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Effect of thermal treatment on ZnO-derived zinc-metal-organic framework for detecting volatile organic compounds

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RESUMO

Este trabalho apresenta a aplicação de ZnO, um óxido metálico semicondutor do tipo n, derivado de estrutura metal-orgânica (MOF), para detecção de compostos orgânicos voláteis microbianos (MVOCs). A detecção rápida, seletiva e em baixos limites de detecção é um dos principais desafios relatados. Além disso, estudos sobre a influência dos tamanhos de cristalitos do óxido metálico no desempenho do sensor ainda são escassos. A proposta e foco desta pesquisa consistem na aplicação de ZnO com diferentes tamanhos de cristalitos no desempenho como sensor de MVOCs. O precursor do ZnO (MOF-5) foi preparado utilizando o método solvotérmico assistido por micro-ondas, empregando o sal metálico $Zn(NO_3)_2.6H_2O$ e ligante orgânico ácido tereftálico em dimetilfomamida (DMF). O ZnO, aplicado como sensor, foi sintetizado pela degradação térmica (400 °C a 800 °C) da MOF-5, resultando em ZnO com tamanhos variados de nanopartículas: 17,8 nm a 450 °C (ZnO-450), 26,8 nm a 600 °C (ZnO-600) e 34,3 nm a 800 °C (ZnO-800). As caracterizações eletrônicas e estruturais evidenciam a formação de ZnO puros e fases cristalinas desejadas. Os sensores foram testados para 100 ppm dos MVOCs: acetona, 2-butanona, m-xileno, tolueno, benzeno e 1-Pentanol, em temperaturas variadas de 200 °C a 450 °C. Todos os sensores apresentaram boa detecção dos MVOCs 1-pentanol e 2-butanona a 400 °C, com destaque para o sensor ZnO-450, que exibiu a maior resposta ao MVOC 1-pentanol, atingindo um valor de resposta de 2680,0. Entretanto, observou-se uma alta sensibilidade e seletividade no sensor ZnO-600, com uma resposta de 2205,0 para 1-pentanol na mesma temperatura de operação, sendo que sua seletividade entre os MVOCs 1-pentanol e 2-butanona foi maior quando comparado ao sensor com tamanho de cristalito de 17,8 nm. Os mesmos parâmetros de seletividade do sensor ZnO-600 foram observados para o sensor ZnO-800, com tamanho de cristalito de 34,3 nm, embora os valores de resposta para os MVOCs 1-pentanol e 2-butanona tenham sido inferiores, 232,0 e 100,01, respectivamente. Portanto, demonstramos que o tamanho das nanoparticulas de ZnO influência diretamente a resposta e o desempenho do sensor, sendo mais seletivo para 1-pentanol a 400 °C o sensor de ZnO calcinado a 600 °C, com tamanho de cristalito de 26,8 nm. Destaca-se também o bom desempenho desse sensor na presença de uma atmosfera úmida e em diferentes faixas de umidade relativa controlada.

Palavras–chave: Semicondurores tipo n. MOF-5. Óxido de zinco. Sensor de gás. 1-Pentanol.

ABSTRACT

This work presents the application of ZnO, an n-type semiconductor metal oxide derived from a metal-organic framework (MOF), for the detection of microbial volatile organic compounds (MVOCs). Rapid, selective detection with low limits of detection is one of the main reported challenges. Furthermore, studies on the influence of metal oxide crystallite sizes on sensor performance are still scarce. The proposal and focus of this research are the application of ZnO with different crystallite sizes to evaluate its performance as an MVOC sensor. The ZnO precursor (MOF-5) was prepared using a microwave-assisted solvothermal method, employing the metal salt $Zn(NO_3)_2 \cdot 6H_2O$ and the organic ligand terephthalic acid in dimethylformamide (DMF). ZnO, applied as a sensor, was synthesized by thermal degradation (400 °C to 800 °C) of MOF-5, resulting in ZnO with varied nanoparticle sizes: 17.8 nm at 450 °C (ZnO-450), 26.8 nm at 600 °C (ZnO-600), and 34.3 nm at 800 °C (ZnO-800). Electronic characterizations and structural analyses confirm the formation of pure ZnO and the desired crystalline phases. The sensors were tested for 100 ppm of the MVOCs: acetone, 2-butanone, m-xylene, toluene, benzene, and 1-pentanol, at varying temperatures from 200 °C to 450 °C. All sensors showed good detection of the MVOCs 1-pentanol and 2-butanone at 400 °C, with particular emphasis on the ZnO-450 sensor, which exhibited the highest response to the MVOC 1-pentanol, reaching a response value of 2680.0. However, high sensitivity and selectivity were observed in the ZnO-600 sensor, with a response of 2205.0 for 1-pentanol at the same operating temperature, and its selectivity between the MVOCs 1-pentanol and 2-butanone was higher compared to the sensor with a crystallite size of 17.8 nm. The same selectivity parameters of the ZnO-600 sensor were observed for the ZnO-800 sensor, with a crystallite size of 34.3 nm, although the response values for the MVOCs 1-pentanol and 2-butanone were lower, at 232.0 and 100.01, respectively. Therefore, we demonstrate that the size of the ZnO nanoparticles directly influences the response and performance of the sensor, with the ZnO sensor calcined at 600 °C and with a crystallite size of 26.8 nm being more selective for 1-pentanol at 400 °C. The good performance of this sensor in the presence of a humid atmosphere and across different ranges of controlled relative humidity is also noteworthy.

