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Chemiresistive Methane Gas Sensing Properties of Triphenylene-based Metal-organic Frameworks

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Summary:
The emission of methane (CH_4), a potent greenhouse gas (GHG), into the atmosphere is one of the causes of global warming and climate change. To address these challenges, we must continue to reduce CH_4 emissions, which ultimately require miniaturised low-power sensor systems with better precision for monitoring, reporting, and validation of CH_4 levels. In this respect, the use of triphenylene-based metal-organic frameworks (TP-MOFs), as sensing materials, to detect CH_4 is described here. Thanks to their high surface area and porosity, TP-MOFs detect low CH_4 levels at room temperature.

Keywords: nanomaterials, MOFs, gas sensors, electrical response, GHGs

Background, Motivation and Objective

Over the last several years, climate change and global warming have been a major concern and are considered to be one of the greatest global threats. Increasing human actions has led to a rapid increase in GHGs emissions, particularly CH_4 and carbon dioxide (CO_2), into the Earth's atmosphere, which has resulted in a gradual warming of the atmosphere [1]. Notably, CH_4 is a potentially explosive gas and it has more than 84 times the warming power of CO_2 [2]. As a result, it is highly responsible for global warming. Therefore, measuring and reliably quantifying CH_4 emissions into the environment is a top priority for tackling the climate change. In this respect, detecting and monitoring CH_4 is the first step in seeking a solution for managing and reducing its concentration in the Earth's atmosphere. In order to meet this demand, substantial research into new materials-based highly sensitive and low-cost gas sensor systems for detecting CH_4 is underway [1-2]. For this, chemiresistive gas sensors are very attractive because they are cost-effective, easy to manufacture, simple to operate, and show response towards various gases. These chemiresistive sensor devices are mostly made from metal oxides, whose properties have been achieved through intensive research on micro- and -nanofabrication of the materials [3]. However, despite considerable efforts, these sensors are still suffering from the drawbacks of poor selectivity, stability, and higher working temperatures. These problems of chemiresistive sensors can be circumvented by replacing metal oxides with advanced MOFs as gas sensing materials. Basically, MOFs are crystalline materials consisting of metal nodes and organic linkers that form a rigid cage-like structure with an extremely high surface area and porosity that makes MOFs an ideal candidate for gas detection, since chemiresistive sensors highly rely on surface reactions [3]. Thus, the main objective of present study is to detect low CH_4 levels using advanced TP-MOFs as detection materials.

Here we used a prominent group of TP-MOFs, which can be chemically altered either with hydroxyl or amino or thiol ligating groups. We targeted the series containing hexahydroxytriphenylene (HHTP) as an organic ligand and Cu^{2+} or Ni^{2+} as metal-ions. We demonstrate that Cu- or Ni-HHTP-based MOFs can be used as sensing materials for detecting low levels of CH_4 at room temperature.

Experimental details

During Cu-HHTP MOF synthesis, suitable amounts of HHTP-ligand and Cu-acetate were mixed in 2 ml of distilled water and sonicated for 10 min. Subsequently, 0.15 ml of dimethylformamide was added into the above mixture and sonicated for another 10 min., after which it was kept in an oven at 80 °C for 6 hrs. After the reaction, the powder product was collected by centrifugation and washed several times with distilled water and ethanol and dried. Similar conditions were applied to the synthesis of Ni-HHTP MOF

with Ni-acetate as metal salt [4]. The chemical structure of Cu/Ni-HHTP MOF is shown in Fig. 1.

