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**Ag/NiO nanocomposites derived from α -nickel
hydroxide for the detection of microbial volatile
organic compounds**

Gabriel Camilo Negrini Vioto

São José do Rio Preto

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

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Comissão Examinadora

Prof. Dr. Diogo Paschoalini Volanti
UNESP – São José do Rio Preto
Orientador

Prof. Dr. Márcio José Tiera
UNESP – São José do Rio Preto

Prof. Dr. Waldir Avansi Junior
UFSCar – São Carlos

São José do Rio Preto
10 de Junho de 2021

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ABSTRACT

Microorganisms are widely studied due to the risks they can cause in human activities. It can damage the economy and health fields, causing infectious diseases or even the deterioration of food. Thus, there is a need for the control and identification of these organisms. An essential characteristic of microorganisms, in general, is that they produce specific profiles of microbial volatile organic compounds (mVOC) in their cellular metabolism, which can be correlated with infectious diseases or even particular microorganisms. In this work, α -nickel hydroxide (α -Ni(OH)₂) and silver (Ag) were used as a precursor of nickel oxide (NiO) and for decorating NiO with different amounts of % mass, respectively. They aim to obtain materials (NiO and Ag/NiO) with pores and silver in their structures. The modifications can guarantee better performance in applying the material both as a sensor for mVOCs and VOCs, through sensitization reactions, caused by the presence of Ag. For selectivity of the samples, acetone, ethanol, 2-butanone, 3-methyl-1-butanol, 2-nonanone, and m-xylene were used; a better selectivity was obtained for 3-methyl-1-butanol, a mVOC. In addition, sensitivity tests were performed, using different concentrations of 3-methyl-1-butanol in a range of 2 to 200 ppm and a test to obtain the optimum operating temperature of the materials.

Keywords: Microbial volatile organic compounds. α -Nickel hydroxide. Nickel oxide. Silver decorating. Nanocomposite.

RESUMO

Os micro-organismos são amplamente estudados devido aos riscos que podem ocasionar nas atividades humanas. Podendo causar danos desde a área da saúde até a área econômica, ocasionando doenças infecciosas ou mesmo a deterioração de alimentos. Dessa forma, surge a necessidade do controle e identificação destes organismos. Uma importante característica dos micro-organismos em geral é que estes produzem perfis específicos de compostos orgânicos voláteis (mCOVs) em seu metabolismo celular, perfis estes que podem ser correlacionados com doenças infecciosas ou mesmo micro-organismos específicos. Neste trabalho, foi utilizado de α -hidróxido de níquel, como precursor para síntese de óxido de níquel (NiO) e do NiO decorado com diferentes quantidades de % massa de Ag, respectivamente. Visando a obtenção de materiais (NiO e Ag/NiO) com morfologias semelhante a pétalas e com prata em suas estruturas. Modificações estas que podem promover um melhor desempenho na aplicação do material tanto como sensor de mCOVs quanto de COVs, possivelmente obtida por reações de sensibilização, ocasionadas pela presença de Ag. Em seguida, foram realizados testes de seletividade para as amostras. Para a seletividade foram utilizados, acetona, etanol, 2-butanona, 3-metil-1-butanol, 2-nonanona e m-xileno, onde foi obtido uma melhor seletividade para o 3-metil-1butanol, um exemplo de mCOV. Além disso, foram realizados testes de sensibilidade, utilizando diferentes concentrações de 3-metil-1-butanol em uma faixa de 2 a 200 ppm. Também foram realizados testes para a obtenção da temperatura de trabalho das amostras.

Palavras-chave: Compostos orgânicos voláteis microbianos. α -Hidróxido de níquel. Óxido de níquel. NiO decorado com Ag. Nanocompósitos.

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LISTA DE ABREVIATURAS E SIGLAS

VOC	Volatile organic compound
mVOC	Microbial volatile organic compound
LMs	<i>Listeria Monocytogenes</i>
MVP	Mechanically ventilated patients
CG-MS	Gas chromatography coupled to a mass spectrometer
SMO	Semiconductor metal oxide
HAL	Hole accumulation layer
TEFLON	Polytetrafluoroethylene
XRD	X-ray diffraction
FTIR	Fourier transform infrared
FESEM	Field-emission scanning electron microscopy
EDX	Energy-dispersive X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy
FWHM	Full width at half-maximum
RH	Relative humidity
2D	Two-dimensional

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1 General introduction and aim of this work

Volatile organic compounds (VOCs) are compounds that have high vapor pressure, which facilitates their boiling at low temperatures (ex: 50 ° C to 260 ° C)[1]. Contact with VOCs can adversely affect human health, short-term or long-term health effects[2]. As the risk of exposure to VOCs increases, strict environmental regulations and indoor air quality[3].

