MOF NANO-CRYSTALS OF ZIF-8 IDENTIFIED AS AMBIENT NO_2 GAS ABSORBENT BY USING RESONANT MICRO-CANTILEVER EXPERIMENT

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ABSTRACT

Based on resonant micro-cantilever measurements, the metal-organic framework (MOF) nano-crystal material of ZIF-8 is, for the first time, identified as an excellent absorbent to capture/fix the automobile exhaust of NO_2 in real atmospheric air. By using MEMS resonant cantilever as material evaluation tool, the adsorbing properties of ZIF-8 to NO_2 gas have been experimentally examined not only for qualitative judgement, but also for thermodynamic-level quantitative evaluation. Such identification can help to real the formation mechanism of NO_2 associated $PM_{2.5}$ particles and acid rain.

INTRODUCTION

Recently, capture and storage of gas molecules in atmospheric environment becomes an important research topic in many fields, especially in environmental protection [1-3]. An important goal of these researches aims to develop high-performance gas adsorbent. Featuring huge specific-surface-area, quite a lot of newly developed nano-materials, e.g., graphene and metal–organic frameworks (MOFs), are considered promising candidates for the application [4]. To comprehensively evaluate or optimize an adsorbing material, it is far from enough to simply observe its apparent parameters like surface area or porosity. Moreover, molecule adsorption in real atmospheric environment is inevitably influenced by ambient interfering factors like humidity. In case of lack of in-depth knowledge, the results of the laboratory can sometimes lead to feint information. For optimally designing an adsorption material, it would be better to look inside into the inherent nature of the material (i.e., the material 'genome').

In order to capture the ambient harmful gases, various nanoporous materials including MOFs have been recently synthesized for fixation of the harmful gas, as the nanoporous structures bear ultra-high specific-surface-area. However, the evaluation experiments were normally performed under anhydrate testing atmosphere by using commercial gas-sorption analyzers [5]. It is worth noting that, as for harmful gas adsorption in real ambient atmosphere, the ubiquitous water molecules in the environment may bring about strong negative effect. Such important factors are difficult to be examined by using the commercial gas-sorption analyzers. Moreover, using the commercial gas-sorption analyzer is really time-consuming and costly. The required amount of the material sample for analysis is also quite large. Nowadays, it is really lack of highly efficient and accurate methodology to evaluate such adsorption properties. The technical bottleneck may retard developing process of such new materials. In addition, using the traditional gas-sorption analyzers can only detect the adsorbed amount at equilibrium state, but cannot be used to continually record the whole adsorbing process. Nowadays, there is really lack of *in situ* detection tool to continually record the adsorbed molecule number during the whole trace-amount adsorption process. The shortage in method for elucidating the competitive adsorption mechanism (e.g., identify the competitive adsorption order) seriously hinders high-efficiency development of adsorbing materials. In order to thoroughly clarify competitive adsorption of the target gas molecules under complex atmospheric environment, it is needed to see the inherent nature through the apparent adsorbing phenomenon. From the perspective of "material genome", the sorption performance of a material is eventually governed by the thermodynamic parameters like enthalpy ΔH° (i.e., isosteric heat) [6]. If such thermodynamic parameters can be quantitatively extracted from the adsorption process, development of sorption material will benefit quite a lot.

We herein propose a micro-gravimetric method to study the adsorption properties of materials to gas molecules in different atmospheres of dry and real ambient air. One typical nanoporous material of ZIF-8, a kind of MOFs, is selected as adsorbing material to be evaluated. With the proposed micro-gravimetric method, the adsorbing properties of ZIF-8 can be systematically evaluated both from qualitative and quantitative aspects. Moreover, in the real atmospheric ambient where water molecules are ubiquitous, a criterion is established to judge the competitive adsorption between the gas molecules and the environmental moisture on the material surface. The micro-gravimetric evaluation method is expected to be helpful for identification of optimal gas-adsorbing materials in real atmospheric environment.

EXPERIMENTAL SECTION

ZIF-8 synthesis. ZIF-8 nanocrystals are synthesized with a modified procedure in literatures [7] and detailed as follows. Firstly, 0.30 g of $Zn(NO_3)_2 \cdot 6H_2O$ (Aldrich) is dissolved in 11 g of anhydrate methanol to form *stock solution I*. Then, 0.66 g of 2-methylimidazole (Aldrich) is added into 11 g of methanol to form *stock solution II*. After 2-methylimidazole is dissolved completely in methanol, *stock solution II* is quickly poured into *stock solution I* under vigorous stirring, and a homogeneous suspension is obtained after 5 min. After that, the abovementioned suspension is transformed into a Teflon lined stainless steel autoclave and kept aging statically at 423 K for 3 hours. After cooling to room temperature, the suspension is transformed in a centrifuge tube with 50mL volume and the solid product is collected by high-speed centrifugation (10,000 rpm) for 2 min. Then, the solid product is washed and purified by repeating the following procedure for three times: dispersed in 20 mL of methanol and centrifugation. Finally, the ZIF-8 nanocrystals are obtained after dry overnight at 343 K.

