

Cerium Based UiO-66 Chemiresistor for the Detection of Carbon Dioxide

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Abstract: Metal-Organic Frameworks are a versatile class of hybrid materials that can offer tantalizing opportunities to tune its structure, chemical composition suitable for gas sensing application. CO₂ - a major greenhouse gas emission is challenging due to its low reactivity. Hence, sensors with more adsorption/ reactive sites and CO₂ activating sites are needed to develop effective CO₂ sensors. Chemiresistive sensors that are based on change in electrical properties (resistance/ conductance) offer simpler instrumentation and are cost effective over other sensing technologies. The surge to develop effective CO₂ sensors have allowed us to demonstrate a simple chemiresistor- UiO-66 (Ce). UiO-66 (Ce) was synthesized and characterized by powder X-ray diffraction, scanning electron microscopy and nitrogen sorption studies. The UiO-66 (Ce) showed a very high response of 88 % at 150 °C. By combining the well-known features of redox active Ce with UiO-66 based MOF, we have converted an innocent MOF into an effective chemiresistive CO₂ sensor. The gas sensing characteristics can be attributed to a greater number of active sites for CO₂ sensing on replacement of Zr with Ce in the nodes of UiO-66.

Keywords: Metal-Organic Frameworks, Chemiresistive gas sensing, Carbon dioxide, Cerium, Redox active.

1. Introduction

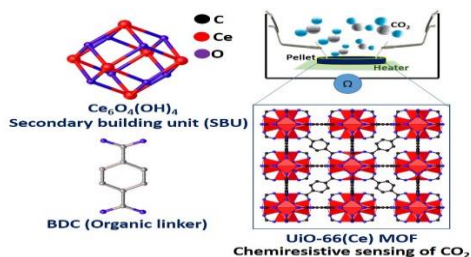
Metal-Organic frameworks (MOFs) are crystalline porous materials composed of bi- or multipodal organic linkers and metal ions /clusters.¹⁻³

Owing to its structural regularity and synthetic tunability MOFs offer a tantalizing consolidation of the components needed for a wide range of applications, including gas storage/separation, catalysis, drug delivery and chemical sensing.⁴⁻⁷ Recently, a good number of studies have been reported for MOFs as potential chemiresistors to sense toxic gases, volatile organic components (VOCs) as well as greenhouse gas like CO₂.⁸⁻¹⁰ ZIF-67 was the first MOF studied for chemiresistive gas sensing of formaldehyde vapors. The operating temperature was 150 °C with a detection limit of up to 5 ppm.¹¹ Also, it was important in sensing of trimethylamine vapors at very low operating temperatures for 2 ppm concentration of analyte.¹² Following this several more studies were developed for chemiresistive sensing using MOFs and MOF based materials.^{5,8}

Gas sensors provide a real time feedback to our surrounding containing different amount of gases that could be hazardous to human health, atmospheric pollutants or of significance to an industrial or medical process¹³. Metal-Organic Frameworks (MOFs) reveal great promise for the development of sensors due to their control over pore dimension, chemical composition, etc. Hence, by choosing an appropriate metal cluster (mono-, di-, tri- and tetravalent based metal ions or their clusters) or by tuning the predesigned linkers with specific interacting functional groups aligned on their pore walls which can act as active sites¹⁴. This can tune their affinity to the substrate interactions/analyte gas and thereby bring detectable changes in the resistance of the MOFs^{5,15}. All this finds its importance in real time gas sensing studies because of the lack of selectivity and surface area of semiconductor metal oxide (SMO), which have long been studied in gas sensing applications¹⁶. SMO like SnO₂ is among the widely studied prototype for oxide-based chemiresistive sensor. The research interest for these SMO had increased due to their promising electronic properties that they offered. Nevertheless, the SnO₂ based sensors require a very high temperature (> 200 °C) to obtain minimal sensitivity to various oxidizing/reducing gases. This is due to the primary connection of their sensing characteristics that depend on the absorption and activation of oxygen species (O⁻, O²⁻)¹⁷⁻¹⁹. Hence the need to develop low temperature gas sensors are rising that can overcome these drawbacks in the state of art gas sensors.

