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Fabíola Costa Paciência

Micrometric Co_3O_4 coated with metal-organic framework ZIF-67 for selective detection of volatile organic compounds

São José do Rio Preto

2024

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Dissertação apresentada como parte dos requisitos para obtenção do título de Mestre em Nome do Programa, junto ao Programa de Pós-Graduação em Nome do Programa, do Instituto de Biociências, Letras e Ciências Exatas da Universidade Estadual Paulista "Júlio de Mesquita Filho", Câmpus de São José do Rio Preto.

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IMPACTO SOCIAL DA DISSERTAÇÃO

O trabalho tem como impacto social a utilização de sensores de gás para detectar seletivamente compostos orgânicos voláteis, possibilitando o desenvolvimento de instrumentos alternativos para monitoramento da qualidade do ar e para a detecção desses compostos. Além disso, o material sintetizado é produzido de maneira simples, econômica, atóxica e sustentável.

DISSERTATION SOCIAL IMPACT

The work has the social impact of using gas sensors to selectively detect volatile organic compounds, making it possible to develop alternative instruments for monitoring air quality and detecting these compounds. In addition, the synthesized material is produced in a simple, economical, non-toxic and sustainable way.

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Micrometric Co_3O_4 coated with metal-organic framework ZIF-67 for selective detection of volatile organic compounds

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RESUMO

O objetivo desse trabalho foi sintetizar o óxido de cobalto (II) dicobalto (III) (Co_3O_4) puro, juntamente com a síntese de Co_3O_4/ZIF-67, para a detecção de moléculas orgânicas voláteis. O estudo foi composto pela avaliação do uso do óxido de cobalto puro como sensor de gás em comparação com o sensor produzido a partir do óxido revestido com nanopartículas de ZIF-67 (Co_3O_4/ZIF-67), a fim de aprimorar a resposta, bem como a seletividade e o tempo de resposta para a detecção de VOCs. O sensor de Co_3O_4 foi preparado empregando o método hidrotérmico assistido por micro-ondas, ao passo que o Co_3O_4/ZIF-67 foi obtido utilizando o método de refluxo, utilizando o óxido puro preparado inicialmente e o ligante orgânico 2-metilimidazol. Os resultados de caracterização desses materiais demonstraram que as amostras não apresentaram impurezas. As respostas dos sensores foram avaliadas na faixa de 100 partes por milhão (100 ppm) dos VOCs: metanol, acetona, 2-butanona, m-xileno, tolueno e benzeno, variando a temperatura de operação na faixa de 200- 275°C. A maior resposta para o sensor Co_3O_4 foi de 20,05 para tolueno a 250 °C, ao passo que para o sensor Co_3O_4/ZIF-67 a maior resposta foi de 61,22 para o tolueno a 250 °C.

Palavras-chave da dissertação: Semicondutores. Sensor de gás. Óxido de cobalto. ZIF-67. Síntese hidrotérmica assistida por micro-ondas.

ABSTRACT

The aim of this work was to synthesize pure cobalt (II) dicobalt (III) oxide (Co_3O_4), together with the synthesis of Co_3O_4/ZIF-67, for the detection of volatile organic molecules. The study consisted of evaluating the use of pure cobalt oxide as a gas sensor in comparison with the sensor prepared from the oxide coated with ZIF-67 nanoparticles (Co_3O_4/ZIF-67) in order to improve the response, selectivity and response time for the detection of VOCs. The Co_3O_4 sensor was prepared by the microwave-assisted hydrothermal method, while Co_3O_4/ZIF-67 was obtained by the reflux method using the initially prepared pure oxide and the organic 2-methylimidazole ligand. The characterizations results of these materials showed that the samples were free from impurities. The sensor responses were evaluated in the range of 100 parts per million (100 ppm) of the VOCs: methanol, acetone, 2-butanone, m-xylene, toluene and benzene, varying the operating temperature in the range of 200-275°C. The highest response for the Co_3O_4 sensor was 20.05 for toluene at 250°C, while the highest response for the Co_3O_4/ZIF-67 sensor was 61.22 for toluene at 250°C.

Dissertation Keywords: Semiconductors. Gas sensor. Cobalt oxide. ZIF-67. Hydrothermal synthesis.