Ink-jet printing technology for ZIF-8 sample loading on resonant micro-cantilever. Featuring 1.5 pg/Hz mass sensitivity and pg-level resolution, our lab-fabricated resonant micro-cantilevers [8] are employed to investigate the adsorption properties of ZIF-8 to CO_2 molecules. About 10 mg of the ZIF-8 sample is added into 1 mL deionized water (under ultra-sonic) to form a crude suspension which is used as ink in the following material deposition experiment. Then, several drops of the inks are printed onto the microcantilever top-surface by using a commercial GIX II Microplotter (Sonoplot Inc.). After that, the micro-cantilever detector is dried in an oven at 333 K for about 2 hours.

Material characterization. Powder X-ray diffraction pattern is obtained with a Rigaku D-MAX/IIA X-ray diffractometer with Cu $K\alpha$ radiation. The scanning range is 5-30° (2θ) and the scanning rate is set as 1.2° min-1. Transmission electron microscopy (TEM) is taken with a FEI Tecnai G20 microscope, where 200 kV accelerating voltage is used. Scanning electron microscopy (SEM) images are taken using an FEI Magellan 400 XHR ultrahigh resolution cold field emission scanning electron microscope.

Experimental set-up. The target gas with desired concentration is diluted by high purity N_2 and is supplied by Shanghai Shenkai Gases Technology Co., LTD. All the MFC (mass flow controller) are calibrated by using digital soap-film flow-meter. The temperature-controlled oven can supply a precise temperature in the range of 233 K to 423 K, with a negligible temperature fluctuation of less than 0.5 K. In order to control the temperature of the flowing gas, a helical-coil tube with a length of 10 m, which is put inside into the temperature controlled oven, is used prior the testing chamber. To diminish the non-specific adsorption of the gas molecules with ultra-low concentration, all the tubes and joints as well as valves used in the set-up are made by high-grade Teflon with ultra-low surface-energy. A lab-developed digital phase-locked loop circuit is used as the key component to construct the data acquisition system.

RESULTS AND DISCUSSION

Fig. 1 shows the schematic setup for the resonant-gravimetric experiment. The setup consists of three parts: gas generator, temperature-varying resonant-gravimetric detection system and data acquisition system. In order to generate simulant ambient gas with various relative humidity, a piece of wet sponge is placed in the bottle-shaped container that is connected with the gas line. The concentration of moisture is determined by both the water amount in the sponge and the gas flow-rate. The value of relative humidity is real-time measured by a commercial humidometer that is placed at the end of the gas line. When the bottle with wet sponge is disassembled from the gas line, the sample of adsorbing material can also be examined under dry gas. An integrated silicon resonant micro-cantilever is used as the core detecting component of the temperature-varying resonant-gravimetric system. Both an electro-thermally micro-heater for resonance excitation and a piezoresistive Wheatstone bridge for frequency-shift signal readout are integrated in the cantilever [8]. Due to the adsorbed gas-molecule mass (Δm) being much smaller than that of the silicon cantilever (m_0), the real-time recorded frequency-shift signal can be accurately proportional to Δm, i.e., $\Delta f/f_0=0.5\Delta m/m_0$ and the mass sensitivity is defined as $S=\Delta f/\Delta m$. By previously implementing calibration experiment, where the mass known micro-beads were loaded on the cantilever for sensing, S=1.5 Hz/pg has been obtained [9]. According to the experimentally achieved lower than 0.5Hz noise-floor of the frequency signal, the mass detection resolution of the cantilever is finer than 1 picogram in atmospheric ambience. Thanks to the precise MEMS technology for batch fabrication of the cantilevers, the mass sensitivity of the batch-fabricated cantilevers is quite uniform. The required material sample for loading on the cantilever is generally in nano-gram level, thus the molecule adsorbing process can be completed quite fast. Therefore, the adsorption induced mass adding process can be real-time detected by recording the frequency-shift signal. The whole evaluation experiment is performed in a temperature programmable oven. Based on the resonant-gravimetric detection data obtained at two different temperatures, the key thermodynamic parameters like enthalpy $\Delta H°$ can be calculated based on classical physical-chemistry theories [10]. By using the setup schematically drawn in Fig. 1, both dry gas and simulated ambient gas (*i.e.* with humidity) can be generated for adsorbing experiment. The method can be used to examine various kinds of adsorbing materials to various gases, including the herein exampled nanoporous MOF of ZIF-8 crystals to NO_2.