Keywords: n-type semiconductors. MOF-5. Zinc oxide. Gas sensor. 1-Pentanol.

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ABREVIATIONS AND ACRONYMS LIST

BET	Brunauer-Emmett-Teller
EDX	Energy-dispersive X-ray
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
HRTEM	High-resolution transmission electron microscopy
MOF	Metal-organic framework
MVOC	Microbial volatile organic compound
RH	Relative humidity
SMO	Semiconducting metal oxide
TEM	Transmission eléctron microscope
TEY	Total eléctron-yield
TFY	Total fluorescence-yield
TGA	Thermogravimetric analyses
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

SYMBOLS LIST

Å	Angstrom
°C	Celsius degree
cm	Centimeter
nm	Nanometer
cm^3/g	Cubic centimetre per gram
eV	Electron volt
g	Gram
h	Hour
keV	Kilo eléctron volt
kV	Kilovolt
mA	Milliampère
mg	Milligram
mL	Milliliter
mmol	Millimol
min	Minute
ppm	Parts per million
s	Second
$m^2\ g^{-1}$	Square meter per gram

SUMMARY

1 INTRODUCTION AND BIBLIOGRAPHIC REVIEW

The development of conductometric sensors based on semiconductor metal oxides (SMOs) has gained prominence in the detection of microbial volatile organic compounds (MVOCs) (BARSAN; KOZIEJ; WEIMAR, 2007; BARSAN; WEIMAR, 2020) compared to other detection methods, such as optical and mechanical ones (SOHRABI et al., 2023), due to their great multifunctionality, morphological diversification, physical, chemical and thermal stability, in addition to low costs (CHATTERJEE; MITRA; MUKHOPADHYAY, 1999; WANG et al., 2020; WAN et al., 2004).

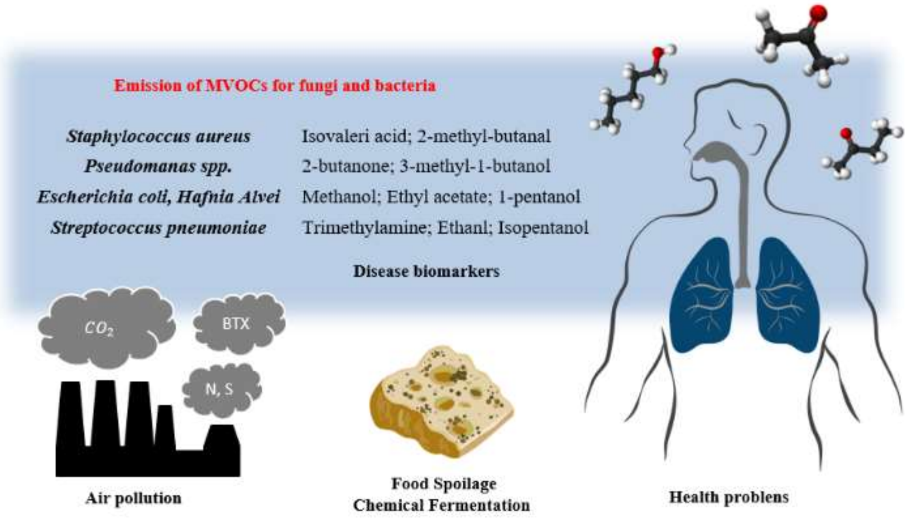
The importance of detecting different chemical classes of these compounds, produced by microorganisms, arises from several factors that directly impact society (ANAND; PHILIP; MEHENDALE, 2014; KAMPA; CASTANAS, 2008; KORPI; JÄRNBERG; PASANEN, 2009; PASANEN et al., 1998; SCHULZ; DICKSCHAT, 2007). Among these factors are food spoilage (WANG et al., 2016) and the danger to human health caused by pathogenic microorganisms (PASQUARELLA; PITZURRA; SAVINO, 2000; SCHÜTZE et al., 2017). Furthermore, there are volatile organic compounds exhaled through respiration that are directly associated with diseases such as cancer and can act as biomarkers, aiding in the diagnosis of potentially undetectable diseases (MACHADO et al., 2015; SCHMIDT; PODMORE, 2015; SUN; SHAO; WANG, 2016).