VOCs can also be used as disease biomarkers. They can be generated in the human body due to changes in metabolic pathways and be emitted in body fluids such as breathing, urine, saliva, and blood[4,5]. The same goes for the cellular metabolism of all living organisms, such as fungi, mold, and bacteria, which can produce a wide variety of extracellular metabolites, some of which are volatile (mVOCs)[6–8]

Microorganisms present in the environment represent a risk for many human activities[9], such as food spoilage[7], pathogenicity[8,10,11]. As a result of the different metabolisms they present, various pathogens produce specific profiles of mVOCs. The analysis of these particular profiles allows the correlation of mVOC with indicative of specific diseases and infections. One of the most critical contamination routes by microorganisms occurs through ingestion, whether accidental or intentional, exposure to contaminated drinking water, wastewater, soil, and food sources[12]. In the last decades, many countries have documented a significant increase in the incidence of diseases caused by microorganisms' presence in food. Contamination of food by microbiological agents is a worldwide public health concern[7].

Some examples related to food spoilage are grains and oilseeds that generate mycotoxins that can cause chronic health problems to humans and animals when stored during an extended period. The detection of specific mVOCs made it possible to use an mVOC sensor to indicate fungal growth[6]. For example, several diseases are related to microorganisms; *Listeria Monocytogenes* (LMs) is a pathogenic microbe present in food, responsible for bacteremia, meningitis, and complications during pregnancy. It grows in foods such as meats, vegetables, seafood, and even in domestic refrigerators. In the case of LMs, the main exhaled volatile organic compound (VOC) is 3-hydroxy-2-butanone[13] and 2-nitrophenol[14] and can be used as a biomarker for indirect detection of this microorganism.

Among infectious lung diseases, pneumonia is the second most common cause of death, second only to lung cancer. Nosocomial pneumonia is also the second most

common cause of nosocomial infections after urinary tract infection[15]. Nosocomial pneumonia complications are associated with mechanically ventilated patients (MVP). The mortality rate for MVP can be relatively high, ranging from 24 to 76%. MVP can be caused by pathogens, such as *Staphylococcus aureus* and *Pseudomonas aeruginosa*[15]; these microorganisms can be identified through the detection of some VOCs, such as acetoin[16], isovaleric acid[16], acetic acid[14,16], and 3-methyl-1-butanol[15] for *Staphylococcus aureus* and 2-nonanone[16,17] and 3-methyl-1-butanol[15] for *Pseudomonas aeruginosa*. Therefore, sensors' application to detect metabolites derived from pathogens, especially in mechanically ventilated patients, is entirely feasible. It is not invasive, and the results are available immediately after the measurement. Due to these concerns, there was an increase in sensor technologies in hospitals, industries, and agriculture[9].

Conventional methods for identifying VOCs and microorganisms are gas chromatography coupled to a mass spectrometer (CG-MS)[8,10,11,18] and cultivation and biochemical tests[6], respectively. However, they become unfeasible because they are expensive, robust[5,11], complicated, and time-consuming[19] techniques. An alternative widely studied to these problems is the development of semiconducting metal oxides (SMOs) for application in detecting VOCs; the interest arises due to the high sensitivity, selectivity, portability, and low cost[5,20–23] that the material can present.

Chemiresistive sensors use a reaction mechanism (oxidation) of the studied mVOCs due to the presence of oxygen species adsorbed on the material surface, which causes a depletion layer (n-type semiconductors) or a layer of accumulation of holes (p-type semiconductors)[24]. As shown in Figure 1c,d, the VOCs detection mechanism occurs through reactions present on the sensor surface. In p-type SMO, when the material is exposed to air, molecular oxygen adsorbs on the material's surface, thus removing electrons—generating ionized oxygen species on its surface and a hole accumulation layer (HAL) the electrons used in the ionosorption. The ionosorbed oxygen species on the surface react with the specific VOC, oxidizing it to CO₂ and H₂O[21,24]. In this way, the electrons previously captured recombine with the holes, thus promoting resistance increasing. When the material is exposed to atmospheric air again, oxygen species will adsorb on the material's surface, forming the HAL, changing the resistance again.

