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Revealing humidity-enhanced NH_3 sensing effect by using resonant microcantilever

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ABSTRACT

High performance NH_3 sensor is of great importance in various application fields such as environmental protection and early diagnosis of stomach cancer. Herein, carboxyl group functionalized mesoporous silica nanoparticles (C-MSNs) with ultrahigh specific surface area are developed as high performance mass-type sensing material for trace-level NH_3 detection. By using inkjet printing technology, C-MSNs material is precisely loaded on our lab-made integrated resonant microcantilever to construct a mass-type gas sensor. Based on the specific acid-base interaction between Brønsted acidic C-MSNs material and basic NH_3 molecules, our sensor exhibits satisfactory NH_3 sensing performance. The experimentally observed detection limit of our sensor reaches parts per billion (ppb) level. Exposed to NH_3 with identical concentration, our sensor outputs a higher response in wet air than that of in dry atmosphere. In real air, hydrate NH_3 molecule (*i.e.* $NH_3 \cdot xH_2O$) has a larger molecular weight than anhydrous NH_3 in absolute dry experimental atmosphere. Therefore, our gravimetric sensor exhibits a higher response in real air. In order to in-depth elucidate the humidity-enhanced sensing effect, the micro-gravimetric sensing data obtained in wet air and in dry experimental environment are compared together. Based on our quantitatively measurement data, the molecular formula of hydrate $NH_3 \cdot xH_2O$ existing in wet air (with 50–80% relative humidity) can be obtained as $NH_3 \cdot 2{\sim}2.4H_2O$.

1. Introduction

Ammonia (NH_3) is one of the small molecules that widely exist in environment such as livestock farms and chemical plant [1]. As a common industrial chemical, NH_3 is extensively used as raw material to produce nitrogenous pharmaceuticals, polyurethane coatings or adhesives, fertilizers, polyamide fibers and so on [2]. As one of endogenous gaseous molecules, NH_3 is recently used as bio-indicator for early diagnose of cancer. For example, catalyzed by *Helicobacter pylori* bacteria, urea can be decomposed to two main kinds of molecules, i.e. NH_3 and CO_2 [3]. Thus, the detection of trace-level NH_3 in exhalation can be used as low cost method for early diagnose of stomach cancer. Besides, liquid ammonia also plays as a refrigerant in large scale industrial applications for more than 120 years. However, it is necessary to pay more attention on the toxicity of ammonia. A painful case of people poisoned by NH_3 is liquid ammonia leakage accident took place at Shanghai, August 31, 2013, leading to 15 people death [4]. Apart from high toxicity, ammonia is considered as environmental harmful gas since it can react with acidic molecules like NO_2 or SO_2 to form $PM_{2.5}$ particles [5]. Therefore, detection of trace-level NH_3 in air is crucial associated with many application fields including agriculture, industry, biomedical technique and environmental protection.

One of the ideal NH_3 detectors is gas sensor with satisfactory performance. Compared with conventional bulky instruments, NH_3 sensor bears merits of small volume, inexpensive, portable and on-site detection [6,7]. However, unsatisfied sensitivity of the available NH_3 sensors still cannot meet the requirements of many kinds of practical usages, especially high demands aimed to biomedical applications. To date, detection capability of reported sensors is mainly focused on the scope of ppm or sub-ppm level in terms of limit of detection (LOD). To the best knowledge of the authors, there are only a few studies reported that their LOD can reach tens of *ppb* level. Besides unsatisfied limit detection, the conventional NH_3 sensor also suffers influence from environmental molecules such as ubiquitous water in real air. During the process of new

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NH_3 sensor design, the environmental interfering factors such as unavoidable humidity change should be taken in account. In order to sense trace NH_3 molecules in ambient atmosphere, it is still a big challenge to develop new NH_3 sensing material with novel sensing effect for further NH_3 sensor design.

Herein, by using resonant microcantilever as gravimetric sensing platform, carboxyl group functionalized mesoporous silica nanoparticles (dubbed as C-MSNs) are successfully developed as a new NH_3 sensing material. Due to the advantages of a huge amount of NH_3 sensing groups loading and huge specific surface area, C-MSNs loaded cantilever sensor can detect *ppb* level NH_3 in ambient atmosphere. According to our researches, our sensor exhibits an enhanced sensing performance in wet air than in dry atmosphere. From the aspect of hydrated and anhydrous molecular structures, the different sensing behaviors of the C-MSNs under wet condition and dry atmosphere are also demonstrated systematically.

2. Experimental

2.1. Co-condensation synthesis of C-MSNs

Cetyltrimethylammonium bromide (CTAB) is purchased from Alfa Aesar. Carboxyethylsilane triolsodium (CES, 25 wt% salt solution) is purchased from Gelest, Inc. Tetraethylorthosilicate (TEOS), methanol, concentrated hydrochloric acid (36 wt%) and NaOH are of analytical grade and purchased from Shanghai Chemical Reagent Corp.

