

MOF (METAL-ORGANIC FRAMEWORK) NANOMATERIAL FOR 400ppb-CONCENTRATION DETECTABLE XYLENE GAS SENSORS

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ABSTRACT

In this paper, metal-organic framework (MOF) is explored as xylene sensing-material for resonant-cantilever gas sensor. Sensing experiment with the MOF nano-material of HKUST-1 demonstrates that 400 ppb xylene can be detected. This limit of detection (LOD) has been lower than the human olfactory threshold. The sensing mechanism is identified as the interaction between MOF and xylene. The specificity of HKUST-1 MOF to xylene is originated from the Cu²⁺ induced moderate Lewis acidity and like-dissolves-like interaction of benzene-ring.

INTRODUCTION

Nowadays, xylene is frequently used in many daily products in people's lives everywhere like various coatings, paints and adhesives, since xylene is an important organic chemical and widely used as solvent. However, as one of typical VOCs (volatile organic compounds), xylene is harmful for human's health because it significantly inhibited the activities of cellular antioxidant enzymes such as superoxide dismutase (SOD), guaiacol peroxidase (POD) and catalase (CAT) in human body [1]. Thus, it is really important for us to pay more attention on the toxic of xylene, especially in the indoor air. Although xylene has a pungent odour at high concentration, it is still difficult for us to directly smell xylene in the indoor atmosphere because the concentration of ambient xylene is usually below the olfactory threshold of human beings of 0.47 ppm (parts per million by volume) [2].

In order to detect trace level xylene, many kinds of techniques have been developed nowadays. Standard analysis methods for xylene detection are based on bulky instruments like gas chromatography (GC). Besides the disadvantages of high cost, labor-intensive and time-consuming, however, a complicated sampling process of pre-concentration is needed prior to GC analysis. In addition, the bulky GC instrument cannot be used for on-site measurement, which hinders the wide application for trace xylene detection. Hence, to meet the fast and on-site detection requirements, it is meaningful to develop portable devices like high performance gas sensor for trace xylene monitoring.

Being widely used as a good gravimetric sensing platform, resonant microcantilever has drawn much attention in the application fields of trace-level molecules detection. Besides the high mass-resolution and small volume (micron scale), resonant microcantilever also features merits of low cost and high constancy because the resonant microcantilevers are batch fabricated by using microelectromechanical systems (MEMS) technique. For

trace molecule detection, sensing materials can be directly loaded onto the sensing region of resonant microcantilever to construct gravimetric sensors. To date, numerous functional materials such as mesoporous silica, graphene oxide, hyper-branched polymer and metal-organic frameworks (MOFs) have been successfully utilized as gravimetric sensing materials and the target molecules been detected including explosives, amines and carbon dioxide [3]. However, due to the chemical inert nature of xylene, it is still a big challenge to detect trace xylene by using conventionally functionalized sensing materials.

EXPERIMENTAL SECTION

Chemicals. Trimesic acid, terephthalic acid, 4,4',4''-benzene-1,3,5-triyltribenzoate(BTB), 2-methylimidazole, Cu(NO₃)₂·3H₂O, N,N-Dimethylformamide (DMF) and N,N-Diethylformamide (DEF) are purchased from Sigma-Aldrich.

Synthesis of MOF crystals. Under vigorous stirring, 1.76 g of Cu(NO₃)₂·3H₂O is added into 24 mL of de-ionized (DI) water. After Cu(NO₃)₂·3H₂O is completely dissolved in DI water, Stock solution (I) is formed. Meanwhile, 0.84 g of trimesic acid is dissolved completely into 24 mL of absolute ethanol under stirring to form Stock solution (II). Then, Stock solution (II) is quickly poured into Stock solution (I). After further stirring for 5 min, the solution is transferred into a Teflon-lined autoclave. The reaction mixture contained Teflon-lined autoclave is heated in an oven at 110 °C for 18 hours. After cooling down to room temperature, the solids are collected by centrifugation and washed sequentially with DI water as well as ethanol for three times. Then, the precipitates are dried at 60 °C overnight and the HKUST-1 products are finally obtained. The other three types of MOFs can be obtained by using the methods in literature [4].

Characterization. The XRD (X-ray diffraction) patterns are obtained by using a Bruker model D8 focus diffractometer equipped with a copper anode to produce X-ray (40kV, 40mA), where the wavelength is 0.154nm. The data are collected in continuous scan mode from 5° to 80°, with a 0.02° sampling interval. The morphologies of the as-synthesized samples are characterized by using FE-SEM (Hitachi S4800). The accelerating voltage is 1 kV. The nitrogen sorption isotherm is measured at 77 K by using a Micromeritics ASAP 2020M system. Specific surface area and pore size distribution are calculated using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The FT-IR experiment is performed with a Bruker Vertex 70v infrared spectrometer (under the vacuum <100Pa) in KBr pellet.