Meanwhile, the metal ions/clusters will contribute to some MOF properties. For instance, due to the lability of most metal ligands bonds, the chemical stability of a MOF will be mainly determined by the metal cluster/node. Stable MOFs generally exist in the oxidation state of +4 as their metal node ligates with a greater number of linkers to neutralize/

balance the charge (as in the case of carboxylate-based linkers). This increases the stability of MOFs in presence of water²⁰. Hence, UiO-66 MOFs that are based on tetravalent metals such as Zr, Ce, Hf, etc. are widely studied materials²¹⁻²³. Ce (IV)-based MOFs are promising materials and one of the most abundant rare-earth elements that have been explored in photocatalysis, redox heterogeneous catalysis and luminescence. By tailoring the oxidation state of Ce (IV/III) redox pairs as demonstrated earlier, one can fine control its redox properties. The low-lying empty 4f orbitals of Ce^{+4} (e.g. CeO_2) are highly reducible to Ce^{+3} hence incorporating f^0 Ce+4 metal ion into the node of MOF^{24,25}. Noteworthy, CO_2 conversion reactions using cerium-based oxide (IV) have been well reported earlier^{26,27}. UiO-66 (Ce) possesses a similar framework topology to UiO-66 (Zr) and hence is isostructural to UiO-66 (Zr). However, owing to the characteristic feature of ceria as a CO_2 activator, improvement in properties (such as redox activity) from the parent Zr-based MOF to Ce-based MOF rationalizes the choice of developing UiO-66 (Ce) MOF as a potential chemiresistor for CO_2 .²⁸ In this work, we have synthesized, characterized and demonstrated UiO-66 (Ce) MOF as a chemiresistive CO_2 sensor (scheme 1). To the best of our knowledge, UiO-66 (Ce) MOF has not been explored for its chemiresistive CO_2 sensing.



Scheme 1. Illustration of chemiresistive sensing of CO_2 gas using UiO-66 (Ce) MOF.

2. Experimental

2.1 Chemicals and Reagents: Cerium ammonium nitrate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, 99% was provided by SDFCL, Mumbai. Zirconium tetrachloride anhydrous (ZrCl_4), Hydrochloric acid (HCl , 35 %), Benzoic acid and Methanol (CH_3OH , 99%) was purchased from Merck Life Science Pvt. Ltd. Mumbai, India. Terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) was provided by SDFCL, Mumbai. N, N Dimethylformamide (DMF, $\text{HCON}(\text{CH}_3)_2$) was bought from Avra Synthesis Pvt. Ltd, Hyderabad, India.

2.2 Synthesis of UiO-66 (Ce): UiO-66 (Ce) synthesized by a modulator free solvothermal method. UiO-66(Ce) material synthesized according reported literature²⁹. 212.4 mg terephthalic acid (1.279 mmol) was dissolved in 7.2 mL of DMF. The solute was dissolved by sonicating for 5 mins. Exactly 2.4 mL of 0.533M $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$ was added using a micropipette. It is then kept in an oil bath at 100°C and stirred for 30 min using a magnetic stirrer. Yellow colored precipitate was formed. After the completion of reaction time, the mixture was brought to room temperature, centrifuged and the supernatant was decanted. Further, the MOF was washed two times using fresh DMF (7mL) followed by washing with acetone 3 times.

