Article

Materials Design, Sensing Performance and Mechanism of Anhydrous Hydrogen Fluoride Gas Sensor Based on Amino-Functionalized MIL-101(Cr) for New Energy Vehicles

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Abstract: To guarantee the security of new energy vehicles (NEV), which include energy storage devices such as batteries, a quartz crystal microbalance (QCM) sensor was designed to detect online the HF gas produced from the leakage of electrolyte in the power system. Based on the chemical properties of HF gas, an amino-functionalized metal–organic framework NH₂-MIL-101 (Cr) was synthesized as a sensing material of a QCM transducer to detect HF gas for NEV safeguard. The sensing materials are designed based on the hydrogen bond interaction between the amino group and HF molecular and were characterized by powder X-ray diffraction, Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA), etc. The performance of this sensor showed high sensitivity, with a limit of detection at 500 ppb, short response/recovery time and good reproducibility for anhydrous hydrogen fluoride (AHF) detection. Additionally, the sensing mechanism of NH₂-MIL-101(Cr) QCM resonator to AHF is revealed to be reversible chemical adsorption by Gaussian 09. It is well-matched with a result of experimental determination through temperature-varying microgravimetric experiments. Therefore, the amino-functionalized MIL-101(Cr) QCM resonator may be a good candidate for an NEV safety monitor due to its rapid response to HF leaked from the decomposition of the electrolyte.

Keywords: quartz crystal microbalance (QCM); MOF; NH₂-MIL-101(Cr); anhydrous hydrogen fluoride gas sensor; gas sensing mechanism

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1. Introduction

Hydrogen fluoride (HF) is a basic fluorine chemical product. It is widely used in industrial production, such as refrigerants, fluororubbers and the production of fine chemicals [1]. HF is also used frequently in the etching of silicon wafers to fabricate glass products [2]. However, it is also a hazardous reagent due to its extreme erosive performance, which could react with metal to generate hydrogen, resulting in a risk of explosion. Moreover, its aqueous solution (hydrofluoric acid) is also highly corrosive to Si-containing materials and metal equipment. Nevertheless, colorless and odorless HF can cause tremendous problems in the human body, as contact with moisture in tissue could burn skin and result in inflammation; people who have been in constant contact with HF can develop chronic poisoning [3,4]. If HF were emitted in large amounts into the atmosphere through various industrial processes, it would be a toxic atmospheric pollutant. For example, electrolytic aluminum industries emit a large amount of HF gas during the production process. A new energy vehicle (NEV) is an electrical vehicle that includes energy storage devices

such as batteries. Electrolytes in lithium-ion power batteries have low flash points, and electrolyte leakage and exposure to oxygen in the air can cause a battery fire or even an explosion [5]. Moreover, the electrolyte in NEV generally contains LiPF_6 or LiBF_4 ; once the electrolyte leaks, the LiPF_6 or LiBF_4 may rapidly react with trace level water vapor to produce phosphorous (POF_3) and HF. So, we can determine whether the battery electrolyte leaks by detecting the presence of hydrogen fluoride gas [5]. Therefore, it is necessary to develop an efficient sensor to detect HF gas in time.

Until now, many methods have been developed to measure HF. Semiconductor tin dioxide-based HF gas sensors have been reported. These could detect HF gas in trace levels, but the best sensitivity to HF molecules is not ensured, and they are affected significantly by temperature [6,7]. SiO_2 microcantilever [4,8], SAW sensors [1], a fiber-optic probe based on reflection-based localized surface plasmon resonance (LSPR) [3] and plastic optical fiber (POF) sensors [9] have also been reported. However, these methods are either nonreversible or sacrifice costly devices and difficult-to-detect HF gas in real time. Apart from this, various fluorescence and colorimetric chemosensors for HF have also been studied; fluorescence requires expensive and complex instrument and colorimetric chemosensors that can only detect HF vapor [2,10,11]. To the best of our knowledge, quartz crystal microbalances (QCM) have not been employed to detect HF gas.

