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Enhanced NH₃ sensing properties of carboxyl functionalized carbon nanocoil

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Abstract

Based on Quartz Crystal Microbalance (QCM) sensing platform, modifying functional groups was usually used to improve the performance of sensing materials. In this work, we reported a novel sensing material, carboxyl functionalized carbon nanocoil by acidification treatment. It was found that carboxyl functionalized carbon nanocoil had excellent reversible response to ammonia (NH₃), and the response to 50 ppm NH₃ was as high as 8.1 Hz. As a contrast, pristine carbon nanocoil had only 2 Hz response to 50 ppm NH₃. The enhanced response should be ascribed to the hydrogen bond adsorption between carboxyl group and NH₃ molecules. These results demonstrated that carboxyl functionalization could improve the NH₃ sensing performance of carbon nanocoil, which has potential in monitoring NH₃ in the future.

1. Introduction

Ammonia (NH₃) is a source of nitrogen for microorganisms. NH₃ originates from dead plan and animals, fertilizers, food, as well as medicine [1, 2]. Occupational Safety and Health Administration has reported that the highest concentration of NH₃ that humans can contact is 50 ppm. NH₃ above 50 ppm is harmful to human organs, such as throat, nose, eyes, skin, and respiratory [3]. As a result, from the perspective of human health, it is necessary to fabricate a high standard gas sensor which can detect 50 ppm NH₃.

In the past, semiconductor sensors based on metal oxides such as In₂O₃, SnO₂, ZnO, and TiO₂ have been used for ammonia detection [4–7]. However, semiconductor gas sensors usually need high temperature to work, which is not conducive to energy saving [8]. Recently, a new type of energy-saving sensor platform, Quartz Crystal Microbalance (QCM), has been developed. QCM can work at room temperature and meet the needs of high sensitivity detection [9]. QCM is a quality sensing platform, and its surface can be modified with a variety of sensing materials [10]. After the gases are adsorbed on the surface of QCM, a frequency shift takes place and that transformation can be quantized using Sauerbrey equation by proper measurement system [11]. Therefore, the rational design and functionalization of sensing materials are conducive to the absorptive sensing of specific target gases with high performance [12].

The research of carbon nanotechnology is popular, and a variety of nano carbon materials, such as graphene, carbon nanotube, fullerene and so on, are emerging in endlessly [13–15]. Carbon nanocoil (CN) is a special carbon nanotube with spiral structure formed by bending around [16]. Because of unique helical shape and nonlinear mechanical response, CN has been widely used in micro nano devices, composite materials and other fields [16–18]. In addition, the large-scale commercial production of CN has provided the possibility for its application exploration and further commercialization [19]. As an emerging sensing material, CN enhanced the performance of many kinds of sensors, such as thermal sensor, humidity sensor, pressure sensor, etc [18, 20, 21].

In this work, a facile acidification route was utilized to prepare carboxyl functionalized carbon nanocoil (CN–COOH) [22]. The CN–COOH based sensor exhibited higher response than pristine CN at lower...
temperature (298 K). The enhanced response should be attributed to the hydrogen bond adsorption between NH\textsubscript{3} molecules and carboxyl groups. Furthermore, the reversibility and selectivity of CN–COOH in the detection of NH\textsubscript{3} are also satisfactory.

2. Fabrication and characterization

2.1. Materials

CN was purchased from XFNANO Inc. (Nanjing, China). All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). QCM resonators were purchased from Chengdu Westsensor Co., China. Its overtone frequency is $1 \times 10^7$ Hz.

2.2. Synthesis of CN–COOH

The commercialized pristine CN (1 g) was first chemically functionalized with a mixture of concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and nitric acid (HNO\textsubscript{3}) (3:1, 60 ml and 20 ml, respectively) under reflux at 80 °C for 1 h (h). Then, the obtained mixture was diluted with distilled water and filtered repeatedly until the pH of the solution was no longer acidic. Finally, the sample was dried at 55 °C for 24 h under vacuum. The finally material was named as CN–COOH, as shown in figure 1.

2.3. Characterizations

The morphology of CN and CN–COOH were observed via using scanning electron microscope (SEM, Quanta 200 FEG). Fourier transform infrared (FT-IR) spectra of CN and CN–COOH were recorded with a KBr pellet on a Nicolet 5700 spectrometer ranging from 400 cm$^{-1}$ to 4000 cm$^{-1}$. Raman spectra was obtained in a Raman spectroscopy meter (Thermo Nicolet Corporation, USA).

