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Co_3O_4-ZnO heterostructure for microbial volatile organic compounds detection

São José do Rio Preto
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Dissertation presented as part of the requirements for obtaining the Master's degree in Chemistry at the Program of Postgraduation in Chemistry at the Institute of Biosciences, Letters and Exact Sciences of the Universidade Estadual Paulista "Júlio de Mesquita Filho," Campus of São José do Rio Preto.

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IMPACTO SOCIAL DA DISSERTAÇÃO

O impacto social deste trabalho está relacionado com a detecção dos compostos orgânicos voláteis microbianos produzidos por microorganismos, possibilitando uma melhor compreensão sobre seus efeitos. Além disso, é um material sintetizado através de um processo não tóxico e sustentável.

DISSERTATION SOCIAL IMPACT

The social impact of this work is related to the detection of microbial volatile organic compounds produced by microorganisms, enabling a better understanding of their effects. Furthermore, it is a material synthesized through a non-toxic and sustainable process.

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RESUMO

O foco desse trabalho foi sintetizar heteroestruturas *p-n* e *n-p* à base de Co_3O_4-ZnO e ZnO-Co_3O_4, derivados de estruturas metal-orgânicas (metal-organic frameworks, MOF) para detectar moléculas voláteis produzidas por micro-organismos (ex.: fungos e bactérias). Entretanto, existem poucos estudos na detecção rápida e com limite de detecção baixo de compostos orgânicos voláteis produzidos por micro-organismos (microbial volatile organic compounds, MVOCs). O estudo foi composto pela avaliação do uso de heteroestruturas *p-n* e *n-p* em comparação com a estrutura pura do óxido de cobalto (Co_3O_4) para aprimorar a resposta, a seletividade e o tempo de resposta na detecção de MVOCs, principalmente para o 3-metil-1-butanol. Os sensores foram preparados a partir da degradação térmica em atmosfera comum das MOFs (ZIF-8/ZIF-67) preparadas previamente por um método hidrotérmico simples, utilizando dos sais $Co(NO_3)_2.6H_2O$ e $Zn(NO_3)_2.6H_2O$ e o ligante orgânico 2-metilimidazol em água deionizada. Os resultados de caracterização desses materiais demonstraram que as amostras não apresentaram impurezas ou surgimento de fases indesejadas. As respostas dos sensores foram avaliadas na faixa de 100 partes por milhão (100 ppm) dos MVOCs: 2-nonanona, etanol, 3-metil-1-butanol, acetona e acetato de etila, variando a temperatura de operação na faixa de 190-350 °C. A maior resposta de 14,6 foi para o 3-metil-1-butanol demonstrado pelo sensor heteroestruturado Co_3O_4-ZnO na temperatura ótima de 270 °C. Além disso, esse sensor apresentou um bom desempenho na detecteção do 3-metil-1-butanol com a presença de atmosfera úmida em diferentes faixas de umidade relativa controlada. Por fim, foi possível observar uma melhora significativa nas propriedades sensoras da heteroestrura *p-n* Co_3O_4-ZnO em comparação ao óxido puro de Co_3O_4.

Palavras-chave da dissertação: Semicondutores. Sensor de gás. Heteroestrutura *p-n*. Óxido de cobalto. Óxido de zinco. 3-metil-1-butanol.

ABSTRACT

This work focused on synthesizing *p-n* and *n-p* heterostructures based on Co_3O_4-ZnO and ZnO-Co_3O_4, derived from metal-organic frameworks (MOF) to detect volatile molecules produced by microorganisms (fungi and bacteria). However, there are few studies on the rapid detection and low detection limit of volatile organic compounds produced by microorganisms (microbial volatile organic compounds, MVOCs). The study consisted of evaluating the use of *p-n* and *n-p* heterostructures in comparison with the pure structure of cobalt oxide (Co_3O_4) to improve the response, selectivity, and response time in the detection of MVOCs, mainly for 3-methyl- 1-butanol. The sensors were prepared from thermal degradation in a typical atmosphere of MOFs (ZIF-8/ZIF-67) previously prepared by a simple hydrothermal method, using the salts $Co(NO_3)_2.6H_2O$ and $Zn(NO_3)_2.6H_2O$ and the organic ligand 2-methylimidazole in deionized water. The characterization results of these materials demonstrated that the samples did not present impurities or the appearance of unwanted phases. Sensor responses were evaluated in the range of 100 parts per million (100 ppm) of the MVOCs: 2-nonanone, ethanol, 3-methyl-1-butanol, acetone, and ethyl acetate, varying the operating temperature in the range of 190- 350 °C. The highest response of 14.6 was for 3-methyl-1-butanol, demonstrated by the Co_3O_4-ZnO heterostructured sensor at the optimum temperature of 270 °C. Furthermore, this sensor performed well in detecting 3-methyl-1-butanol in a humid atmosphere in different ranges of controlled relative humidity. Finally, it was possible to observe a significant improvement in the sensing properties of the Co_3O_4-ZnO *p-n* heterostructure compared to pure Co_3O_4 oxide.