LIST OF FIGURES

LIST OF TABLES

ABREVIATIONS AND ACRONYMS LIST

BET	Brunauer-Emmett-Teller
EDX	Energy-dispersive X-ray
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission electron microscopy
MOF	Metal-organic framework
VOC	Volatile organic compound
RH	Relative humidity
SMO	Semiconducting metal oxide
TEY	Total eléctron-yield
XAS	X-ray absorption spectroscopy
XRD	X-ray Diffraction

SYMBOLS LIST

°C	Celsius degree
cm	Centimeter
µm	Micrometer
cm^3 /g	Cubic centimetre per gram
eV	Electron volt
g	Gram
h	Hour
keV	Kilo eléctron volt
kV	Kilovolt
mg	Milligram
mL	Milliliter
min	Minute
ppm	Parts per million
s	Second
m^2 g^{-1}	Square meter per gram

SUMMARY

1 INTRODUCTION AND BIBLIOGRAPHIC REVIEW

Volatile organic compounds (VOCs) represent a significant environmental concern due to their adverse effects on human health and the natural environment (LI et al., 2021). These compounds are recognized as toxic and are linked to the development of allergic reactions. It is therefore of great importance to be able to detect gaseous pollutants, such as volatile organic compounds, in a number of different fields, including the pharmaceutical industry, the food industry, environmental monitoring and public safety. In light of these developments, it is important to acknowledge the emergence of gas sensors as a tool for the detection of environmental contaminants, including gases and volatile organic compounds. Considering the multitude of gas detection technologies that have emerged in recent years, it is imperative to underscore the growing prominence of metal oxide semiconductors (MOSs) and their nano composites for the detection of gases and volatile organic compounds. This is largely due to their high porosity, which enhances their gas detection capacity, and their heightened sensitivity (WANG et al., 2023).

Metal oxide semiconductor gas sensors have broad application prospects in various fields due to their characteristics of small size, low cost, fast response speed, and real-time in situ detection (HU et al., 2024). However, the field of gas sensors has developed mainly based on *n*-type semiconductors, with little research and application of the detection properties of *p*-type oxide semiconductors. (LIU; ZHANG; WU, 2011) This is due to the high sensitivity and short response range of n-type semiconductors, which is advantageous for a significant proportion of research. However, due to their elevated operating temperature, they are not suitable for practical applications. While *p*-type semiconductors exhibit excellent stability and a low operating temperature range, they display reduced sensitivity (YAO et al., 2022). Among the *p*-type MOS, Co_3O_4 is a multifunctional semiconductor that exhibits sensitivity to gas detection due to the fact that the Co^{2+} present in the oxide can be readily oxidized to a higher oxidation state, thereby facilitating the adsorption of oxygen molecules on the material's surface, which is advantageous for gas detection (HU et al., 2024).

Moreover, a gas sensor's capacity to selectively VOCs is of paramount importance. Additionally, the ability to detect gases at exceedingly low concentrations (ranging from ppb to ppm) in mixtures devoid of interference from other substances is a crucial attribute. (VAN DEN BROEK et al., 2021). Despite the efficacy of p-type semiconductors as VOC catalysts, the issue of low detection sensitivity persists, a challenge that is particularly prevalent in cobalt oxides. To enhance the sensitivity of the sensor, modifications are essential.

It bears noting that recent studies have explored the potential of metal-organic frameworks (MOFs) as filtration materials to enhance the detection of MOSs. This improvement is often attributed to a size-screening effect (LUO et al., 2023). By leveraging this effect, it is possible to modify and adjust the pore size to achieve greater selectivity for specific gases, taking into account both the diameter of the MOF utilized and the gas under analysis. Therefore, the utilization of filters is intended to enhance the selectivity of the sensor, as they transform undesired interferents into inactive or less responsive substances, while the target analytes remain ideally unaffected. However, the utilization of filters can also enhance the sensitivity of the sensor by rendering certain analytes more responsive (WEBER; GÜNTNER, 2022).

1.1 Detection of volatile organic compounds

Volatile organic compounds are a class of organic substances that can be produced by both natural and synthetic processes. They are one of the primary classes of pollutants, both internally and externally. The World Health Organization (WHO) has identified a number of adverse effects of VOCs on human health, including the triggering of various chronic and acute diseases. Additionally, these compounds have been linked to destructive effects on the central nervous system (CNS), (HAJIVAND et al., 2024). Furthermore, VOCs have been shown to have a detrimental impact on the environment. In light of these considerations, it is evident that the detection of volatile organic compounds is a crucial endeavor in contemporary research.

Sensitive analytical techniques have been developed and employed for the quantification of VOCs, including spectrophotometry, gas chromatography (GC), and high-performance liquid chromatography (HPLC) (MIRZAEI; LEONARDI; NERI, 2016). However, despite their accuracy, these techniques have some disadvantages, including high cost, high energy demand, low yield, and the necessity for complex pre-treatment steps, which renders them unsuitable for scenarios where VOC monitoring is required rapidly and at a low cost. Consequently, research has been conducted over time with the aim of developing high-performance, user-friendly, and cost-effective gas detection devices that exhibit high sensitivity, selectivity, and stability for specific applications. These studies have resulted in the development of a diverse array of sensors based on MOFs, microporous materials whose surface functionality can be tailored to provide stronger and more selective binding sites for the targeted adsorption of VOC molecules through suitable coordination bonds or based on electrostatic interactions. These sensors demonstrate superior potential for detection when compared to other types of sensors, due to their high responsiveness and ease of integration.