Sensor fabrication and sensing experiment. The MOF material (10 mg) 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.). Thereafter, the microcantilever is dried in an oven at 60 °C for about 2 h. The chemical sensing properties are measured using similar method as described in our previous report.

RESULTS AND DISCUSSION

In this research, four kinds of typical MOFs including MOF-5, HKUST-1, ZIF-8 as well as MOF-177 are synthesized and employed as micro-gravimetric sensing material for trace-level para-xylene (p-xylene or PX) detection. The phases of the as-synthesized four MOFs are firstly characterized by powder X-ray diffraction (XRD) and the results are shown in Fig. 1, respectively. The sharp diffraction peaks of the corresponding sample are in accordance with the standard XRD patterns as previously reported in literatures [4, 5], which indicate that all the four samples with pure phase have been synthesized successfully. Based on the N₂ sorption experiments, specific surface area, porosity and pore size can be obtained. In this study, all of the four MOF samples have a Langmuir surface area around 2000m²/g and the pore size is in the range of 2–4 nm.

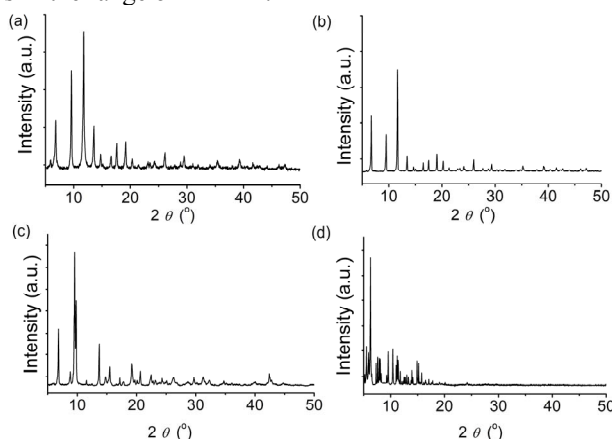


Figure 1: XRD characterization results of the four MOF samples: (a) HKUST-1, (b) ZIF-8, (c) MOF-5 and (d) MOF-177.

Herein, the lab-made resonant microcantilevers with 1.5 Hz/pg mass-sensitivity are used as gravimetric transducers. Due to the MEMS batch fabrication, the consistency of the microcantilevers in mass-sensitivity and fundamental frequency can be well controlled. To form resonant gravimetric sensors, the MOF material should be precisely loaded onto the sensing area of the free end of the microcantilevers. In this study, a commercial available ink-jet printer equipped with an optical microscope is used to deposit MOF material onto the designated micro-region. Before depositing, MOF material is ultra-sonically dispersed onto de-ionized (DI) water to form a special ink. In-situ manipulated under the microscope, several drops of MOF dispersion with known volume are precisely

deposited onto the free-end of the cantilever. After the solvent of DI water evaporated completely, the MOF-based gravimetric sensor is constructed and can be used for the following xylene detection. Fig. 2 shows the scanning electron microscopy (SEM) image of the fabricated gravimetric sensor where MOF material of HKUST-1 crystals are precisely deposited onto the free-end of the cantilever.

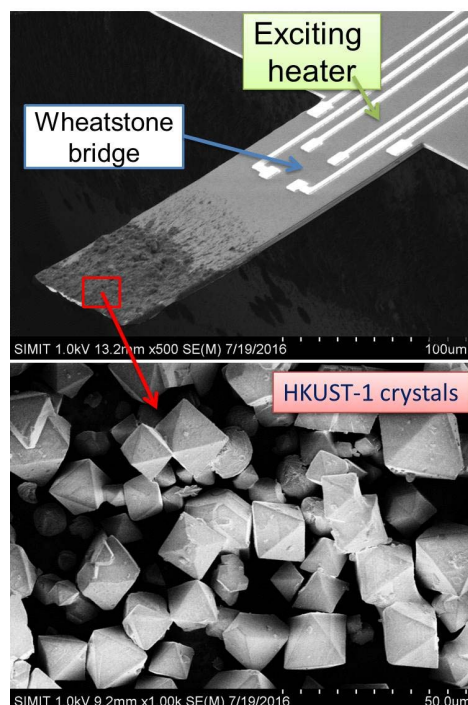


Figure 2: SEM image of the MOF-loaded resonant micro-cantilever sensor, where the MOF sensing material of HKUST-1 is regio-selectively deposited onto the free end of the cantilever.