A QCM gas sensor is a kind of mass-sensitive detector, which has many advantages, such as its low cost, stability, reliability, good selectivity, high precision and fast response; in particular, it has a high sensitivity and can achieve nanogram-level detection [12–15]. QCM gas sensors detect gas by the change of the resonant frequency of the quartz crystal caused by the mass change on the surface of the crystal after gas adsorption [16–20]. The core component of the QCM gas sensor is a quartz crystal, which is extremely stable and insoluble in hydrochloric acid, sulfuric acid and nitric acid at room temperature, but it is soluble in hydrofluoric acid. As the reaction between hydrofluoric acid and quartz crystal is a liquid–solid reaction, quartz crystal does not easily react with anhydrous hydrogen fluoride gas. Therefore, we can employ a QCM gas sensor to detect whether anhydrous hydrogen fluoride (AHF) gas exists.

The performance of a QCM gas sensor depends on the gas adsorption capacity of the sensing material coated on the quartz resonator [21,22]. So, the key is to design sensitive materials for detecting special gas. In recent years, metal–organic frameworks (MOFs) with a large surface area, high porosity and unsaturated metal sites have been employed in gas storage, catalysis and sensing [23–26]. This may have potential as a sensing material for mass-sensing devices based on gas adsorption. In order to design a QCM-based AHF sensor, we prepared two MOFs including MIL-101(Cr) and NH_2 -MIL-101(Cr) for comparison and understanding of its sensing mechanism. The molecular structures and crystal structures of MIL-101(Cr) and NH_2 -MIL-101(Cr) are confirmed and shown in Figure S1.

2. Experimental

2.1. Materials

All reagents used were analytical grade except the special instructions. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH, methanol, ethanol, 1,4-benzenedicarboxylic acid (H_2BDC), sodium acetate trihydrate (CH_3COONa) and N,N-dimethylformamide (DMF) are purchased from Sigma-Aldrich (Shanghai, China). 2-aminoterephthalic acid (2- NH_2 -BDC) was purchased from Shanghai Dibai Biotechnology (Shanghai, China). Deionized water was used in all experiments.

2.2. Materials Synthesis

2.2.1. Synthesis of MIL-101(Cr)

The hydrothermal method was employed to synthesize MIL-101(Cr) as described previously [27]. Briefly, 0.82 g of H_2BDC , 2 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 25 mL (0.05 mol/L) of CH_3COONa solution were introduced into a mixing vessel and stirred for 30 min. Then, the resulting mixture was transferred into a Teflon-lined stainless steel reactor, capped tightly and heated at 493 K for 480 min. After that, the mixture was filtered, and washed with

ethanol and deionized water three times. The resulting green solid was dried in vacuum at 423 K for 12 h.

2.2.2. Synthesis of NH₂-MIL-101(Cr)

NH₂-MIL-101(Cr) was synthesized by a mild solvothermal process [28–30]. Typically, 800 mg (2 mmol) Cr(NO₃)₃·9H₂O and 360 mg (2 mmol) 2-aminoterephthalic acid were added slowly into a 15 mL H₂O solution containing 0.16 g NaOH. The mixture was stirred at room temperature for 30 min and then transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 423 K for 10 h. After natural cooling, the obtained mixture was collected by centrifugation at 10,000 rpm for 10 min. The obtained green powder was washed several times with distilled water, DMF and methanol, respectively, and then further purified by solvothermal treatment in ethanol at 373 K for 24 h to remove the unreacted raw materials in the tunnel. After supercritical drying, the NH₂-MIL-101(Cr) was obtained. The schematic diagram of synthesis procedure of NH₂-MIL-101(Cr) shown in Figure S2.

2.3. Characterization

Powder X-ray diffraction, Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) were used to characterize the synthesized materials. For detailed parameters, please refer to the supporting information.