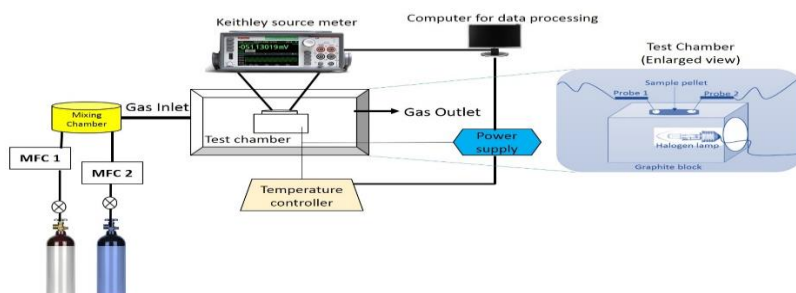
2.3 Synthesis of UiO-66 (Zr): In a typical synthesis, ZrCl_4 (0.233 g, 0.99 mmol) was dissolved in 0.16 mL of conc. HCl and 10 mL DMF solvent in a 30 mL screw-cap glass vial. This was followed by the addition of terephthalic acid (0.181 g, 1.08 mmol) and benzoic acid (0.244 g, 1.99 mmol) to the above solution. Once all the precursors were dissolved, the vial was sealed and placed in the oven at 120 °C for 48 hrs. The precipitate was washed with DMF and methanol thrice and dried under vacuum to give a white colour product of UiO-66.

2.4 Preparation of the pellets for sensing measurements: 150 mg of UiO-66 (Ce) and UiO-66 (Zr) each were pressed into individual pellets of uniform thickness of approximately 1 mm with a diameter of 1 cm. Further contacts are given by using a silver conductive adhesive paste purchased from Alfa Aesar with Sheet resistance: $<0.025 \text{ ohm/square @ } 0.001 \text{ in thick}$. The diameter of the silver dots is approximately 1 mm. All the pellets of UiO-66 (Ce) and UiO-66 (Zr) are prepared using this procedure.

2.5 Chemiresistive gas sensing measurements: The CO_2 sensing measurements of UiO-66 (Ce) and UiO-66 (Zr) is conducted by using a two probe chemiresistive gas sensing station as illustrated in scheme 2. The gas sensing station is equipped with a Keithley source meter (Model No. 2450), Alicat Mass Flow Controllers (MFCs), a mixing chamber, two tungsten needle probes of 10 μm thickness, gas reactor chamber, control panel, hollow graphite block with heating element, temperature control unit and a computer-controlled data acquisition system^{10,30}.

The gas sensing measurements were carried out by using the two-probe sensing station. Argon gas was chosen as a diluting as well as a balance gas along with CO_2 for all the measurements. After the palletization of the materials, the pellets were placed into the gas reaction chamber. A

temperature of 150 C was optimized for all the pellets in the presence of Ar gas. A steady state baseline was obtained under Ar gas prior to the switching on the CO₂ gas. The gas flow was controlled using the two MFCs, one specified for the balance-Ar gas (MFC 1) and the other for CO₂ gas (MFC 2). The mixing chamber of 500 SCCM capacity was used to mix the target and the balance gas. Finally, the difference in the resistance with respect to Ar and CO₂ was measured using the source meter^{10,30}.



Scheme 2. A schematic illustration of two probe chemiresistive gas sensing station.

2.6 Calculation of response percentage, response time and recovery time: The Response of the sensor was defined as

$$\% \text{ Response} = \frac{[R_a - R_g]}{R_a} \times 100$$

Where, R_a = Resistance of the sample in the presence of Argon, R_g = Resistance of the sample in the presence of CO₂

The Response Time (Speed of response) is defined as the time required for a sensor to reach 90 % of total response of the signal such as resistance upon exposure to the target gas. $T_R = T_2 - T_1$, Where, T_2 = Time taken by the sample to reach a steady state baseline in presence of CO₂, T_1 = initial time in presence of Ar and before switching on CO₂. The Recovery Time is defined as the time required for a sensor to return to 90 % of original baseline signal upon removal of target gas.

$$\text{Recovery Time} = T_4 - T_3$$

Where, T_4 = Time taken by the sample to reach a steady state baseline in absence of CO₂ and as soon as CO₂ gas has been switched off.

