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Evaluation of the PhD thesis of Martyna Manka to receive the PhD of Adam Mickiewicz University in Poznań and Universite de Strasbourg

Specialty: Chemistry

" Amino-Functionalized MOF based thin films as sensory platform for detection of aldehydes"

The topic developed in the PhD thesis manuscript focuses on fabrication of MOF/ZIF-functionalized films for electrochemical sensors for the detection of aldehydes. This project provides great flexibility for the generation of systems and functional devices ranging from complex molecular mixtures, coordination or porous organized surfaces. These strategies are easily accessible and lead to studies of great scientific value in several areas of chemistry.

The manuscript is basically divided in 4 main chapters,

1. State of the art of ZIF/MOF synthesis and use as different experimental platforms, including sensor devices;

2. Experimental techniques used for characterization ;

3. Synthesis and characterization of Zeolite Imidazolate Frameworks- ZIF films for aldehyde electrochemical detection from aqueous solution using electrodes for capacitor application;

4. Synthesis and characterization of Metal Organic Frameworks- MOF films for aldehyde electrochemical detection from aqueous solution using electrodes for capacitor application;

The last two experimental chapters focus the development of four distinct ZIF-Nafion and three MOF-Nafion composite films for aldehyde sensing. Four ZIF systems are synthetized for the purposed described in the manuscript from 2-methyl imidazole or 2 amino benzimidazole and Zn^{2+} or Co^{2+} as metal ions at room temperature. The design include several structural variants as metal ion nature important for electrochemical detection, amino groups used for imine bond formation with the aldehyde analytes and aromatic groups for network rigidity and non-covalent interaction with aldehyde guests. The three MOF systems were synthetized from 2-aminoterephtalic acid and Cu^{2+} Ni^{2+} or Co^{2+} to determine the impact of metal ions on MOF-Nafion films sensitivity

The physico-chemical characterization has been performed in a similar manner for both ZIF-Nafion and three MOF-Nafion classes by using X-ray diffraction (XRD) in accordance with molecular simulations via DFT calculations in order to check the crystallinity and polymorphic nature of ZIFs. X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared

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spectroscopy (FTIR), thermal analysis (ATG) provided information about the chemical bond formation in ZIFs or MOFs and their interaction with aldehydes. Scanning electron microscopy (SEM) was used to determine the crystalline morphology and the dimension of ZIF or MOF nanoparticles. The porosity was evaluated by using Nitrogen adsorption-desorption measurements and important differences have been observed on the determined porosity of ZIFs obtained from 2-methyl imidazole (high porosity) or 2 amino benzimidazole -low porosity) linkers. For MOF based systems the porosity is similar for all synthetized MOFs and do not depends on metal ion nature. Then the ZIF-Nafion and MOF-Nafion films were prepared by casting them on glassy carbon electrodes and used for aldehyde detection by using electrochemical impedance spectroscopy. In all cases the capacitance increase with the aldehyde enzyme concentration reaching a saturation level for high concentration of 100 µm . the results show that the fabricated to ZIF and MOF based sensors show excellent recovery rates and robust performances even for real sample analysis of tap water. Various structural and morphological factors can affect the aldehyde diffusion and imine bond formation within porous frameworks. This result encourages future pursuits in designing electronic devices containing organic species with very good conductive properties.

As a general conclusion on the PhD manuscript, one can notice the high interest of the systems investigated and characterized through a large spectrum of analytical methods, that were appropriately and successfully used. Also, the manuscript is of high quality of format and layout.

At the same time, due to the high quality of experimental results included in the doctoral dissertation, reliable and systematic implementation, innovative solutions that will certainly impact on the development of the studied field, I recommend for its distinction.

Therefore, I recommend Martyna Manka to receive the doctorate degree of Adam Mickiewicz University in Poznań and Universite de Strasbourg

Montpellier, September 04th, 2025

Mihai Barboiu, PhD.

Directeur de Recherche