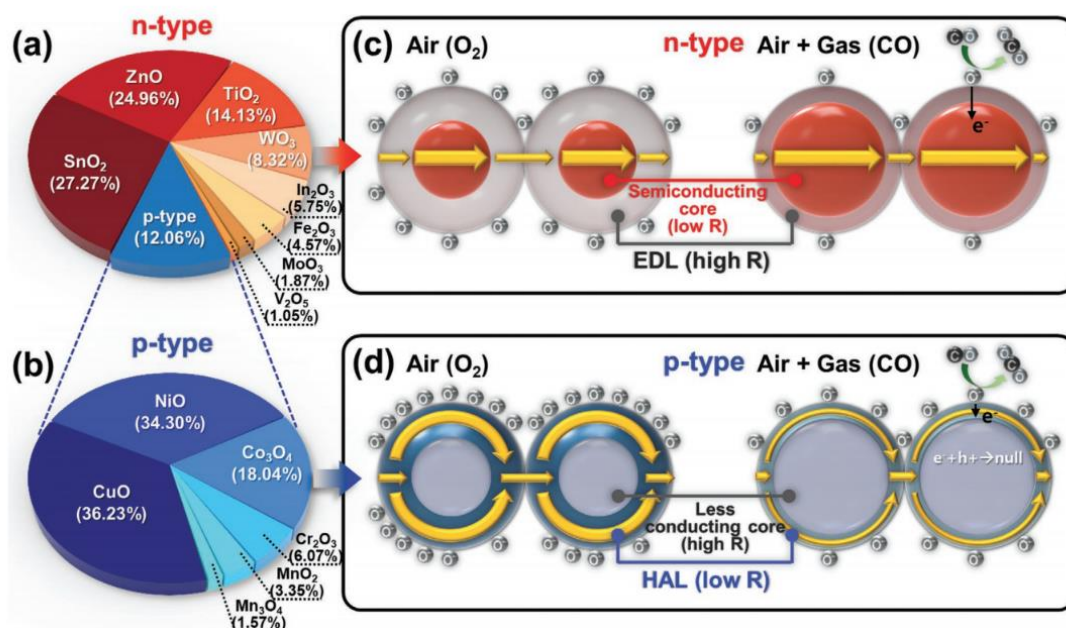


Figure 1. a,b) Papers of n-type and p-type oxide semiconductor gas sensors reported in the literature. c,d) Formation of electronic core-shell structures in n-type and p-type metal oxide semiconductors. **Reference:** JEONG, KIM, LEE, 2020[24].

P-type SMOs usually have an inadequate response as a sensor than n-type SMOs, making it difficult to commercialize. Despite the smaller number of studies related to p-type sensors as presented in Figure 1a,b, an area of active research appears to increase the performance of these sensors. The application of p-type SMO should not be underestimated and overlooked, as most p-type semiconductors are widely used as valuable catalysts. The choice of metal oxide and characteristics such as surface area, and morphology can directly affect the sensor's performance [24].

NiO is widely studied for applications such as electrochromic [25], supercapacitor [26], and battery systems [27]. In addition, it was presenting high physical stability and good electrical properties[28], making it an exciting material for gas sensing. Besides, several alternatives can be explored to improve the performance of SMOs as a sensor, including the use of methodologies for morphology control and functionalization methods with noble metals, aiming at increasing the material's contact surface and sensitization reactions, respectively.

α -Ni(OH)₂ has a hydroxyl-deficient, thus positively charged, with a structure similar to hydrotalcite. The interlayer distance is approximately 7 Å, more significant than that presented by its polymorphs. α -Ni(OH)₂ contains intercalated air anions and water molecules in its interlamellar spacing; their layers are oriented randomly, giving a

greater degree of disorder. The large interlamellar distance directly influences the characteristics of α -Ni(OH)₂, resulting in interlayer chemistry and electrochemical activity. Thus, presenting electrochemical features superior to β -Ni(OH)₂, in addition to being a material that can be easily transformed into a p-type semiconductor. However, α -Ni(OH)₂ is unstable and difficult to prepare, as this phase may change rapidly to beta form during synthesis or storage[29,30].