2.4. QCM Sensors Fabrication and Measuring Equipment

The QCM sensors fabrication and measuring were carried out as described previously [31,32]. An AT-cut QCM resonator ($f_0 = 10^7$ Hz) containing quartz crystal, silver electrode and crystal support was purchased from West Sensor Co., Chengdu, China. In the Sauerbrey equation in Equation (1), f_0 is the essential resonant frequency of QCM, Δm is the mass change on the electrode, A is the active area and Δf is the frequency shift of QCM. The A and f_0 are constant for a particular quartz crystal. The resonance frequency of the quartz crystal decreases in proportion to an increase in mass.

$$\Delta f = -2.3 \times 10^{-6} f_0^2 \Delta m / A \quad (1)$$

Before the sensitive material was dropped on the surface of the quartz crystal, the quartz crystal was cleaned to ensure the sensitive material was tightly bonded to the quartz crystal. QCM electrodes were ultrasonically cleaned in acetone, ethanol and deionized water for 30 min, respectively, and then dried at 60 °C. Thereafter, 2 µL of the suspension (material mass: deionized water volume = 1 mg:1 mL) was drop-cast onto the QCM electrode to form a sensitive film while drying at 40 °C. In a typical measurement, the as-prepared QCM sensors were vertically suspended in a sealed chamber with a gas inlet/outlet, and the air was used as a carrier gas. The tested HF gas was obtained from Dalian Date Gas Co. Ltd. (Dalian, China); the purity of all gases was up to 99.5%. The QCM sensor was exposed to the dry air stream until a stable baseline was established, then the target gas was injected into the testing chamber. After the adsorption of AHF, a stable response was obtained within tens of seconds. After that, the air was re-introduced into the chamber to reestablish the baseline. Repeating the above operation can obtain responses with different gases or concentrations. The schematic of the testing system is shown in Figure 1. All these measurements were conducted at room temperature (25.0 ± 1.0 °C) unless for measuring adsorption isotherm at different temperatures to determine experimentally the adsorption enthalpy of AHF on sensing materials.

Figure 1. Schematic of a gas testing system.

2.5. Gaussian Simulated Calculations

To understand AHF adsorption and sensing mechanism, we utilized Gaussian simulation to calculate the adsorption enthalpy and the geometries of the AHF molecules. The simulation and calculation were conducted by a Gaussian 09 software with the hybrid B3LP functional and 6-33++G (d, p) basis set. The optimized structures were confirmed to be minima on the potential energy surface via vibration frequency analysis. The simulated adsorption enthalpies of HF molecules and MIL-101(Cr) and NH₂-MIL-101(Cr) were calculated with Equations (2) and (3).

$$\begin{aligned} & \Delta H_{\text{MIL-101(Cr)-HF}} \left(\text{kJ mol}^{-1} \right) \\ &= 2625.5 \left[H_{\text{MIL-101(Cr)+HF}} - H_{\text{MIL-101(Cr)}} - H_{\text{HF}} \right] \end{aligned} \quad (2)$$

$$\begin{aligned} & \Delta H_{\text{NH}_2\text{-MIL-101(Cr)-HF}} \left(\text{kJ mol}^{-1} \right) \\ &= 2625.5 \left[H_{\text{NH}_2\text{-MIL-101(Cr)+HF}} - H_{\text{MIL-101(Cr)}} - H_{\text{HF}} \right] \end{aligned} \quad (3)$$

3. Results and Discussion

3.1. Structure Characterization

The structures of MIL-101(Cr) and NH₂-MIL-101(Cr) were confirmed by powder X-ray diffraction (PXRD) (Figure 2). The diffraction peaks of the MIL-101(Cr) are in good agreement with its simulated pattern, indicating the successful synthesis of MIL-101(Cr). Compared with the simulated pattern of MIL-101(Cr), the pattern of NH₂-MIL-101(Cr) shows a phenomenon of broad Bragg reflection caused by its nanometer size effect. However, in general, the pattern of our sample is similar to the simulated one and is consistent with that reported in the literature [28], confirming that amino-functionalized MIL-101(Cr) did not change the crystal structure and form isorecticular MOF.

