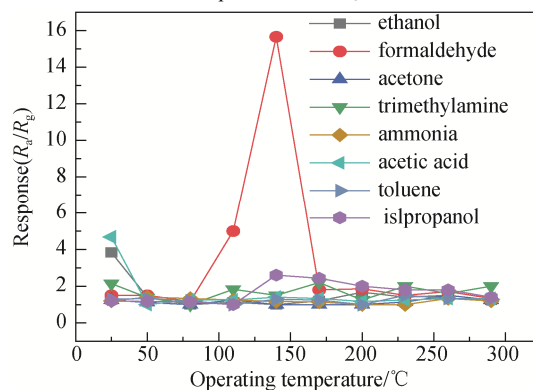
Fig. 3 N_2 adsorption-desorption isotherms and pore size distribution of CdSnO_3 and sample WSC-2

2.2 气敏性能

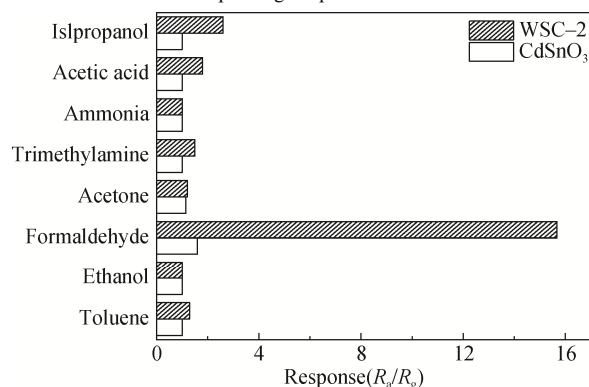
图 4 为样品气敏性能测试结果。由图 4a 可见, 在不同工作温度下, CdSnO_3 与一系列 $\text{WS}_2\text{-CdSnO}_3$ 复合材料对 0.01% 乙醛气体的灵敏度曲线, 样品



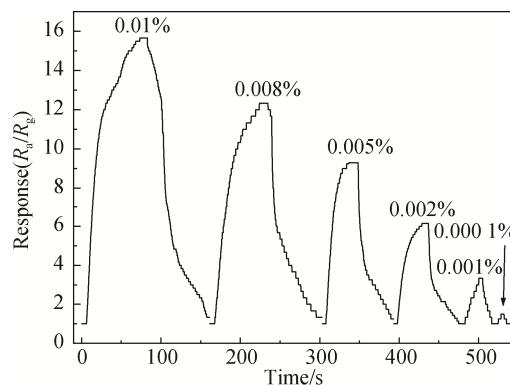
(a) Formaldehyde (0.01%) gas sensing response of CdSnO_3 and a series of sample $\text{WS}_2\text{-CdSnO}_3$



(b) Response of sample WSC-2 to 8 kinds of gases of 0.01% under different operating temperature



(c) Gas sensing properties comparison at $140\text{ }^\circ\text{C}$



(d) Response and recovery curves of sample WSC-2 to different concentration formaldehyde vapor at $140\text{ }^\circ\text{C}$

图 4 样品气敏性能测试结果

Fig. 4 Results of gas sensing tests

WSC-2 在 140 °C 时对 0.01% 甲醛的响应值最高, 为 15.7, 而 CdSnO_3 的最佳工作温度是 260 °C, 响应值为 3.8, 样品 WSC-1、样品 WSC-3、样品 WSC-4 在 140 °C 时对甲醛的响应值仅为 2.0、1.8、2.3, 表明 WS_2 的最佳复合量为 3.5%, 说明通过与适量 WS_2 复合可以显著提升 CdSnO_3 材料的灵敏度, 而且降低了其工作温度。由图 4b 可见, 样品 WSC-2 在不同的工作温度下对多种气体都有一定的响应, 而在 140 °C 时, 对甲醛的响应值最高, 表明样品 WSC-2 对甲醛气体有较好的选择性。为了检验所制备的 WSC-2 传感器的潜在实际应用, 在 140 °C 的工作温度下测试了传感器对不同气体的选择性和灵敏度, 通过图 4c 对比可知, 样品 WSC-2 对 0.01% 的甲醛的响应值是 CdSnO_3 材料的 9.8 倍, 对 0.01% 的异丙醇气体的响应值仅有 2.6, 因此, WS_2 的添加不仅改变了 CdSnO_3 材料的气敏选择性, 也提高了灵敏度。由图 4d 可见, 该材料对 0.01% 的甲醛的响应/恢复时间为 51.0s/71.0s, 且对甲醛的检测限为 0.0001%, 其响应值为 1.5。

