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Abstract

Zn-Based Triphenylene Metal–Organic Frameworks as a Chemiresistive Platform for Methane Detection †

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Abstract: Methane (CH_4) emissions are a leading cause of global warming, and precise monitoring of and reduction in these emissions are important. To achieve these goals, miniaturized low-power sensor systems with improved precision are necessary. To this end, we present a novel room-temperature chemiresistive CH_4 gas sensor that employs Zn-hexahydroxytriphenylene-based metal–organic frameworks (Zn-HHTP MOFs) as detection materials. The high surface area and porosity of Zn-HHTP MOFs enable effective detection of low atmospheric levels (1.2 ppm) of CH_4.

Keywords: nanomaterials; Zn-MOFs; gas sensor; greenhouse gases; CH_4 detection

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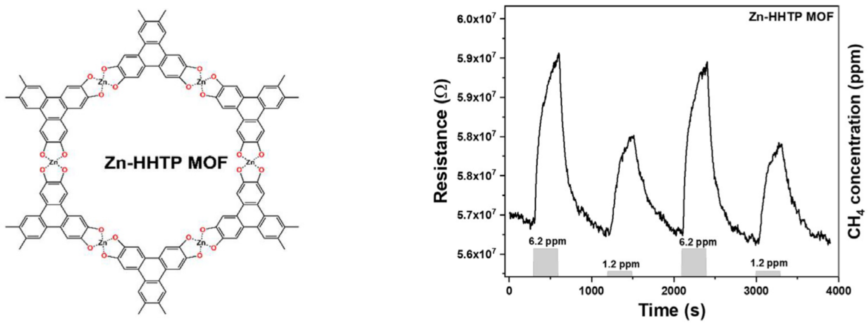
1. Introduction

CH_4 is a potent greenhouse gas, and detecting low concentrations of odorless CH_4 is challenging due to its non-polarity and high enthalpy of C–H bonds [1]. Therefore, developing miniaturized low-cost and sensitive gas sensors remains an active research goal. Although electrochemical, infrared, and chemiresistive are the most common gas detection technologies, chemiresistive sensors are advantageous thanks to their low cost, simple operation, high sensitivity, and lifetime [2]. Despite intensive research on advanced materials, metal oxide-based chemiresistive sensors, which are used most, still face major challenges related to poor selectivity and high working temperature [2]. Replacing traditional metal oxides with advanced conductive MOFs as detection materials could address these challenges. MOFs, made up of metal nodes and organic linkers, have a rigid cage-like structure with a high surface area, porosity, and crystallinity [3]. These properties make them excellent for gas detection, particularly for chemiresistive sensors that rely on surface reactions. Therefore, the primary goal of this study is to detect low levels of CH_4 by utilizing advanced MOFs as the detection material. In this respect, Zn-HHTP MOFs were synthesized by coordinating a prominent group of triphenylene with Zn^{2+} ions using a simple solvothermal method, and they were employed for the first time as active sensing material to detect low levels of CH_4 at room temperature.

2. Materials and Methods

To synthesize Zn-HHTP MOFs, a mixture of HHTP-ligand and Zn-acetate in distilled water (DW) was sonicated for 10 mins, and then dimethylformamide was added and sonicated for another 15 min. After incubating at 80 °C for 6 h, the powder was collected by centrifugation, washed with DW and ethanol, and dried. The chemical structure of the

Zn-HHTP MOFs is shown in Figure 1a. For sensor fabrication, 1 mg of Zn-HHTP MOF powder was dispersed into 1 mL of distilled water and sonicated for 30 min. Later, the suspension was deposited on the interdigited chips with Au electrodes and dried in air prior to being used as a detection element.



(**a**) (**b**)

Figure 1. (**a**) Chemical structure of Zn-HHTP MOF; (**b**) chemiresistive study of Zn-HHTP MOF sensor to 6.2 and 1.2 ppm of CH_4 at room temperature, proving its reversibility.

3. Discussion

Room-temperature chemiresistive gas sensing measurements on Zn-HHTP MOFs were performed regarding various CH_4 concentrations via a dynamic gas sensing setup under laboratory conditions. A sensor response was calculated as the ratio between the resistance of Zn-HHTP MOF in air (Ra) to the resistance of Zn-HHTP MOF in CH_4 gas (Rg), i.e., response (%) = $[|Ra - Rg|/Ra] \times 100$. Before CH_4 exposure, the Zn-HHTP MOF sensor was stabilized by aging in dry synthetic air for 3 hours. Figure 1b shows the reversibility plot of the Zn-HHTP sensor to successive 6.2 and 1.2 ppm of CH_4 at room temperature, where the sensor electrical resistance values were found to be increased upon the interaction of CH_4 gas with complete recovery features. Notably, the Zn-HHTP sensor is capable of effectively detecting a very low CH_4 concentration down to 1.2 ppm (response = 2.5%), which is lower than the atmospheric CH_4 concentration (1.9 ppm) specified by the Global Monitoring Laboratory for the year 2022 [4]. The observed response is mainly due to the MOF's high surface area, porosity, and crystallinity, enabling effective surface reactions with CH_4 molecules. Furthermore, the sensor's affinity for CH_4 may have been enhanced by the coordination of triphenylene with Zn^{2+} ions. Overall, based on our findings, Zn-HHTP MOFs show promise as advanced sensing materials for room-temperature chemiresistive CH_4 sensors. Our current focus is to study the influence of interfering gases, such as water vapor, on the sensor response, considering its practical applications.

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