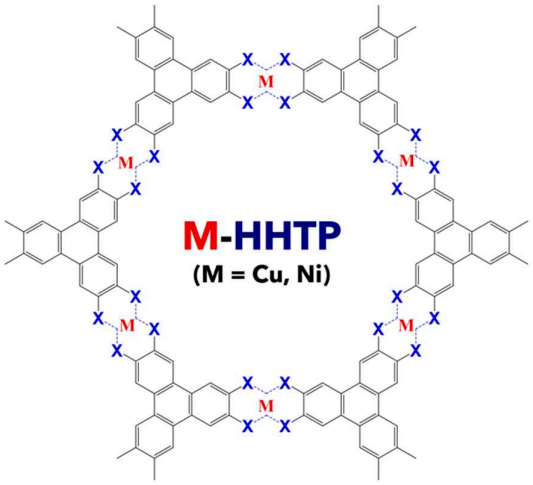

Fig. 1. Chemical structure of Cu/Ni-HHTP MOF.

Gas sensing results

Gas sensing studies on Cu/Ni-HHTP MOFs were conducted, using dynamic gas measurement setup, towards different concentrations of CH_4 at room temperature. The electrical resistance change of Cu/Ni-HHTP MOFs upon CH_4 interaction was recorded and plotted over time. For electrical resistance measurement, chips with interdigited electrodes (90 pairs of Au-electrodes) were used. For sensor fabrication, a small amount of Cu/Ni-HHTP powders were dispersed into the distilled water and sonicated for 20 minutes. Afterwards, 10 µl (≈1 drop) of the suspension was drop-casted onto the interdigited chips and dried, before being used as sensing element. During gas sensing measurements, prior to CH_4 injection, Cu/Ni-HHTP sensors were stabilized for 2 hrs in dry synthetic air. A sensor response was calculated as: Response=[$|R_a$-$R_g|/R_a$]*100, where, R_a and R_g are the resistances of Cu/Ni-HHTP sensors in air and CH_4 gas, respectively. Fig. 2 shows the response of Cu- and Ni-HHTP sensors to various CH_4 concentrations at room temperature, wherein resistance values of both the sensors found to be increased upon CH_4 interaction, with complete recovery kinetics. A higher response was observed for the Cu-HHTP sensor relative to the Ni-HHTP sensor. The calculated response, at 12.5 ppm CH_4 is 10% for the Cu-HHTP sensor, which is almost 9 times that of the Ni-HHTP sensor (1.15%), suggesting excellent response to CH_4 with Cu-HHTP MOFs. More importantly, the Cu-HHTP sensor detects very low CH_4 concentration, 1.2 ppm, which is below the atmospheric CH_4 concentration (1.9 ppm) reported by Global Monitoring Laboratory for the year 2022 [5]. Thus, the sensing results clearly illustrate the potential of TP-HHTP MOFs as active sensing materials in the development of low-power chemiresistive sensors to detect GHGs, especially CH_4.

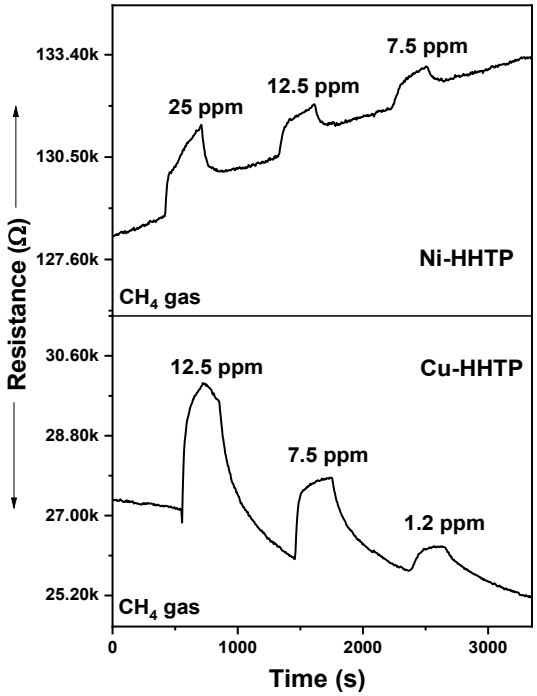

Fig. 2. Dynamic resistance plot of Cu/Ni-HHTP MOF sensor at various levels of CH_4 at room temperature.

Acknowledgements

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