2.4. Sensor fabrication

The gas sensing experiment was tested at room temperature (298 K). First of all, we put 1 mg of the material into 1 ml of ethanol, and after ultrasonic treatment, a homogeneous dispersion can be obtained. 1 μl of the above as-synthesized homogeneous dispersion samples were drop-cast onto the surface of QCM electrode, and the as-made sensor was put into a vacuum oven for 1 h. The vacuum of the oven is set to 0 MPa and the temperature is set to 45 °C. In order to explore the capability of NH\textsubscript{3} detection, a reported man-made classic measure setup is sketched in figure 2\textsuperscript{[23]}. The sensor was tested in a designed chamber which was placed in a constant temperature room (25 °C). First, the sensor was exposed to 15 sccm nitrogen (N\textsubscript{2}) stream until obtained a stable baseline. The tested gas was introduced by using a microliter syringe. Then, the sensor was exposed to the tested gas stream until a stable response was occurred. Finally, N\textsubscript{2} stream was introduced again to drive away the tested gas measured in the chamber, so that the baseline can be reproduced.

2.5. Gaussian calculations

Gaussian 09 software was used with a DFT method, the hybrid B3LYP functional, and 6-311++G(d,p) basis set to optimize the geometries of the molecules\textsuperscript{[24]}. The optimized molecular structures were confirmed to be minima on the potential energy surface by vibration frequency analysis. In order to simulate the adsorption method between the material and the gas, the adsorption enthalpy ($\Delta$H) between NH\textsubscript{3} molecule and CN–COOH was calculated according to the following equation (1).

$$\Delta H_{CN-COOH-NH_3} (kJ/mol) = H_{CN-COOH-NH_3} (kJ/mol) - H_{CN-COOH} (kJ/mol) - H_{NH_3} (kJ/mol)$$ (1)
3. Experimental results

3.1. Materials characterization

As shown in figures 3 (a), (b), SEM studies the surface morphology of the CN before and after carboxyl functionalization. The pristine CN are entangled, and the width was more than 50 nm. Obviously, the length and helical structure of CN have no obvious change after carboxyl functionalization. Compared with pristine CN, CN–COOH possesses a lower degree of entanglement, which should be attributed to the fact that in the

Figure 2. The sketch diagram of gas sensing system. Reprinted from [23], Copyright (2017), with permission from Elsevier.

Figure 3. SEM images of (a) pristine CN and (b) CN–COOH. (c) FT-IR spectra of pristine CN and CN–COOH. (d) Raman spectra of pristine CN and CN–COOH.
process of functionalization, stirring and other operations break up the entangled CNs. In general, the surface morphology of CN before and after functionalization was not significantly different. Therefore, we used infrared spectroscopy to characterize the surface functional groups. As shown is figure 3(c), the peak at 1645 cm\(^{-1}\) is assigned to the C=C stretching, indicating the graphite structure of CN. Compared with CN, an emerging peak around 1729 cm\(^{-1}\) appears in the spectra of CN–COOH, which should be assigned to CO stretching of the carboxyl groups [25]. The peaks at 1032 cm\(^{-1}\) and 3442 cm\(^{-1}\) should be assigned to CO and OH stretching vibrations of carboxyl groups, respectively [26]. Besides, the peaks at 2925 cm\(^{-1}\) and 2853 cm\(^{-1}\) should be attributed to symmetric and asymmetric CH\(_2\) stretching. The analysis of the above infrared peaks indicates the carboxyl has been introduced onto the surface of CN. Besides, the peak at 528 cm\(^{-1}\) should be assigned to small amount of sulfonic groups. Figure 3(d) shows the Raman analysis of CN and CN–COOH. The two materials show D band (1341 cm\(^{-1}\)) and G band (1570 cm\(^{-1}\)). The relative intensity ratio of D band and G band (I\(_D\)/I\(_G\)) was estimated as 0.65, which was known as a ratio of amorphous/disordered carbon relative to graphitic carbon [27, 28]. A higher I\(_D\)/I\(_G\) value (0.84) indicates a greater disruption of the graphitic carbon atoms to amorphous/disordered carbon atoms, indicating that there are more carbon atoms in CN–COOH that are not graphene carbon, which may belong to carboxyl groups [29].

3.2. NH\(_3\) sensing result

We first explored the response of CN and CN–COOH to NH\(_3\). As shown in figure 4, CN–COOH possesses higher response to NH\(_3\) with different concentrations (50 ppm, 100 ppm, 150 ppm, 200 ppm, and 250 ppm) than CN. Besides, CN–COOH is more than twice as responsive to NH\(_3\) as CN. This advantage should be attributed to the carboxyl groups of CN–COOH, which can adsorb NH\(_3\) molecules by hydrogen bond adsorption. It is indicating that CN–COOH is a better sensing material than CN for the purpose of detecting NH\(_3\), so we choose CN–COOH to evaluate the NH\(_3\) sensing performance in a deeper level.