Figure 3a,c show SEM images of the NH₂-MIL-101(Cr) and MIL-101(Cr) samples. From the figure, we can see that MIL-101(Cr) shows a uniform regular octahedral structure. However, the NH₂-MIL-101(Cr) sample exhibits a dependent and irregular crystal structure, indicating a weaker crystallinity property due to the pores being filled with amino groups. The TEM images (Figure 3b) reveal that the particle size of the NH₂-MIL-101(Cr) sample is uniform in the range of 30–40 nm and smaller than the MIL-101(Cr) (70–80 nm). Figure S3 exhibits the elemental analysis result of NH₂-MIL-101(Cr) examined by EDS. Additionally, the mapping of Cr, O, N, C show that all element distribution is homogeneous, and the N is lower than the other components. Figure S4 shows that the element analysis of MIL-101(Cr) including Cr, O, C, H, and the distribution of the element is well-proportioned. Additionally, SEM images of the thickness and surface of MIL-101(Cr)- and NH₂-MIL-101(Cr)-deposited

films on QCM resonators were displayed in Figure S5. The thicknesses of the two sensitive films were found to be 1.67 μm and 1.625 μm , respectively.

Figure 2. Powder XRD patterns of MIL-101(Cr) (theoretical pattern), MIL-101(Cr) and NH_2 -MIL-101(Cr).

Figure 3. SEM images of (a) NH_2 -MIL-101; (c) MIL-101; and TEM images of (b) NH_2 -MIL-101; (d) MIL-101.

To prove the successful synthesis of NH_2 -MIL-101(Cr), the FT-IR spectra of the two samples are also presented in Figure 4. As shown in Figure 4, the double peaks at 3456 cm^{-1} and 3371 cm^{-1} correspond to the asymmetric and symmetric vibration of amino N-H on the phenyl ring. Due to the bending vibration adsorption of the amino groups, the FT-IR has a peak at 1661 cm^{-1} . The peak at 1343 cm^{-1} is attributed to the C-N stretching of the

aromatic ring. The other two peaks at 1494 cm^{-1} and 1435 cm^{-1} can be assigned to $-(\text{O}-\text{C}-\text{O})-$ stretching vibrations. The peak of the stretching vibration of the C-H on phenyl ring at 2931 cm^{-1} and relevant C-H deformation vibration bands were at 1258 cm^{-1} , 1100 cm^{-1} and 768 cm^{-1} , respectively. The peak at 600 cm^{-1} belonged to the symmetric stretching of Cr-O. Thus, we can conclude the successful formation of $\text{NH}_2\text{-MIL-101}(\text{Cr})$ and a retained structure of MIL-101(Cr).

Figure 4. FT-IR Spectra of $\text{NH}_2\text{-MIL-101}(\text{Cr})$ and $\text{MIL-101}(\text{Cr})$.

To obtain the microstructural features, the sample was analyzed by an N_2 adsorption-desorption experiment and the isotherms are shown in Figure 5. $\text{MIL-101}(\text{Cr})$ and $\text{NH}_2\text{-MIL-101}(\text{Cr})$ both exhibited a type IV isotherm character of mesoporous materials, according to the IUPAC classification of adsorption isotherms. The calculated surface area and total pore volume of $\text{NH}_2\text{-MIL-101}$ are $2541.74\text{ m}^2\text{g}^{-1}$ and $1.61\text{ cm}^3\text{g}^{-1}$, respectively; this is comparable with the $\text{MIL-101}(\text{Cr})$ ($2890.37\text{ m}^2\text{g}^{-1}$, $1.80\text{ cm}^3\text{g}^{-1}$). The inset of Figure 5a,b presented the pore size distribution of the samples; the pore diameter distribution shows a peak at 4.5 nm in $\text{NH}_2\text{-MIL-101}$, which is smaller than that in $\text{MIL-101}(\text{Cr})$ ($4.8, 4.9\text{ nm}$) due to the amino groups projecting into the pores.