The synthesis of C-MSNs is detailed as follows: 0.5 g of CTAB is firstly dissolved into 240 mL of deionized water under stirring at 80 °C. Then, 1.75 mL of NaOH aqueous solution (2 mol/L) is added and allowed to react for 5 min. Thereafter, 2.5 mL of TEOS is slowly added into the solution for 10 min. 0.3 mL of CES is then added into the abovementioned solution. Subsequently, at 80 °C, the resultant mixture is further allowed to react for 2 h. The product is filtered and washed with deionized water, then overnight dried at room temperature to obtain —COOH functionalized MSNs precursor. The molar composition of the reaction mixture is tuned in the range of 1 TOES: (0–0.02) CES: 0.27 NaOH: 0.1 CTAB: 1000 H_2O. Acid extraction of the CTAB surfactant is conducted at 90 °C by placing the as-obtained C-MSNs precursor in the mixture of methanol (150 mL) and concentrated hydrochloric acid (9.0 mL) for 24 h. The C-MSNs is then filtered, washed with water/methanol and dried under vacuum at 80 °C. After drying for 12 h, the C-MSNs product is obtained.

2.2. Material characterization

N_2 sorption isotherms are measured with a surface area and porosity analyzer (ASAP 2020, Micromeritics, USA) at the temperature of 77 K. The specific surface area of the C-MSNs material is calculated according to Brunnauer-Emmett-Teller (BET) equation. Small angle X-ray diffraction patterns are obtained with a Rigaku D-MAX/IIA X-ray diffractometer with Cu Kα radiation and the scanning range is 0–5° (2θ). Scanning electron microscopy (SEM) images are taken using an FEI Magellan 400 XHR ultra-high resolution cold field emission scanning electron microscope. Transmission electron microscopy (TEM) is taken with a FEI Tecnai G20 microscope, where 200 kV accelerating voltage is used. Fourier transform infrared (FT-IR) spectra are obtained under vacuum in a Bruker Vertex 70v spectrometer. Thermo-gravimetry and differential scanning calorimetry (TG-DSC) is carried out using a NETZSCH STA 449 F3 simultaneous thermal analyzer. To characterize the content of organic groups in the sample, TG-DSC is measured in an oxygen-enriched atmosphere (containing 40% O_2 and 60% N_2 in volume). The temperature program of the TG-DSC experiments is set in the range of 30–800 °C, with a 5 °C/min heating rate.

2.3. Experimental set-up

The lab-established set-up consists of three main parts: gas generator, temperature-controlled oven and data acquisition system. NH_3 with desired concentration is prepared from a commercial available standard vapor generator (Molecular Analysis series 8000S, Taiwan), which is equipped with a temperature programmable oven. One commercial available NH_3 permeation tube (KinTec, USA), with the permeation rate precisely calibrated by gravimetric determination of weight loss as 454 ng/min, is prior put inside into the oven of the vapor generator. High pure N_2 is used as carrier gas, where the flow rate is set as 1000 ± 1 sccm (standard cubic centimeter per minute). After stabilization at 35 °C for 3 days, the N_2-diluted NH_3 stream with constant concentration is generated. Using another mass flow controller, the NH_3 stream can be further diluted by pure N_2 down to the desired concentration and, then, is introduced to a testing chamber where the cantilever is prior put inside. The temperature-controlled oven can supply a precise temperature in the range of −50 to 150 °C, with a negligible temperature fluctuation of less than 0.5 °C. 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.

2.4. Inkjet printing technology for C-MSN sensing material loading on resonant microcantilever

Our lab-made resonant microcantilever with 1.5 pg/Hz mass sensitivity and *pg*-level resolution is employed as mass-type transducer to evaluate the NH_3 sensing performance of the prepared C-MSN material. The fabrication process of resonant microcantilever can be found in our previous report [8]. About 10 mg of the C-MSNs is dispersed into 1 mL deionized water (under ultra-sonic) to form a crude suspension. Then, 0.1 μL of the suspension is precisely loaded onto the cantilever top-surface by using a commercial inkjet printer (SonoPlot Microplotter GIX II, USA). After that, the microcantilever sensor is dried in an oven at 333 K for about 2 h.

3. Results and discussion

Co-condensation method with CTAB as template is widely applied for mesoporous silica nanoparticles (MSNs) synthesis [9–13]. By using co-condensation method, MSNs with numerous organic group functionalized have been successfully prepared [14–16]. In order to prepare −COOH functionalized MSNs (denoted as C-MSNs) for NH_3 sensing applications, CES is utilized as the key reagent to introduce −COOH groups in the matrix of MSNs in this research. Compared with the method as reported in literatures, our one-step method is more effective since it does not need to take the step of acidic or oxidization treatment [17]. Considering the organic reagent of CES may bring negative effect to the order degree of mesoporous structure, small angle X-ray diffraction is herein used to characterize the order degree of the prepared C-MSN samples. Fig. 1a shows the small angle XRD patterns of the four C-MSN samples synthesized with different CES amount. The small angle XRD results indicate that ordered mesoporous structure can be well maintained with the molar ratio of CES: TEOS in the range of 0–0.03 and the corresponding XRD patterns can be indexed as