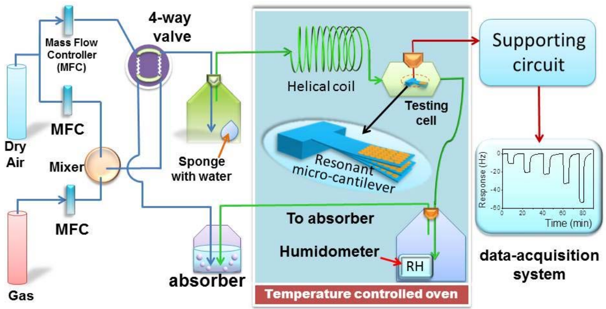

Figure 1: Experimental setup of the micro-gravimetric identification method.

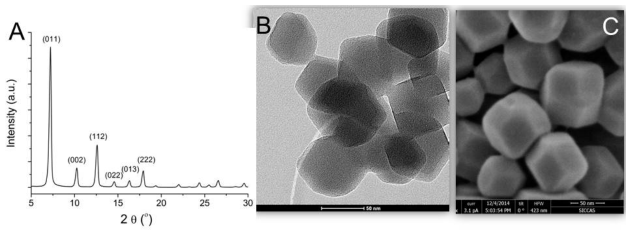

Figure 2: Characterization results of the synthesized ZIF-8 nanocrystals. (A) XRD pattern. (B) TEM image. (C) SEM image.

Fig. 2 shows the characterization results of the herein exampled ZIF-8 material. As shown in Fig. 2A, the sharp diffraction peaks of the corresponding samples are in accordance with the standard XRD pattern of ZIF-8 material that was previously reported [7]. The TEM image in Fig. 2B clearly shows the tiny nanoporous structure of the well-dispersed ZIF-8 nanocrystals. The SEM image in Fig. 2C depicts the candy-like polyhedron profile of the prepared ZIF-8 nanocrystals. Both TEM and SEM characterization results indicate that the diameter of the ZIF-8 nanocrystals is approximately 70nm. By using ink-jet printing technology, the ZIF-8 nanocrystals can be easily deposited on the desired micro-region of the resonant cantilever for the following evaluation.

Fig. 3 shows the qualitative results of ZIF-8 material to NO_2 gas at both dry atmosphere (i.e. 0% RH) and ambient atmosphere (i.e. with moisture). At room-temperature of 298 K, The test chamber for accommodating the ZIF-8 loaded cantilever is firstly under absolutely dry atmosphere for gas adsorbing experiment. Then, the dry atmosphere is switched to the wet atmosphere of 70% RH, and the cantilever is repeatedly tested with the gas introduced under the wet atmosphere. Fig. 3 records a very large frequency drop of the cantilever when moisture is introduced to replace the impractical dry atmosphere. We preliminarily attribute the large frequency-shift represented strong adsorption of the ZIF-8 to the very high concentration water vapor. As is also shown in Fig. 3, the cantilever clearly shows the responses to 0.5 ppm NO_2 gas under both dry and wet atmosphere. The results in Fig. 3 qualitatively indicate that, the ZIF-8 material may be a promising candidate for ambient NO_2 adsorption.

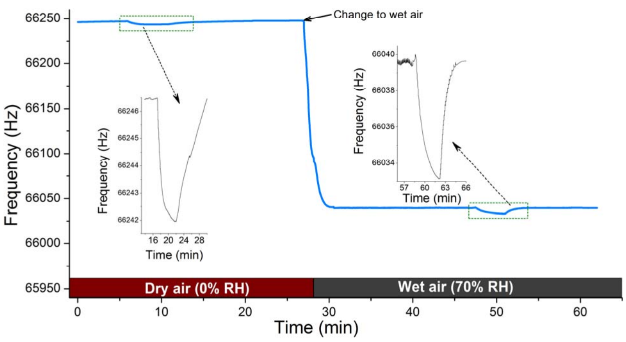

Figure 3: Qualitative judgment of ZIF-8 material to adsorb NO_2, under both dry atmosphere (i.e. 0% RH) and moisture-containing atmosphere (70% RH).