Figure 5. Nitrogen adsorption-desorption isotherms of (a) $\text{MIL-101}(\text{Cr})$; (b) $\text{NH}_2\text{-MIL-101}(\text{Cr})$ and pore size distributions of the pristine are presented in the inset, respectively.

Figure 6 displays the thermogravimetric curves of the $\text{MIL-101}(\text{Cr})$ and $\text{NH}_2\text{-MIL-101}$ samples. For $\text{NH}_2\text{-MIL-101}$, three main weight losses can be seen when heated up to $800\text{ }^\circ\text{C}$ in a nitrogen atmosphere. The first weight loss up to about $100\text{ }^\circ\text{C}$ is attributed to the volatilization of water absorbed in the air. The second part, between $100\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$, corresponds to the loss of bound water. The third section, higher than $200\text{ }^\circ\text{C}$, belongs to the decomposition of terephthalic acid and the destruction of the structure. Simultaneously, it should be noted that $\text{MIL-101}(\text{Cr})$ possesses a higher decomposition temperature compared with $\text{NH}_2\text{-MIL-101}(\text{Cr})$, indicating that amino functionalization reduces the thermal stability of the metal-organic framework $\text{MIL-101}(\text{Cr})$.

Figure 6. Weight loss vs. temperature TGA curve of MIL-101(Cr) and NH₂-MIL-101(Cr) heated up to 800 °C in nitrogen.

In order to investigate the element categories of MIL-101(Cr) and NH₂-MIL-101 samples, the XPS was carried out. As presented in Figure 7a, the sample of NH₂-MIL-101 comprised C, N, O and Cr elements, and MIL-101(Cr) does not contain an N element. From Figure 7a, we can see the same element has the same peak position. The Cr³⁺ 2p consists of two peaks at 577.18 and 586.18 eV in Figure 7b, which are in accordance with the signal of Cr³⁺ 2p_{3/2} and Cr³⁺ 2p_{1/2}, suggesting the existence of Cr-O. The 284.6 eV binding energy obtained by XPS analysis is a standard result for specimens C1s as the reference, and the peak in 288.3 eV is attributed to the ether carbon in O-C-O, while the peak in 284.2 eV is associated with the aryl carbon from the benzene ring in Figure 7c. The O 1s emission spectrum (Figure 7d) can be divided into two peaks, where the peak at 531.6 eV shows typical metal-oxygen bonds, and the peak at 532.4 eV may be attributed to the -OH group from the adsorbed H₂O molecules. In addition, Figure 7e shows the XPS spectrum of N1s, with the peak at 400.6 eV, characteristic of an amino group, indicating that NH₂-MIL-101 has been successfully synthesized, and where the peak at 399.0 eV can be attributed to the C-N bonds.

3.2. Sensing Behaviors of These QCM Sensors toward HF Gas

Two QCM gas sensors were constructed based on MIL-101(Cr) and NH₂-MIL-101(Cr) porous materials, respectively. Figure 8 shows the response curves of the above two QCM gas sensors toward 2.5 ppm HF. Before the gas sensing test, a smooth baseline of resonating frequency was established in an air atmosphere. When AHF gas was introduced to the setup, the frequency shifts appeared, representing the adsorption process of AHF on the surface of the gas sensors. It was rapidly evident that the response no longer changed, indicating that the adsorption-desorption equilibrium-state had built up. Then, air was reintroduced to the chamber to break the balance, and the desorption process was started. As seen from Figure 8, the MIL-101(Cr) and NH₂-MIL-101(Cr) thin film-modified gas sensors have responses of 464 Hz and 281 Hz for 2.5 ppm AHF, respectively. The response time of NH₂-MIL-101(Cr) is 4 s, and the recovery time is 12 s, and the response and recovery time of MIL-101(Cr) is slightly less than for NH₂-MIL-101(Cr). The result shows that these sensors have rapid response and recovery dynamics. So, the MIL-101(Cr) and NH₂-MIL-101(Cr) composite-modified QCM sensors could be used for further experiment and analysis.