Dissertation Keywords: Semiconductors. Gas sensor. *P-n* heterostructure. Cobalt oxide. Zinc oxide,. 3-methyl-1-butanol.

ABBREVIATIONS AND ACRONYMS LIST

2-MI	2-methylimidazole
3M1B	3-methyl-1-butanol
BET	Brunauer-Emmett-Teller
DI	Deionized
EDX	Energy-dispersive X-ray
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
MOF	Metal-organic framework
MVOC	Microbial volatile organic compound
RH	Relative humidity
SMO	Semiconducting metal oxide
TEY	Total electron-yield
TFY	Total fluorescence-yield
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZIF	Zeolitic imidazole framework

SYMBOLS LIST

Å	Ångström
°C	Celsius degree
cm	Centimeter
cm^3/g	Cubic centimetre per gram
eV	Electron volt
g	Gram
h	Hour
keV	Kilo electron 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

CHAPTER 1: General introduction and aim of this dissertation.

Over the years, problems related to human health have become a big concern in society. Among these problems, the presence of micro-organisms in the spoilage process of food and diseases in people caused by these pathogens are relevant discussions (THORN; GREENMAN, 2012). In this way, this present study sought to synthesize a material capable of assisting in the presence of fungi and bacteria detection. The micro-organisms produce microbial volatile organic compounds (MVOCs) during metabolism, with different organic compositions (POVEDA, 2021). Semiconductor oxides (SMOs) are materials suitable to apply as gas and MVOC sensors, such as Co_3O_4 (XU; CHENG, 2016) and ZnO (ZHANG et al., 2019). However, the pure oxides as sensors generally present low responses and poor selectivity. The *p-n* heterojunction is an excellent alternative to improve these sensing properties (LIU et al., 2022). So, MVOC detection using SMOs is a crucial way to improve health conditions and bring a database of these compounds.

The main objective of this study is to improve the pure Co_3O_4 sensing performance as an MVOC sensor with a *p-n* heterojunction of Co_3O_4-ZnO or the *n-p* heterostructure of ZnO-Co_3O_4, using the MOF-derived synthesis method. For the secondary objectives: (a) study the influence of the *n-p* and *p-n* heterojunction of ZnO and Co_3O_4 for MVOC detection; (b) application of an MVOC sensor in different operation conditions, such as varying the relative humidity (R.H.) and temperature in the working atmosphere; (c) the synthesis of a material capable of detecting MVOCs at low concentrations (ppm) with high selectivity, fast response time, stability, and reversibility.

For a better understanding of the structure of this study, it is divided into four chapters. Chapter 1 is the present one, with a general discussion and the principal objectives of this work. Subsequently, Chapter 2 presents the bibliography review and the references used. Chapter 3 is the article content to be published in a sensor journal, containing all the materials and methods used and the results produced in the laboratory. Finally, Chapter 4 exhibits the dissertation conclusions, challenges to overcome, and future studies.

CHAPTER 4: Conclusions and future challenges

The present study explored the potential of a heterostructured material suitable for MVOC detection at different operation conditions. As discussed in Chapter 2, MVOCs cause several problems related to human health, especially the presence of pathogens composed of fungi and bacteria. In this way, MVOC detection with high selectivity and low cost contributes to mitigating these social situations, creating a database of MVOCs. The synthesized Co_3O_4-ZnO exhibited an excellent sensing performance, especially for 3-methyl-1-butanol detection, with a simple synthesis method (Chapter 3). Besides, this *p-n* heterostructure presented a higher response for 3M1B at the optimal temperature, lower response time, and higher selectivity ratio between all the synthesized sensors (Co_3O_4 and ZnO-Co_3O_4).

The upcoming challenges are summarized in a better characterization of the synthesized Co_3O_4-ZnO, such as Transmission Electron Microscopy (TEM) and band-gap energy value measurement. These techniques can bring more information about the material and understand the electronic changes caused by the *p-n* heterojunction. The sensing performance for 3M1B, as discussed in Chapter 3, can be better explained by the mechanism occurring at the surface of the material and band-gap study. Moreover, it is essential to study the selectivity measurements with MVOCs produced by a specific bacterium, such as the compounds liberated by the *Pseudomonas spp* discussed in Chapter 2 (3-methyl-1-butanol, 2,4-dimethyl-1-heptane and 2-butanone).

Finally, this study can assist other people in the group who pretend to work with *p-n* heterostructures, MOFs as precursors for SMO synthesis, ZnO and Co_3O_4 characterizations, and 3M1B detection. The increase in MVOCs database is an exciting aim of the group. So, with more information about these compounds and how one can influence a selectivity factor, more knowledge and growing up with the use of sensors. Besides, measurements with conditions close to real, such as temperature and relative humidity, are also challenging to overcome.

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