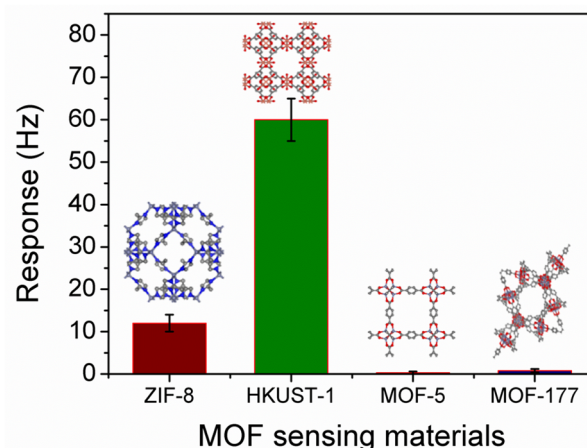


Figure 3: Resonant-cantilever sensing results of the four MOFs to the xylene vapor with identical concentration of 50ppm. The insets individually show the nano-crystal structures of the four MOFs.

In order to obtain a MOF material with better xylene sensing performance, the four kinds of MOF materials are used to detect p-xylene vapour under the same detection condition. Fig. 3 summarizes the detection results of the four MOF-based sensors to p-xylene vapour with identical concentration of 50 ppm. From Fig. 3, it can be found that

HKUST-1 shows the highest response among the four kinds of MOF materials. Sensing results in Fig. 3 imply that, all with similar carboxyl-based linker, HKUST-1 constructed with Cu^{2+} units has the more moderate Lewis acidity than MOF-5 and MOF-177 (both with Zn^{2+} as building blocks) for p-xylene detection. Compared with ZIF-8 (a kind of zinc imidazolate), HKUST-1 has the benzene-ring which can detect xylene based on “like dissolves like” interaction. Therefore, HKUST-1 is chosen as p-xylene sensing material for the following systematically investigations in terms of sensitivity, selectivity and stability.

Fig. 4a shows the real time sensing curve of the HKUST-1 to p-xylene vapours with concentrations in the range of 0.5~250 ppm. As shown in Fig. 4a, the HKUST-1 based sensor outputs a remarkable frequency shift (i.e. response) of 50 Hz to 50 ppm p-xylene vapour at room temperature. As shown in the inset of Fig. 4a, when the sensor is allowed to expose p-xylene vapour with the concentration down to 400 ppb (parts per billion by volume), it still outputs a response signal of 0.1 Hz which is five times higher than the noise-floor of $\pm 0.01\text{Hz}$. Thus, we can make a safely conclusion that the limit of detection (LOD) to p-xylene of the HKUST-1 based sensor is better than 400 ppb.

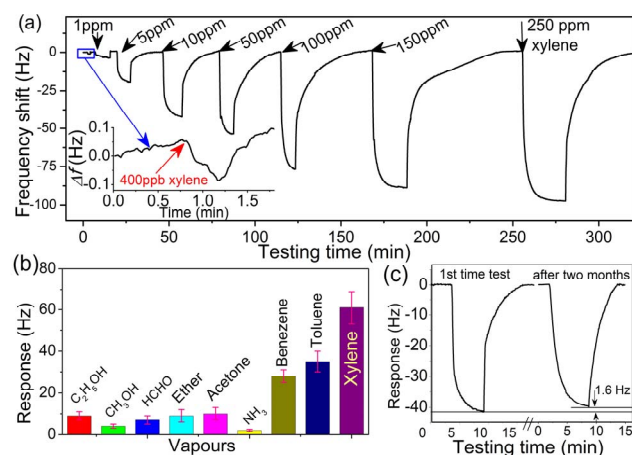


Figure 4: (a) Resonant-gravimetric sensing curve of HKUST-1 nano-crystals to the p-xylene vapor with the concentration ranged from 400ppb to 250ppm. The inset shows the resolvable sensing signal to 400ppb p-xylene. (b) Responses of the HKUST-1 sensor to nine kinds of interfering vapours for evaluating selectivity. (c) Two sensing results are sequentially obtained, with a time interval of two months, for evaluating long-term stability.

To investigate the selectivity of the HKUST-1 based sensor, herein, eight kinds of common vapours including ethanol, methanol, acetone, formaldehyde, ether, acetone, ammonia, benzene and toluene are chosen as interfering gases. Fig. 4b shows the selectivity results of the sensor to various gases. When 50 ppm of interfering gas such as ethanol, acetone, ammonia, ether, or formaldehyde exposed to the sensor, the sensor only outputs a negligible response, which indicates that the sensor exhibits a satisfied selectivity to such interfering gases. However, to the other two interfering gases of benzene and toluene, the sensor outputs relative high responses as shown in Fig. 5b.