Still with the resonant-gravimetric experiment, the quantitatively extracting the key thermodynamic parameter of $\Delta H°$ is explored to reveal the interfacial interaction mechanism between the adsorbing material and the target gas molecules. The value of $\Delta H°$ can directly reflect the interfacial molecule capture ability of the examined material to the target gas. Knowing this material inherent nature (i.e., the so-called "material genome") is very helpful for clarifying the competitive adsorption mechanism of the gas molecules on the ZIF-8 material. The resonant-gravimetric signals obtained for different gas concentrations can be transformed into molecule-adsorption induced mass-addition. With the known molecular weight, the mass-addition can be quantitatively converted into adsorbed molecule number. According to the experimental data, the relationship between molecule uptake and gas partial pressure can be quantitatively obtained and plotted into a curve of thermodynamic sorption isotherm. With the two isotherms obtained in two experiments at two temperatures of T_1 and T_2, the value of $\Delta H°$ can be obtained by solving Clausius-Clapeyron equation [10] of

$$\Delta H° = \frac{RT_1T_2}{T_2\text{-}T_1}\ln\frac{p1}{p2} \tag{1}$$

With the nano-porous MOF material of ZIF-8 loaded on the resonant-gravimetric cantilever, the experimentally obtained isotherms for adsorbing NO_2 and H_2O are shown in Fig. 4. Shown in Figs. 4A or 4B, the horizontal dotted-line has two intersection points with the two isotherms. The two points correspond to identical mass uptake but different gas pressures of $p1$ and $p2$. By substituting the data of the two points into Eq.1, the -$\Delta H°$ values of the ZIF-8 nanocrystals to NO_2 and H_2O are calculated as 164 kJ/mol and 73 kJ/mol, respectively. The quantitatively extracted -ΔH° values clearly show the order of $(-\Delta H°)_{NO2} > (-\Delta H°)_{H2O}$. According to the definition of enthalpy -$\Delta H°$, which is also called adsorption/reaction heat, its value directly determines the type and degree of strength of the interfacial interaction. As for the competitive adsorption of ZIF-8 to the two gases of NO_2 and H_2O, from strong to weak the adsorption-capability order is $NO_2 > H_2O$.

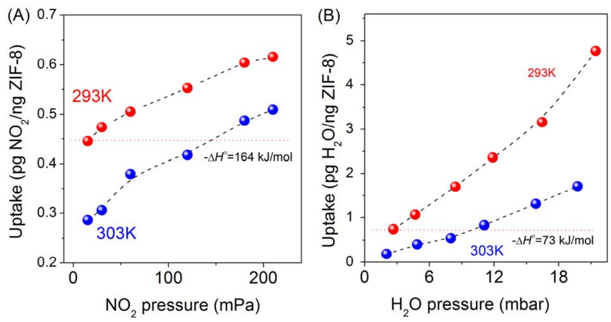

Figure 4: Quantitative extraction of the thermodynamic-parameter data of enthalpy ($\Delta H°$) based on the resonant-gravimetric experiments. According to the resonant-gravimetric experiments, two isotherms for the two temperatures are plotted in (A) and (B), respectively.

Based on thermodynamic theories, the interesting adsorbing phenomena observed in Fig. 3 can be reasonably explained. In moisture-containing real atmosphere, the ZIF-8 nano-material can be used to capture the harmful NO_2 due to the much higher -$\Delta H°$ value of NO_2 than that of H_2O. By using the resonant-gravimetric experiment method, the ZIF-8 nano-crystal material is, for the first time, sufficiently proved being able to efficiently capturing/fixing environmental NO_2 and reasonably proposed for the applications of automotive-exhaust treatment.

CONCLUSIONS

In summary, micro-gravimetric method is successfully proposed to study the adsorption properties of materials to gas molecules in different atmospheres of dry and real ambient air. With the micro-gravimetric sensing data, the adsorbing performance of ZIF-8 material to NO_2

at both dry atmosphere (i.e. 0% RH) and ambient atmosphere (i.e. with moisture) can be qualitatively investigated. Still using the micro-gravimetric method, the inherent nature (i.e. material'genome') of the adsorbing material is quantitatively evaluated based on the extracted thermodynamic parameter of $-\Delta H°$. According to the obtained thermodynamic parameters, the solid-gas interfacial interactions between ZIF-8 material and the selected gas molecules (i.e. NO_2 and H_2O) are compared quantitatively. The obtained interaction-order reveals that, there is no significant influence of water for NO_2 adsorbing on ZIF-8 nanocrystals. The results of this study can be used to select the potential application scope of the nanoporous materials like ZIF-8 material.

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