In this context, this research aimed to synthesize and apply ZnO-based SMO sensors for detecting MVOCs. SMOs are materials with unique and highly versatile electrical characteristics, mainly when derived from metal-organic frameworks (MOFs) (WANG et al., 2020), ensuring high surface area, porosity, absorptivity, and crystallinity (KUMAR; MASRAM, 2021). These properties have great potential for application in toxic gas detection (SOHRABI et al., 2023). The sensor properties are directly linked to their morphology, particularly the crystallite size of the material (REN et al., 2022), which directly influences the material's active sites and gas adsorption capacity (XU et al., 2000), thereby altering the sensor performance.

1.1 Microbial volatile organic compounds (MVOCs)

Identifying and controlling the emission of atmospheric pollutants known as volatile organic compounds (VOCs) is of great importance due to their impact on society (HAO et al., 2024). VOCs correspond to organic compounds with boiling points below 250 °C and high vapor pressures, evaporating quickly (ANAND; PHILIP; MEHENDALE, 2014; HE et al., 2019). They are responsible for the reduction of air quality (KAMPA; CASTANAS, 2008), and

Figure 1 – Overview of volatile organic compounds and their interactions.



Source: adaptation from literature (KAMPA; CASTANAS, 2008; SCHÜTZE et al., 2017; SUN; SHAO; WANG, 2016).

Furthermore, some MVOCs are produced by specific microorganisms, which, when exhaled by the respiratory system, can be directly associated with diseases, acting as biomarkers and aiding in the diagnosis of potentially undetectable diseases (DUFFY; MORRIN, 2019; MACHADO et al., 2015; SCHMIDT; PODMORE, 2015). Currently, conventional methods cannot meet monitoring and safety requirements as they require expensive and time-consuming processes to identify microorganisms and MVOCs (ZHU et al., 2019), such as the use of gas chromatography coupled with mass spectrometry, as well as chemiluminescent and fluorescent sensing techniques. Therefore, the application of semiconductor metal oxide sensors can address these issues in a simple and cost-effective way, enabling the rapid, practical, efficient, and selective detection of MVOCs, while also facilitating the integration of information that can assist in disease diagnosis and food safety risk assessment

1.2 Semiconductor metal oxides based on ZnO for MVOC detection

Semiconductor metal oxides (SMOs) comprise a class of materials with excellent electrical characteristics and are widely used in several areas, such as catalysis and photocatalysis (DJURIŠIĆ; LEUNG; CHING NG, 2014; ZHANG; LIN, 2014), supercapacitors, energy storage, and conversion (WU et al., 2011), and primarily as sensors for detecting toxic gases (KRISHNA et al., 2022; SOHRABI et al., 2023; WANG et al., 2020). SMOs are classified as n-type or p-type according to the type of receptor and conduction mechanisms (KIM; LEE, 2014). N-type and p-type semiconduction arise from extrinsic defects.

3 CONCLUSION AND NEXT CHALLENGES

This research aimed to develop ZnO sensors for the detection of MVOCs under various operating conditions. In line with this objective, Chapter 2 provides a review of key topics, specifically MVOCs and conductometric sensors based on semiconductor metal oxides (SMOs). Detecting MVOCs is crucial due to the environmental and social problems caused by various classes of bacteria and fungi. The rapid and selective identification of these compounds, using low-cost materials, drives the search for new alternatives. The synthesized ZnO proved to be an excellent material for MVOC detection, especially for 1-pentanol, when the crystallite size of the nanoparticles was modified. Chapter 3 describes the fabrication of ZnO through the thermal treatment of a MOF-5 precursor, synthesized via a microwave-assisted solvothermal method. Varying the crystallite size enhanced sensor performance. At the optimal operating temperature, ZnO with intermediate crystallite size demonstrated increased selectivity, improved detection of 1-pentanol, and the shortest response time among all the sensors studied.

Future challenges include better characterization of the synthesized material using Transmission Electron Microscopy (TEM) to obtain more detailed structural information, as well as a more in-depth investigation of the electronic and surface properties of ZnO through X-ray absorption spectroscopy and X-ray photoelectron spectroscopy analyses. These analyses will provide clearer insight into the detection mechanism. Furthermore, this study aims to support future research into the development of simple ZnO sensors derived from MOF-5, while demonstrating the importance and influence of nanoparticle size on sensor performance, whether for 1-pentanol or other MVOCs produced by specific bacteria and fungi. This will contribute to the development and expansion of the MVOC database. Improving selectivity and sensor applications under real-world temperature and humidity conditions remains a significant challenge in this field.

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