T_3 = final time in presence of CO₂ achieved after obtaining a steady state baseline and before switching off CO₂

3. Results and Discussion

The crystalline phases of the materials were characterized with powder X-ray diffraction (PXRD) {Bruker with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$)}, operating at 20 kV and 10 mA. The PXRD spectrum of UiO-66 (Ce) and UiO-66 (Zr) matches well with that of the simulated (Figure 1a). The morphology of the materials was characterized by scanning electron microscopy (Field Emission Scanning Electron Microscopy (FESEM)-TESCAN- MIRA 3). The FESEM image of UiO-66 (Ce) (Figure 1b) and UiO-66 (Zr) (Figure 1c) showed the presence of irregular and octahedral-like shaped particles (200- 400 nm size). The specific surface area of the samples was measured using a BELSORP-mini II instrument by obtaining N₂ adsorption isotherms at 77 K. All the samples were degassed at 100 °C overnight prior to measurements and showed type I isotherm of microporous nature. Further by using the Brunauer-Emmett- Teller (BET), the surface area of UiO-66 (Ce) and UiO-66 (Zr) was estimated to be 1084 m²g⁻¹ and 1326 m²g⁻¹, respectively. (Figure 1d).

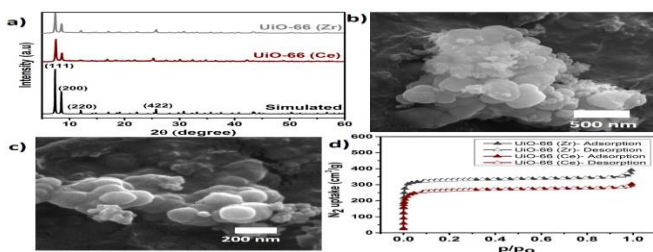


Figure 1: Characterization of UiO-66 (Ce) and UiO-66 (Zr): a) powder XRD patterns, scanning electron microscopy images: b) of UiO-66 (Ce) and c) of UiO-66 (Zr) and d) N₂ sorption isotherms.

The CO₂ sensing behavior of all the materials were studied by monitoring the resistance change in the presence and absence of CO₂ gas by using a two-probe sensing station as described in the experimental section. The samples in the form of thin pellets were placed in the probe station provided with heater and gas supplying channel controlled with temperature control unit and MFCs. We tested the response of materials at three different concentrations including 100 %, 50 % and 30 % CO₂ at 150 °C under argon flow. Argon gas was chosen both as reference and diluting gas with respect to the

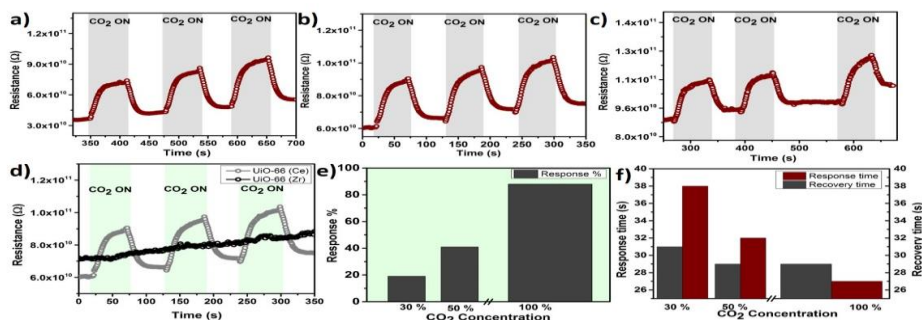


Figure 2: Gas sensing performance of UiO-66 (Ce) at an operating temperature of 150 °C. a) 100 % CO₂, b) 50 % CO₂, c) 30 % CO₂, d) Comparison of gas sensing performance of UiO-66 (Ce) and UiO-66 (Zr) at 150 °C for 50 % CO₂; comparison of gas sensing characteristics- e) % response and f) response time and recovery time for different concentrations of CO₂.