Metal-organic frameworks are microporous materials whose surface functionality can be adapted to provide stronger and more selective binding sites for targeted adsorption of volatile organic compounds through suitable coordination bonds or electrostatic interactions. This adaptability confers superior potential for detection when compared to other types of sensors, due to their high responsiveness and ease of integration.

1.2. Semiconductors metal oxides of Co_3O_4 for VOC detection

Metal oxide semiconductors are a prominent emerging technology in the field of gas detection. Derived from MOFs, MOSs possess high porosity, which enhances their capacity for gas detection. In comparison to alternative detection methodologies, these sensors demonstrate enhanced sensitivity and stability, reduced manufacturing costs, straightforward applicability, and a diverse range of structures and morphologies (WANG et al., 2023).

In this regard, among the various sensors derived from semiconducting metal oxides, Co_3O_4 is a notable transition metal oxide. Its status as a p-type semiconductor material has led to extensive research on its potential as a material for gas sensors, given its high thermal stability. Additionally, its oxygen absorption capacity (LETSHOLATHEBE et al., 2021) qualifies it as an effective gas detector, as the conversion of Co^{2+} and Co^{3+} between different valence states enhances the material's sensitivity to gas detection (XU; CHENG, 2016).

Moreover, research suggests that the gas detection capabilities of Co_3O_4 micro and nanostructures are significantly influenced by their surface area, porous structure, and morphology. As documented in the findings of numerous researchers, the synthesis of diverse nanostructures of the material, including nanowires (BAI et al., 2013), nanotubes (FEI et al., 2012; ZHONG et al., 2020) and nanorods (YAN et al., 2017), in order to enhance the material's performance. The resulting structures have demonstrated differing detection responses, suggesting that the material's performance can be tailored through structural engineering. (LI et al., 2021). Consequently, the gas detection properties of Co_3O_4 structures - micro and nano - are contingent upon the modification of one of the aforementioned properties (XU; CHENG, 2016).

Therefore, the main objective of this work is to study the micrometric Co_3O_4 oxide morphology. This structure was selected over the manometric structure with the intention of more effectively covering the material with a metal organic framework (MOF) and enhancing the sensor's sensitivity by incorporating ZIF-67 into the material. Secondary objectives include: (a) A comparison of selectivity in the presence and absence of ZIF-67; (b) An examination of the application of a VOC sensor at different working temperatures (in different operating conditions, such as relative humidity (RH) and atmospheric working temperature; and (c) the synthesis of a material capable of detecting VOCs at low concentrations (ppm) with high selectivity, fast response time, low recovery time, stability and reversibility.

3 CONCLUSION AND NEXT CHALLENGES

The objective of this research was to develop Co_3O_4 sensors, in the presence and absence of ZIF-67, in order to examine the impact of incorporating a MOF into the sensor material on the detection of VOCs under diverse operational conditions. Chapter 2 presents a review of the principal topics, with a particular focus on VOCs and sensors based on semiconducting metal oxides (SMOs). The detection of volatile organic compounds (VOCs) is of paramount importance, given that these compounds are responsible for a few health issues affecting the general population, in addition to posing a significant environmental hazard. The synthesized Co_3O_4/ZIF-67 composite was found to be an excellent material for the detection of VOCs, particularly toluene. Chapter 3 outlines the synthesis of Co_3O_4 utilizing the microwave-assisted hydrothermal method, and the synthesis of Co_3O_4/ZIF-67 employing the reflux method. The incorporation of ZIF-67 resulted in enhanced sensor performance. At the optimal operating temperature, Co_3O_4/ZIF-67 exhibited heightened selectivity and superior toluene detection, although it demonstrated the longest response time. However, its recovery time was shorter in a dry environment.

Future challenges include the better characterization of the Co_3O_4/ZIF-67 sample using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This is necessary to obtain more detailed structural information on ZIF-67. This is because, of the characterization techniques carried out, it was only possible to identify the nitrogen present in the ZIF-67 ring using XAS. These analyses have contributed to a more nuanced understanding of the material's detection mechanism. Furthermore, this study seeks to facilitate future research into the advancement of *p*-type sensors through the incorporation of MOFs to enhance selectivity, while elucidating the impact of increasing porous materials, such as Co_3O_4/ZIF-67, on sensor performance, whether for toluene or other VOCs. Enhancing the selectivity and applications of sensors in authentic temperature and humidity conditions remains a significant challenge in this field.

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