Also, noble metals such as Ag, Pd, Au, and Pt can cause SMO synergistic effects, thus improving the material's performance in the application as a gas sensor. These synergistic effects can occur in two main ways, through electronic and chemical sensitization reactions. In electronic sensitization, Figure 2a, the metal in its oxidized state removes electrons from the SMO, inducing the formation of an electron-depleted space-charge layer close to the surface between the metal and the SMO. Thus, reducing the layer of hole accumulations and changing the resistance. When the material is exposed to analytic gas, the metal is reduced, and the electrons return to the SMO. Chemical sensitization, Figure 2b, occurs through the spill-over effect, resulting from a catalytic surface reaction. The deposited metal activates the analyzed gas molecules, facilitating their subsequent reaction with ionosorbed oxygen on the sensor surface. In this situation, the metal does not affect the sensor's resistance and can cause an increase in sensitivity, increasing the reaction rate of chemical processes[31-33].

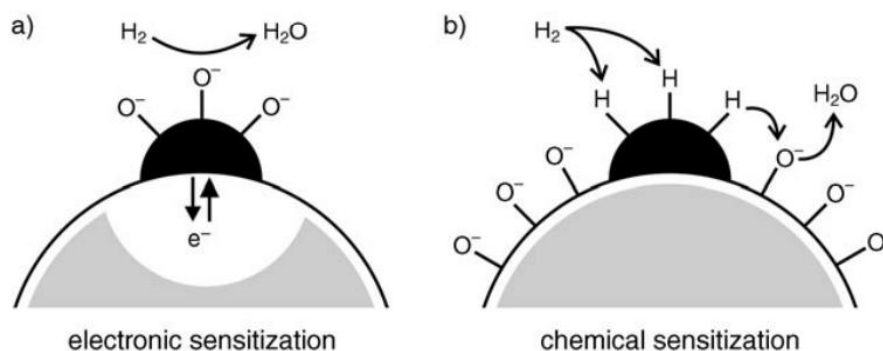


Figure 2. Sensitization mechanism. a) Electronic sensitization b) chemical sensitization.

Reference: FRANKE; KOPLIN; SIMON, 2006.

Therefore, this dissertation aims to explore Ag decorated NiO (p-type semiconductor), derived from α -Ni(OH)₂ to detect mVOCs. The overall structure of the dissertation takes the form of three chapters, including the present chapter. Chapter 2 provides new insights into the methodologies for the synthesis of NiO and Ag/NiO, which will be given for carrying out VOCs-sensing tests, the characterization of

materials, in addition to VOCs-sensing properties for NiO and Ag/NiO 5%. Finally, chapter three presents the general conclusion of the dissertation.

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3 General conclusions

The main concepts (e.g., VOC and mVOCs) and principles for understanding the work, the importance, and the need to develop alternatives for detecting these compounds were presented in the first chapter. The reason SMOs are an excellent alternative as a group for detecting mVOCs. Other essential points were also addressed, such as the need and importance of techniques for obtaining materials with a high specific morphology, a characteristic explored by the use of α -Ni(OH)₂ as a precursor, which may directly influence the performance of the SMO as a mVOC sensor. Besides the use of Ag for decorating NiO and obtaining possible sensitization reactions which may positively impact the selectivity, sensitivity, and even the material's optimum operating temperature.

In the second chapter, the syntheses for obtaining the materials were presented, in addition to characterizations such as XRD, XPS, FTIR, and FESEM, ensuring the obtaining, purity, and morphology of the desired materials. VOC-sensing tests were also carried out for NiO and Ag/NiO 5%, presenting an optimal working temperature of 250 and 200 °C, respectively. In addition, selectivity of ~2.70 and ~2.60 for 100 ppm of 3-methyl-1-butanol. This response is 1.40 and 1.66 times higher than the compound with the second-best response, ethanol. It was also confirmed that the materials could detect low concentrations and perform their function in humid environments, as shown in the sensitivity graphs.