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Vinícius Ferreira Lopes

Sensors of volatile organic compounds based on Co3O4 and V2O5 and their composites with graphene oxide

São José do Rio Preto
2020

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Àqueles que acreditam que na ciência como peça fundamental
para as mudanças que mais ansiamos

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RESUMO

O avanço na ciência e tecnologia de sensores de compostos orgânicos voláteis (VOCs) é importante para o desenvolvimento sustentável de materiais funcionais. A dissertação de mestrado refere-se à avaliação do uso de óxido de grafeno (GO, sigla em inglês) em óxido metálicos (OM) tipo-n (V_2O_5) e tipo-p (Co_3O_4) para melhorar a sensibilidade, a seletividade e o tempo de resposta dos sensores. O GO teve uma modificação sendo submetido a um processo oxidativo. Os OMs nano ou microestrurados foram preparados a partir de seus sais ou por processos de ressolubilização dos óxidos. Por fim, os compósitos GO-OM foram preparados após os percursores ficarem em suspensão com o GO por 24 horas. O GO aumentou a adsorção gasosa dos compostos resultando em maior seletividade e sensibilidade. Por outro lado, os principais benefícios das estruturas nano e microestrutruradas dos OMs seriam a maior área superficial do material resultando em melhores propriedades gasosas, resultando em mais sítios ativos para adsorção do oxigênio e das moléculas do gás analito. As respostas sensoras foram avaliadas na presença de diferentes concentrações (nas faixas de ppm e ppb) de VOCs (ex.: acetona, acetaldeído, etanol, metanol, benzeno, xileno e tolueno) em atmosfera seca.

Palavras–chave: óxido de vanádio, óxido de cobalto, óxido de grafeno, sensor gasoso, composto orgânico volátil

ABSTRACT

The advancement in science and technology of volatile organic compounds (VOCs) sensors is essential for the sustainable development of functional materials. The master's thesis refers to the evaluation of the use of graphene oxide (GO) in metallic oxides (OM) type-n (V_2O_5) and type-p (Co_3O_4) to improve sensitivity, selectivity and the response time of the sensors. The GO had a modification being subjected to an oxidative process. The nano or microstructured OMs were prepared from its precursors. Finally, the GO-OM composites were prepared after the precursors were in suspension with the GO for 24 hours. The GO increased the gaseous adsorption of the compounds resulting in greater selectivity and sensitivity. On the other hand, the main benefits of the nanostructured and micro-structured structures of OMs would be the greater surface area of the material resulting in better gaseous properties, resulting in more active sites for adsorption of oxygen and analyte gas molecules. The sensory responses were evaluated in the presence of different concentrations (in the ppm and ppb ranges) of VOCs (e.g., acetone, acetaldehyde, ethanol, methanol, benzene, xylene and toluene) in a dry atmosphere.

Keywords: vanadium oxide, cobalto oxide, graphene oxide, gas sensor

LISTA DE ILUSTRAÇÕES

LISTA DE ILUSTRAÇÕES

LISTA DE TABELAS

LISTA DE ABREVIATURAS E SIGLAS

A.C	Aromatic Compounds
B.C	Branched Compounds
D.C	Difunction Compouns
EDL	Electron Depletion Layer
FESEM	field-emission scanning electron microscopy
GA	Graphene Acid
GB	Gas Basicity
GO	Graphene Oxide
HAL	Hole-Accumulation Layer
HO	Hofmann
HU	Hummers
MA	Microwave-assisted
MC	Microcrystal
MOS	Metal Oxide Semiconductor
SMO	Semiconducting Metal Oxide
ST	Staudenmaier
TEA	Triethylamine
TEM	transmission electron microscopy
VOA	Volatile Organic Amine
VOC	Volatile Organic Compound
XRD	X-ray diffraction

LISTA DE SÍMBOLOS

ppm	Parte Por Milhão
cm	Centímetro
mmol	Milimol
g	Grama
ºC	Graus celsius
kJ	Quilo joules
GHz	Gigahertz
W	Watt
kV	Quilo volts
V	Volts
W / m^2	Potência por área

SUMÁRIO

1 General Introduction and Objectives

In an actual urban lifestyle and even in rural lifestyle, the population is exposed to a vast number of potentially harmful substances. In the atmosphere, for instance, contaminants like sulfur dioxide, carbon monoxide, ozone, and nitrogen dioxide are presented in different concentrations.[1] Nonetheless, even in non-industrialized food, the number of non-nutrients, which could be toxic or anti-nutrient, is astonishing. Tomato, for instance, has 350 of non-nutrients, and some of them are known toxic (tomatine and cycasin).[1] Considering the constant development of technologies and new products released practically every day, monitoring the maximum of possible substances seems to be vital for the population.

In this context, one class of substances is considerably dangerous: the volatile organic compounds (VOCs). VOCs are defined as any organic substance which has a boiling point between 50ºC and 260ºC[2]. VOCs, due to its volatile, rapidly spread vapor for the atmosphere, facilitating the intoxication process. The common sources of contagion of VOCs have stored meat, food dustbins, and sewers[3,4]. According to the World Health Organization (WHO)[5], the exposure to benzene, naphthalene, hydrocarbons polycyclic aromatics, and formaldehyde (all VOCs) could cause topical irritation, lung cancer, and leukemia. Besides these VOCs, the Products of Incomplete Combustion (PIC), which are in them majority VOCs, are the principal lung cancer agent (excluding tobacco substances).[1] PICs are presented in the majority of culinary activities. Despite its common source of contagion and health damage, VOCs generally are not quantified. The biggest problem with VOC analysis is the cost and time involved. Traditionally, VOCs analysis are made by gas chromatography[6–9], liquid chromatography[10] or/and optical spectrophotometric techniques[10,11].

To obtain a fast and cheap method to analyze the VOC concentration in an environment, one possible way is to apply chemiresistor materials as gas sensors. Chemiresistor material is a class of materials that have them electronic resistance changed in the presence of a certain substance. The semiconducting metal oxides (SMO) are one of the most explored materials with chemiresistor property performing as gas sensors [12–17]. In this work, intending to find a suitable SMO to VOC gas sensor, vanadium pentoxide (V_2O_5) and cobalt (II, III) oxide (Co_3O_4) were synthesized in pure form and with graphene oxide (GO). The V_2O_5 based compounds were mainly tested to volatiles amines (VOA), and Co_3O_4 based compounds were primarily studied as alcohol gas sensors. The VOA and alcohol could also be classified as VOCs. The materials were designed to reach the largest surface area and gas adsorption, which was obtained with nano and microstructure and GO addition, respectively.

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