Figure 7. X-ray photoelectron spectra of (a) MIL-101(Cr); and $\text{NH}_2\text{-MIL-101(Cr)}$; (b) Cr 2p; (c) C 1s; (d) O 1s; (e) N 1s.

Figure 8. Response and recovery curves of two QCM gas sensors based on MIL-101(Cr) and $\text{NH}_2\text{-MIL-101(Cr)}$ to 2.5 ppm HF gas.

In Figure 9a, two samples exhibited fast responses for the same 500 ppb HF in three cycles, and the response–recovery cycle lasted less than 60 s. The response curves are similar, implying that MIL-101(Cr) and NH₂-MIL-101(Cr) both have good repeatability for AHF detection. Because the reversible chemical adsorption exists between the amino group of the NH₂-MIL-101(Cr) and AHF, the NH₂-MIL-101(Cr) gas sensor shows a higher response rate with high selectivity.

Figure 9. (a) Short-term repeatable and reversible rapid sensing response to 500 ppb AHF gas based on MIL-101(Cr) and NH₂-MIL-101(Cr) samples; (b) real-time dynamic frequency response curve of MIL-101(Cr) and NH₂-MIL-101(Cr) QCM sensor exposure to AHF with increasing concentration; (c) linear relationships between the maximum response frequency difference value of MIL-101(Cr), NH₂-MIL-101(Cr) modified QCM gas sensors and concentration of AHF gas, respectively; (d) frequency response values of MIL-101(Cr) and NH₂-MIL-101(Cr) based sensor towards various gases (the concentration of these gases was 5 ppm).

Figure 9b depicts a typical frequency shift of the sensors to 5, 2.5, 1, 0.5 ppm of AHF in air (15 sccm) at room temperature. It demonstrates that the frequency shift of the sensor increases by increasing the concentration of AHF, and all responses were similar in shapes. When the concentration is only 500 ppb, the response of a NH₂-MIL-101(Cr) sensor can achieve 291 Hz, and a MIL-101(Cr) sensor can achieve only 154 Hz, indicating that the detection limit of these sensors is lower than 500 ppb.

At low concentrations, i.e., at concentrations of HF from 50 ppb to 500 ppb, there is a good linear relationship between the response and gas concentration. The calibration curves of MIL-101(Cr)- or NH₂-MIL-101(Cr)-modified QCM gas sensors, regarding the dependence of the frequency response to different HF gas concentrations, are shown in Figure 9c. The calibration curves reveal the conformance of the Sauerbrey equation. The fitting relationship of an MIL-101(Cr) modified sensor is $y = 224.89x + 43.89$ with a correlation coefficient (R^2) of 0.9882, and NH₂-MIL-101(Cr) shows a sharper increase ($y = 463.87x + 63.87$) with $R^2 = 0.9887$. The limit of detection (LOD) value of the sensors was calculated by the equation: $LOD = \frac{3\sigma}{S}$, where S is the sensitivity of the sensor against the gas, and σ is the noise level [33–35]. The logical detection limits of MIL-101(Cr) and NH₂-MIL-101(Cr) were obtained from frequency shift curves and are 13.2 ppb, 6.4 ppb, respectively.