图 5 为相对湿度对样品 WSC-2 在 140 °C 时检测 0.01% 甲醛气体的影响。由图 5 可见, 样品 WSC-2 的灵敏度随着相对湿度的增加而提高, 当空气中的相对湿度处于 20% 到 45% 时, 材料对甲醛气体的响应值缓慢上升, 当相对湿度大于 45% 时, 曲线趋势开始急剧上升, 这表明湿度对气敏材料的灵敏度影响很大, 主要表现为: 当待测环境湿度增大时, 其表面吸附的水分子就越多, 而水分子则会促进样品 WSC-2 对水溶性气体甲醛的吸附, 从而增强气体传感性能^[24]。

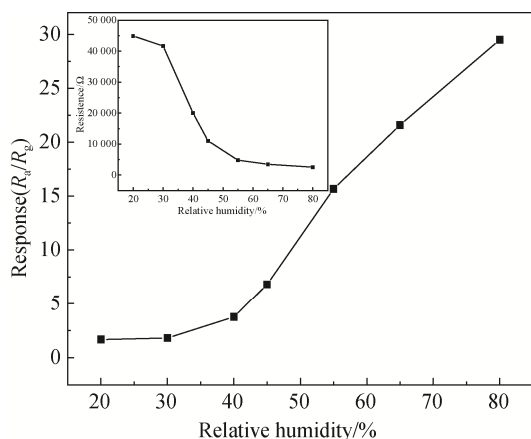
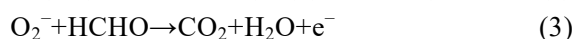
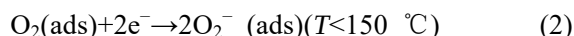


图 5 在 140 °C 时相对湿度对样品 WSC-2 检测 0.01% 甲醛气体的影响

Fig. 5 Influence of relative humidity on detection of 0.01% formaldehyde vapor at 140 °C for sample WSC-2

2.3 气敏机理

样品 $\text{WS}_2\text{-CdSnO}_3$ 的气体传感机理可以从反应气体分子在传感器表面的吸附和解吸方面来解释^[25-26]。当接触到空气环境时, 空气中的氧分子会在传感材料的表面被化学吸附, 而氧分子则从氧化物的导带中捕获电子, 产生化学吸附氧(O_2^-), 如反应式(2), 产生了电子耗尽层, 从而增大了传感器的电阻。与 CdSnO_3 相比, 样品 WSC-2 对甲醛表现出更好的气体传感性能, 主要是由于 WS_2 的加入使样品 WSC-2 具有较多的氧空位和较大的比表面积, 而丰富的氧空位能吸附更多的氧分子, 产生 O_2^- , 甲醛气体与 O_2^- 发生反应形成二氧化碳和水, 如反应式(3), 同时将被捕获的电子释放回导带中, 减少了电子耗尽层的厚度, 降低了传感器的电阻^[27-30]。气体传感过程发生在传感材料的表面, 由于 WS_2 具有层状结构, WS_2 的加入使样品 WSC-2 的比表面积增加, 较大的比表面积可能促进氧/甲醛分子的吸附。当 WSC-2 传感器暴露在潮湿的环境中时, 水分子被吸附在样品 WSC-2 材料的表面, 氧空位可以加速水的分解, 产生更多的 $\cdot\text{OH}$ 基团, 甲醛与 $\cdot\text{OH}$ 反应可以生成 H_2COO , 释放 $\cdot\text{OH}$ 占据的吸附-反应位点, 而 H_2COO 进一步与活性氧反应生成二氧化碳和水, 从而增大对甲醛气体的响应^[31-32], 降低了暴露于甲醛环境下的传感器电阻。这些反应可以表示如下:



3 结论

采用超声混合分散法成功制备了一系列不同质量比例的 $\text{WS}_2\text{-CdSnO}_3$ 复合材料, 气敏性能测试结果表明: 3.5% $\text{WS}_2\text{-CdSnO}_3$ 对甲醛气体的选择性最优异, 在 140 °C 的工作温度下气敏性能最佳, 对浓度为 0.01% 的甲醛气体的灵敏度是纯 CdSnO_3 材料的灵敏度的 4.2 倍, 响应/恢复时间为 51.0 s/71.0 s, 且最低检测限为 0.0001%。

综上所述, 复合 WS_2 显著提高了样品对气体的响应和选择性。本工作为提高 CdSnO_3 材料的气敏性能提供了一种策略, 并对甲醛气体监测和改善室内生活环境具有重要意义。

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Preparation and Formaldehyde Sensing Properties of WS₂-CdSnO₃ Composite Materials

LIU Xingxing¹, HU Mengting¹, LIU Cuicui¹, LI Jiahao¹, CHU Xiangfeng¹, LIANG Shiming²

(1. School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, Anhui;