Figure 5(a) plots the relationship between the response (y) of CN–COOH based sensor and NH\(_3\) concentration (x). The corresponding equations is \( y = -0.1332 \times + 1.94 \), and the regression coefficients (R\(^2\)) is 0.99768. It is indicating that CN–COOH based sensor exhibited linear relationship between the response and NH\(_3\) concentration. The three consecutive responses of CN–COOH to 50 ppm NH\(_3\) are shown in figure 5(b), indicating its excellent short-term reversibility. Besides, as shown in figure 5(c), the response of CN–COOH to 50 ppm NH\(_3\) is more than 8 Hz, its response time and recovery time are 24 s and 119 s, respectively. Furthermore, we also explored the long-term stability of the sensor. The test target was fixed (250 ppm NH\(_3\)). After each test, we put the sensor in a dry box. Before the next test, the sensor was removed and then placed in the vacuum oven (45°C, 0 Mpa) for 1 h. As shown in figure 5(d), the response of the CN–COOH to 250 ppm NH\(_3\) is less fluctuating within 8 weeks, indicating that the CN–COOH based NH\(_3\) sensor has favorable long-term reversibility.

The selectivity is also important for gas sensors. In figure 6, the contrastive responses of CN–COOH are listed upon exposure to NH\(_3\) (250 ppm) and other six kinds of gases (250 ppm), including carbon dioxide (CO\(_2\)), hydrogen sulfide (H\(_2\)S), carbon monoxide (CO), nitrogen dioxide (NO\(_2\)), oxygen (O\(_2\)), and hydrogen (H\(_2\)). The carrier gas is 15 sccm nitrogen (N\(_2\)) stream. Obviously, the sensor has a great advantage in response to NH\(_3\), indicating this NH\(_3\) sensor exhibits a good selective detection capacity. It is worth noting that there are several papers which show the resistance detection of NO\(_x\) gases with sulfonated nanotubes at room temperature [30, 31]. However, the response of CN–COOH to NO\(_2\) is far less than that to NH\(_3\). This result may be due to the...
fact that the sulfonic group and the amino group of CN–COOH can absorb NH₃ at the same time, while only the sulfonic group can absorb NO₂.

The detection mechanism of QCM platform is the adsorptive interaction between sensing material and gas. In order to explore the adsorption mode between CN–COOH and NH₃, we utilized Gaussian 09 software to simulate. First, hydrogen bond adsorption can occur between the oxygen atom of carboxyl group and the hydrogen atom of NH₃. Besides, the hydroxyl group of carboxyl group can absorb ammonia atom of NH₃ via hydrogen bond adsorption. Furthermore, the FT-IR spectra of CN–COOH (figure 3(c)) shows that the material contains some sulfonic groups and the hydroxyl group of the sulfonic group can also adsorb ammonia atom of NH₃ by hydrogen bond adsorption. The thermodynamic parameters of the above three adsorption processes were simulated by Gauss 09 software. As shown in figure 7, the enthalpy variation (ΔH) can be extracted as

![Figure 5](image1.png)

**Figure 5.** (a) The linear relationship between the response and the NH₃ concentration within 50–250 ppm. (b) Short-term repeatability of CN–COOH based sensor with three cycles to 50 ppm NH₃. (c) The response time and recovery time of CN–COOH based sensor to 50 ppm NH₃. (d) Long-term stability measurements of the CN–COOH based sensor to 250 ppm NH₃.

![Figure 6](image2.png)

**Figure 6.** Response of CN–COOH based sensor to different gases at 25 °C.

![Figure 7](image3.png)
According to the adsorption theories, reversible physical adsorption can be qualitative when the $\Delta H$ is in the range of $-40$ to $0 \text{ kJ/mol}$. Strong chemical reaction can be qualitative when the $\Delta H$ is less than $-80 \text{ kJ/mol}$. Weak chemical adsorption can be qualitative when the $\Delta H$ is in the range of $-80$ to $-40 \text{ kJ/mol}$ [32]. Based on the simulation results, NH$_3$ molecules will interact with sulfonic and carboxyl groups after contacting the surface of the materials. Meanwhile, the interaction with sulfonic group belongs to weak chemical adsorption, while that with carboxyl group belongs to physical adsorption.

### 4. Conclusion

In this work, we reported a novel sensing material, carboxyl functionalized carbon nanocoil, for detecting NH$_3$ based on QCM system, which worked at low temperature with detection limits down to 50 ppm level. Because of carboxyl functionalization, the NH$_3$ sensing performance of carboxyl functionalized carbon nanocoil had been improved than pristine carbon nanocoil. The improved sensing performance of the reported sensor can be attributed to the hydrogen bond adsorption between carboxyl and NH$_3$, which will have application potential in the detection of NH$_3$.

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