balance gas present with the CO₂ target gas. Gas sensing performance of UiO-66 (Ce) is shown in figure 2. From the response-recovery plots shown in figure 2a-c, it was evident that UiO-66 (Ce) responded to 100 %, 50% and 30 % CO₂. The resistance increased in the presence of CO₂, displaying an oxidizing behavior of CO₂ upon interaction with the surface of the MOF. However, once the CO₂ gas supply was switched off, the resistance of the MOF was restored to its initial value. Thus, displaying a reversible sensing phenomenon. On the contrary, UiO-66 (Zr) did not show any detectable changes in the resistance when exposed to CO₂ gas (figure 1d). This could be attributed to the absence of inactive Zr species in UiO-66 (Zr) unlike the redox active species available in UiO-(Ce) MOF. As evident from figure 1e, UiO-66 (Ce) showed a response of 88 %, 41 % and 19 % for 100 %, 50% and 30 % CO₂, respectively. The response times and recovery times were summarized in figure 1f. For 100 % CO₂, the response and recovery times were 27 s and 29 s, respectively. Further, the response and recovery time for 50 % and 30 % CO₂ were in the range of 29- 38 s which in comparison with other reports are very low³¹⁻⁴⁰. Hence, all the key sensing characteristics of high response and low response and recovery times have demonstrated UiO-66 (Ce) as an effective chemiresistor for CO₂ detection.

Due to the low reactivity and good thermodynamic stability, CO₂ sensing is challenging but very important. To further, understand the performance of the UiO-66 (Ce), CO₂ uptake measurements were carried out at room temperature and 120 kPa using BELSORP-mini II instrument and CO₂ (99.999%). UiO-66 (Ce) was pretreated at 100 °C under vacuum for 120 min before analysis (activation). The gas adsorption of CO₂ was

carried out under pressure up to 1.23 atm (123 kPa). The measured CO₂ uptake of UiO-66 (Ce) was 30 cm³/g (Figure 3).

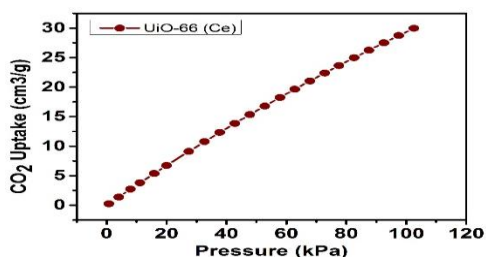


Figure 3. CO₂ adsorption of UiO-66 (Ce)

The replacement of Zr with Ce into nodes of UiO-66 MOF structure has led to the change in the chemiresistive properties of the material. It is evident from the measurements that CO₂ interacts with UiO-66 (Ce) via Ce based secondary building unit. Predominantly Ce in 4+ oxidation state is present, however some amount of Ce in 3+ oxidation state cooperatively present has also been identified^{41,42}. The presence of Ce (IV) in UiO-66(Ce) offers abundant absorption sites for CO₂, unlike in the case of Zr in the nodes.

4. Conclusion

Cerium based UiO-66 MOF was obtained via solvothermal synthesis by using cerium ammonium nitrate and benzene dicarboxylate acid linker. UiO-66 (Ce) was characterized by powder X-ray diffraction where the phases matched well with its simulated pattern. The isostructural MOF-UiO-66 (Zr) was synthesized and characterized by PXRD, SEM and N₂ sorption studies. SEM images gave evidences on the morphology of the MOF and the N₂ sorption studies of UiO-66 MOF proved the microporous nature. Further, UiO-66 (Ce) was demonstrated as an effective chemiresistive CO₂ sensor at an operating temperature of 150 °C. On the other hand, UiO-66 (Zr) did not show any significant response to CO₂. For the CO₂ concentration of 100 %, 50 % and 30 % the response % of 88 %, 41 % and 19 % for UiO-66 (Ce) was observed. Quick response and recovery times in the range of 27- 38 s were also observed. Hence, by a replacement of Zr with Ce in the metal node of UiO-66 we have demonstrated a proof of concept study for developing effective sensors for CO₂.

Conflict of interest: The authors declare no conflict of interest.

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