Selectivity is a key factor for the gas sensor in practical applications. It was also investigated through exposing MIL-101(Cr) and NH₂-MIL-101(Cr) gas sensors to a variety of gases (AHF, CO₂, CO, NO, H₂S, H₂ and CH₄) under a concentration of 5 ppm. Figure 9d exhibits the frequency response values of MIL-101(Cr) and NH₂-MIL-101(Cr) sensors toward different gases. The sensor based on NH₂-MIL-101(Cr) had the largest response to HF among all the interfering gases, which reached about 575 Hz, much larger than the second highest response to CO₂, which reached 315 Hz. In addition, the response of NH₂-MIL-101(Cr) toward acetone was investigated further in Figure S6. As shown in Figure S6, the response is less than AHF, and the recovery time is 25 s, which is longer than the AHF gas recovery time, so NH₂-MIL-101(Cr) was suitable for detecting AHF. As for the MIL-101(Cr) gas sensor, selectivity toward AHF gas was not found, and the response value is smaller than for the NH₂-MIL-101(Cr) QCM sensor. This may be caused by the specific interaction between -NH₂ functional groups and AHF molecules; introducing an -NH₂ group into MIL-101(Cr) enhances the response of AHF. The NH₂-MIL-101(Cr) sensor with high AHF response and gas selectivity can be considered a promising candidate to detect AHF. Furthermore, the response was tested in a different relative humidity, as shown in Figure S7 (adetailed description is in the Supplementary Information).

According to classical adsorption theories, when the value of the heat of adsorption is between $-40 \text{ kJ}\cdot\text{mol}^{-1}$ and $0 \text{ kJ}\cdot\text{mol}^{-1}$, the interaction between the materials and gas molecules belongs to weak reversible physical adsorption, and this adsorption is basically not selective. An irreversible chemical reaction occurs when the value of the heat of adsorption is in the range of $-80 \text{ kJ}\cdot\text{mol}^{-1}$ to $-40 \text{ kJ}\cdot\text{mol}^{-1}$, and the adsorption of target molecules onto the sensing materials is selective and reversible [12,19,36–45]. To explore the sensing mechanism of HF, Gaussian 09 was used to simulate the adsorption energy of HF molecules on MIL-101(Cr) or NH₂-MIL-101(Cr). Considering the site of the action of HF and the molecular structure of the two materials, we calculated the adsorption enthalpy (ΔH) by simulating an HF molecule adsorbed on different sites of MOFs, as shown in Figure S8. Between metal Cr framework and HF, the simulated ΔH is $-27.8277 \text{ kJ}\cdot\text{mol}^{-1}$; we mainly focused on the interaction of organic molecules and HF molecules here. As shown in Figure 10, for HF-H₂BDC, HF-NH₂-H₂BDC, the simulated ΔH were -19.6218 and $-47.3201 \text{ kJ}\cdot\text{mol}^{-1}$. The results show that HF-NH₂-MIL-101(Cr) belongs to chemisorption, and that HF-MIL-101(Cr) is physically adsorbed. Therefore, the NH₂-MIL-101(Cr) would be an excellent candidate for the applications of AHF sensors. Typically, the relative sensitivity and selectivity could be attributed to the introduction of amino groups provided by the mesoporous NH₂-MIL-101(Cr), which was believed to facilitate the gas adsorption.

An experimental method (temperature-varying micro-gravimetric method) was also used to obtain an adsorption isotherm for extracting ΔH of AHF and CO₂ adsorption onto sensing materials. It could verify the correctness of calculation results. At first, two adsorption isotherms at different temperatures (Figure 11a,b) of the NH₂-MIL-101(Cr)-based QCM sensor towards various AHF concentrations were recorded, respectively. Then, the corresponding linear plots calculated at 298 K and 313 K were drawn in Figure 11c. At last, the ΔH value of NH₂-MIL-101(Cr) to HF, calculated from the Clausius–Clapeyron equation in Equation (4), was $-48.6 \text{ kJ}\cdot\text{mol}^{-1}$

$$\Delta H^\theta = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_1}{P_2} \quad (4)$$

meaning that reversible chemical adsorption exists between NH₂-MIL-101(Cr) and HF molecules. The result is consistent with that of a Gaussian 09 simulation, again declaring the key role of an amino group in enhancing AHF sensing. The ΔH value of NH₂-MIL-101(Cr) to CO₂ was calculated based on Figure 11d–f, and is $-35.83 \text{ kJ}\cdot\text{mol}^{-1}$. It is smaller than that of HF, indicating that the interaction between an NH₂-MIL-101(Cr) material and CO₂ is physisorption and CO₂ is a non-competitive adsorptive gas for HF. This is consistent with the previous selectivity results.