2. School of Materials Science and Engineering, Linyi University, Linyi 276005, Shandong, China)

Extended Abstract

Introduction Organic compound formaldehyde (HCHO) is a toxic volatile gas with an irritating odour, which is mainly derived from building materials, furniture and various adhesive coatings. Living in an environment containing formaldehyde gas for a long time can cause a series of hazards to human health, such as headaches, allergies, nausea, and even genetic mutations and leukaemia. It is thus necessary to design a gas sensor with a superior sensing performance to detect formaldehyde in real time. ABO₃ type chalcogenide metal oxides have attracted much attention in sensor research, but their application is restricted due to the drawbacks such as poor sensitivity and high operating temperature. Many studies indicate that the modification of metal oxides with two-dimensional transition metal dichalcogenides (2D TMDs) is one of the effective strategies to improve the gas sensing performance, and among the 2D TMDs materials, WS₂ has aroused much interest in sensor research because of its high specific surface area, good thermal stability and excellent electron mobility. The gas sensor performance of metal oxides can be improved via the combination of WS₂ to form a novel nanocomposite material. Hence, in this paper, a series of WS₂-CdSnO₃ composites with different mass ratios were prepared by an ultrasonic mixing method. The microstructure, crystal structure, and valence state structure of WS₂-CdSnO₃ composite material were characterized, and the gas sensing performance of the composite material was analyzed.

Methods CdSnO₃ was prepared with Cd(NO₃)₂·4H₂O (AR, Shanghai Sarn Chemical Technology, China) and SnCl₄·5H₂O (AR) (Shanghai Aladdin Reagent Co., China). CdSnO₃ was ultrasonically compounded with WS₂ (99.9%) to obtain WS₂-CdSnO₃ composites. The physical phase composition, surface morphology, elemental composition, valence and pore size distribution and specific surface area of the composites were characterized by a model SmartLab SE X-ray diffractometer (XRD, Rigaku Co.,), scanning electron microscope (SEM, Tescan Mira Lms), a model K-Alpha X-ray photoelectron spectrometer (XPS, Thermo Scientific Co., USA), and a model ASAP 2460 fully automated specific surface and porosity analyser (BET, Micromeritics Co., USA).

For the determination of gas sensing performance of WS₂-CdSnO₃ composite material, WS₂-CdSnO₃ composite material was put into a mortar with 1 - 2 drops of terpineol, and thoroughly mixed and ground. The paste was evenly applied to the outer wall of the alumina ceramic tube with a small brush, and an Ni - Cr heating wire put through the ceramic tube and welded firmly to the hexagonal base. The operating temperature was indirectly controlled via adjusting the amount of power added to the two sections of the heating wire. The sensitivity to gases is expressed as a ratio of the stable resistance value of the gas sensing material in air to a stable resistance value in the gas tested. The gas sensing performance of the composites was investigated at a relative humidity of 55% (except for humidity tests).

Results and discussion From the SEM images, the microcube appeared is CdSnO₃, and the cubes structure is agglomerated on the surface of layered WS₂. Based on the EDS analysis, there are five elements Cd, Sn, O, W and S in the composites. It is indicated that WS₂-CdSnO₃ can be prepared. According to the XPS analysis, there are more oxygen vacancies in the sample WSC-2, which can provide more sites for oxygen adsorption, so that more target gases participate in the reaction on the surface of the material. The introduction of WS₂ increases the specific surface area of the sample WSC-2, and the material with a larger specific surface area has more gas adsorption active sites, thus improving the gas sensing performance of the sensor. The sample WSC-2 has the maximum response value of 15.7 for 0.01% formaldehyde at 140 °C. To check the potential practical application of the prepared WSC-2 sensor, the selectivity and sensitivity of the sensor to different gases were investigated at 140 °C. The results show that the sample WSC-2 has the optimum selectivity for 0.01% formaldehyde, and the response value is 4.2 times higher than that of CdSnO₃.

Conclusions A series of WS₂-CdSnO₃ composites with different ratios were prepared via ultrasonic dispersion mixing. WS₂-CdSnO₃ had a large specific surface area, which was beneficial for gas adsorption and diffusion. The gas sensing performance of CdSnO₃ with different ratios of WS₂-CdSnO₃ composites were investigated, and the results showed that 3.5% WS₂-CdSnO₃ had the optimum selectivity for formaldehyde and the superior gas sensing performance at 140 °C, and the sensitivity for 0.01% formaldehyde was 4.2 times higher than that of CdSnO₃ material, and the detection limit was 0.0001%. Therefore, the 3.5% WS₂-CdSnO₃ composite had potential applications in indoor formaldehyde detection. This study indicated that the modification of metal oxides by two-dimensional TMD could be one of the effective strategies to improve the gas sensing performance.

Keywords tungsten disulfide; cadmium metastannate; formaldehyde; gas sensing