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Conductive MOFs for Chemoresistive Sensing of Greenhouse Gases Suitable for Internet of Things

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Summary:

The importance of monitoring greenhouse gas (GHGs) levels with miniaturized and efficient devices has become an important challenge which remains unresolved. In this work, we make use of the recently growing field of metal-organic frameworks (MOFs) to develop conductive materials and test them as room-temperature chemiresistive sensors for CO_2, CH_4 and N_2O.

Keywords: Gas sensors, Greenhouse Gases, metal-organic frameworks, conductive MOFs, chemoresistive.

Background, Motivation an Objective

The direction of sustainability and overall health concerns in which society is moving towards has brought an increasing demand of reliable and affordable new materials-based sensing systems capable of monitoring key Greenhouse Gases (GHGs). However, significant challenges remain for the precise and efficient monitoring GHGs since current monitoring systems are complex, bulky and expensive, having them bound to few fixed locations.

Most solid-state gas sensing technologies come from devices that are made from semiconducting metal oxides (MOX), whose improved properties have been achieved through intensive research on advanced material micro/nanofabrication. Despite these large efforts, two major drawbacks remain: their relatively high operating temperature (above 150 ºC) and their poor selectivity, i.e., their inability to correctly discriminate and quantify the concentration of a specific gas within a mixture [1]. Improvement in the operation temperature has been achieved by replacing MOX by metal-organic frameworks (MOFs) as sensing material in chemoresistors [2].

MOFs are organic-inorganic hybrid crystalline materials consisting in a regular array of metal "nodes" surrounded by organic "linker" molecules that form a cage-like structure with extremely high surface area and porosity. The huge structural and chemical diversity provided by the available metals and linkers allows almost infinite possibilities of tuning the properties of MOFs. This porosity, together with the strong interaction between the material and the surrounding ambient, has made MOFs ideal material for gas capture and conversion [3], as well as very interesting candidates for sensing. Among the different properties that MOFs can present, a reduced subfamily, known as conductive MOFs, present an electrical conductivity which is comparable to that of solid-state semiconducting materials. In addition, some of them present the ability to change their conductance by the chemical atmosphere surrounding them [4].

In this work we will present the results of our study of triphenylene derivative MOFs for chemiresistive gas sensing of CO_2 and CH_4.

Description of the New Method or System

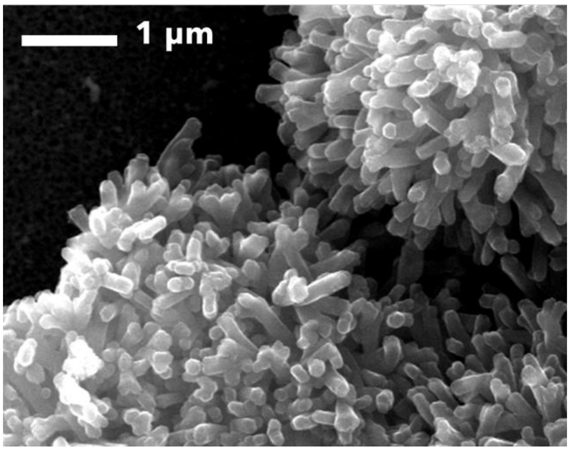
Triphenylene derivative MOFs with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 2,3,6,7,10,11-hexaaminotriphenylene (HITP) were synthesized by a modified solvothermal approach in relation to that published in literature [5], obtaining $M_3(HOTP)_2$ and $M_3(HITP)_2$ respectively (where M=Co(II), Ni(II), Cu(II), Zn(II)). We have optimized the synthesis parameters and we have studied, as well, the use of different coordinating solvent to modulate the growth and to yield high-quality crystalline MOF nanoparticles, as shown in Figure 1a.

For the sensor fabrication, a suspension of the corresponding MOF in water was drop-casted onto interdigitated electrodes (IDE) to obtain a thin layer of deposited MOF.

Results

The synthesized material typically present rod-like shape, as shown in Figure 1a, for the $Cu_3(HHTP)_2$ MOF. Similar structures have been observed for most of the synthesized MOFs, with a slight variation as a function of both the organic ligand and the metal and its salt. Most of these materials present chemoresistive response to the two most important GHGs, namely to CO_2 at concentrations between 100 to 700 ppm and to CH_4, from 0.5 to 15 ppm. For both cases these gas concentration values are comparable to the background ambient concentration. Figure 1b shows the response of one of these sensors to CH_4, between 0.5 and 2 ppm.

In the presentation we will discuss the gas sensing results as a function of the MOF constituents (ligand and metal) and of the gases to be detected.



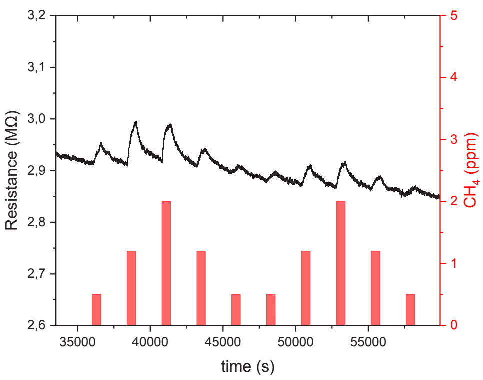


Fig. 1. (a) SEM image of $Cu_3(HHTP)_2$ nanoparticles. (b) Resistance variation of $Cu_3(HHTP)_2$ when exposed to CH_4 pulses of different concentrations.

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