The reason lies on that, just like xylene, there also exists a similar host-guest interaction between the HKUST-1 sensing material and guest molecules of benzene or toluene. Due to the smaller molecular weight of benzene and toluene, the sensor outputs a lower response to benzene or toluene than p-xylene vapour with identical concentration. Based on this reason, HKUST-1 based sensors can be also utilized for detecting of benzene-homologues, what is also called BTX (i.e. benzene, toluene and xylene).

Fig. 4c shows two sensing curves of the same sensor to p-xylene vapour obtained before and after two months. As shown in Fig. 4c, compared with the first time detection, the sensor outputs a slightly lower response (<5% in value) to p-xylene vapour with same concentration after two months. The degradation of the sensing performance may be caused by the non-specific adsorption of the HKUST-1 crystals to interfering gases like H_2O exist ubiquitous in ambient atmosphere. During our researches, we found that the sensing performance of the HKUST-1 based sensor can be recovered successfully by using some sample treatment methods like high temperature activation or UV-light radiation.

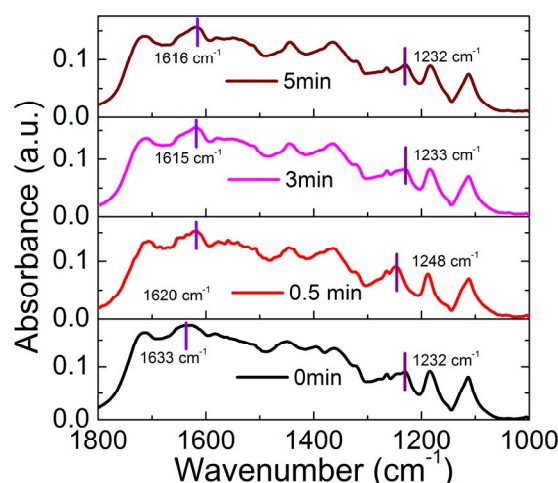


Figure 5: In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results, indicating that the infrared adsorption bands of HKUST-1 are influenced by the adsorbed p-xylene molecule.

In order to elucidate the p-xylene adsorbing induced mass-type sensing mechanism, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is utilized to investigate the interaction between HKUST-1 crystals and the p-xylene guest molecules. Fig. 5 plots the DRIFTS results of the HKUST-1 crystals before and after p-xylene exposing. Due to the electron-rich characteristic of p-xylene molecules, the adsorbed p-xylene molecules will enhance the electron-donor property of benzene-ring in BTC linker of HKUST-1 and thus, will strongly influence the infrared adsorption bands of HKUST-1 crystals. The in-situ DRIFTS results in Fig. 5 indicate that the characteristic peaks of HKUST-1 are indeed affected by the adsorbed xylene molecules. For example, one peak

located at 1633 cm^{-1} which can be assigned to asymmetric stretching vibration of -COO^- group of BTC linker shifts to lower wavenumber. Such blue-shift phenomenon can be also observed in another peak located at 1449 cm^{-1} which is attributes to the symmetric stretching vibration of -COO^- group. In DRIFTS characterization, the blue-shift phenomenon is brought by the weakened bond-force constant. In this research, due to the adsorbed p-xylene molecules, the electron-donor property of benzene-ring is enhanced and therefore, the p-xylene-adsorbed benzene-ring can weaken the bond-force constant of the neighbouring -COO^- group in the BTC linker. The in-situ DRIFTS characterization confirms that p-xylene molecules can be indeed adsorbed on HKUST-1 crystals, which brings satisfied mass-type sensing performance as shown in Fig. 4.

CONCLUSIONS

In summary, the p-xylene sensing performances of MOF materials have been investigated systematically within the gravimetric sensing platform of resonant microcantilevers. According to our researches, typical MOF material of HKUST-1 crystals with Langmuir surface area nearly $2000\text{ m}^2/\text{g}$ shows satisfied sensing performance to trace p-xylene vapour. The LOD of the HKUST-1 based sensor reaches about 400ppb. The sensor also shows a good selectivity to eight kinds of common interfering vapours. After two months later, the sensor response to same concentration xylene only generates a 5% response degradation which indicates that the long-term stability of the sensor is also good. This research approves that MOF materials exhibit potential usages for high performance chemical sensors applications and more attention should be focused on this interesting research area.

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