Figure 10. Optimized geometries and interactions between HF molecules and ligands of MIL-101(Cr) and NH₂-MIL-101(Cr).

Figure 11. Gravimetric curves of NH₂-MIL-101(Cr) based QCM at (a) 298 K and (b) 313 K to AHF with different concentrations of 250, 100 and 50 ppb, respectively; (c) based on the experimental results in (a,b), two isotherms are plotted to calculate the adsorption heat ($-\Delta H$); gravimetric curves of NH₂-MIL-101(Cr) based QCM at (d) 298 K and (e) 313 K to CO₂ with different concentrations of 1 ppm, 500 ppb and 250 ppb, respectively. (f) based on the experimental results in (c,d), two isotherms are plotted to calculate the adsorption heat ($-\Delta H$).

4. Conclusions

In our work, MIL-101(Cr) and NH₂-MIL-101(Cr) were synthesized by a facile hydrothermal method and employed to construct a QCM-based HF sensor. The sensing results indicate that the sensor of NH₂-MIL-101(Cr) exhibits excellent response characteristics in low concentration HF gas (ppb level) and shows a better selectivity, sensitivity and repeatability to AHF gas than its parent MIL-101(Cr). At the same time, the detection limit of the sensor to AHF was lower than 50 ppb. The amino-functionalization of MIL-101(Cr), together with rich organic functional groups and high surface area, enhances the response toward AHF gas of MIL-101(Cr). According to the thermodynamic experiments and Gaussian simulation, the adsorption heat ($-\Delta H$) of HF molecules on NH₂-MIL-101(Cr) is located in the range of reversible chemical adsorption (about 48.6 kJ/mol), which is

suitable for sensor application. The results not only reveal the adsorption and sensing mechanism of an AHF sensor, resulting in a chemosensing performance, but also illustrate that an amino-functionalized MIL-101(Cr) might be a potential candidate for the further development of sensors for AHF detection in many areas. For practical applications, inevitably, the interference of humidity and the need for more investigation and additional drying treatments need to be considered.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/coatings12020260/s1>, Figure S1: The molecular structure of (a) MIL-101 (Cr) and (c) NH₂-MIL-101 (Cr); The crystal structure of (b) MIL-101 (Cr) and (d) NH₂-MIL-101 (Cr), Figure S2: Schematic diagram showing synthesis procedure of NH₂-MIL-101(Cr) employing hydrothermal reaction method, Figure S3: Mapping of different elements of NH₂-MIL-101(Cr), Figure S4: Mapping of different elements of MIL-101(Cr), Figure S5: SEM images of the thickness of (a) MIL-101(Cr) and (b) NH₂-MIL-101(Cr) deposited films on QCM resonators, Figure S6: Response and recovery curves of QCM gas sensor based on NH₂-MIL-101(Cr) to 1 ppm C₃H₆O gas, Figure S7: (a) Frequency shift curves of the NH₂-MIL-101(Cr) and SH NH₂-MIL-101(Cr) from low RH to high RH; (b) Response of the NH₂-MIL-101(Cr) and SH NH₂-MIL-101(Cr) sensor at different humidity, Figure S8. The gaussian simulations of adsorption between HF and: (a) Metal framework, (b) 1,4-BDC, (c) NH₂-BDC, (d) NH₂-BDC (H-bonding adsorption).

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