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Metal-Organic Frameworks-Based Materials for Volatile Organic Compounds Sensing Applications: Strategies to Improve Sensing Performances

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Abstract : Volatile organic compound (VOC) emissions represent a serious risk to human health and the integrity of the ecosystems, especially at high concentrations. For this reason, it is very important to continuously monitor environmental quality and develop fast and reliable portable sensors to allow analysis on site. Chemiresistors have become promising candidates for VOC sensing as their ease of fabrication, variety of suitable sensitive materials, and simple sensing data. A chemoresistive gas sensor is a transducer that allows to measure the concentration of an analyte in the gas phase because the changes in resistance are proportional to the amount of the analyte present. The selection of the sensitive material, which interacts with the target analyte, is very important for the sensor performance. The most used VOC detection materials are metal oxides (MOx) for their rapid recovery, high sensitivity to various gas molecules, easy fabrication. Their sensing performance can be improved in terms of operating temperature, selectivity, and detection limit. Metal-organic frameworks (MOFs) have attracted a lot of attention also in the field of gas sensing due to their high porosity, high surface area, tunable morphologies, structural variety. MOFs are generated by the self-assembly of multidentate organic ligands connecting with adjacent multivalent metal nodes via strong coordination interactions, producing stable and highly ordered crystalline porous materials with well-designed structures. However, most MOFs intrinsically exhibit low electrical conductivity. To improve this property, MOFs can be combined with organic and inorganic materials in a hybrid fashion to produce composite materials or can be transformed into more stable structures. MOFs, indeed, can be employed as the precursors of metal oxides with well-designed architectures via the calcination method. The MOF-derived MOx partially preserved the original structure with high surface area and intrinsic open pores, which act as trapping centers for gas molecules, and showed a higher electrical conductivity. Core-shell heterostructures, in which the surface of a metal oxide core is completely coated by a MOF shell, forming a junction at the core-shell heterointerface, can also be synthesized. Also, nanocomposite in which MOF structures are intercalated with graphene related materials can also be produced, and the conductivity increases thanks to the high mobility of electrons of carbon materials. As MOF structures, zinc-based MOFs belonging to the ZIF family were selected in this work. Several Zn-based materials based and/or derived from MOFs were produced, structurally characterized, and arranged in a chemo resistive architecture, also exploring the potentiality of different approaches of sensing layer deposition based on PLD (pulsed laser deposition) and, in case of thermally labile materials, MAPLE (Matrix Assisted Pulsed Laser Evaporation) to enhance the adhesion to the support. The sensors were tested in a controlled humidity chamber, allowing for the possibility of varying the concentration of ethanol, a typical analyte chosen among the VOCs for a first survey. The effect of heating the chemiresistor to improve sensing performances was also explored. Future research will focus on exploring new manufacturing processes for MOF-based gas sensors with the aim to improve sensitivity, selectivity and reduce operating temperatures.

Keywords : chemiresistors, gas sensors, graphene related materials, laser deposition, MAPLE, metal-organic frameworks, metal oxides, nanocomposites, sensing performance, transduction mechanism, volatile organic compounds
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