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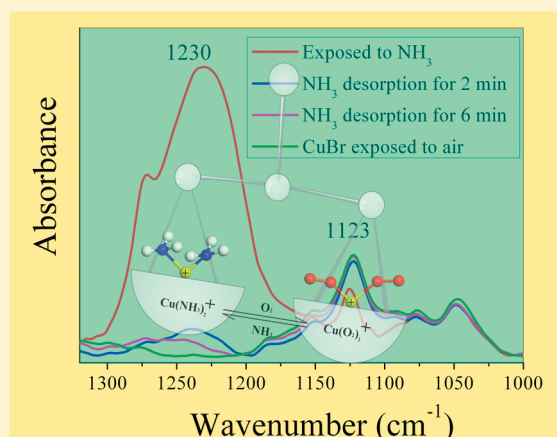
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NH₃ Sensing Mechanism Investigation of CuBr: Different Complex Interactions of the Cu⁺ Ion with NH₃ and O₂ Molecules

Yuan Zhang,^{†,§} Pengcheng Xu,[‡] Jiaqiang Xu,^{*,†,‡} Hui Li,[§] and Wenjie Ma[†][†]Department of Chemistry, Shanghai University, Shanghai 200444, China[‡]State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Shanghai 200050, China[§]Department of Physics, Shanghai University, Shanghai 200444, China

ABSTRACT: Copper(I) bromide (CuBr) was considered to be a good gas sensing material with a high sensitivity and selectivity to ammonia (NH₃) at ambient temperature. The NH₃ sensing mechanism was generally considered to be a result of the strong interaction between NH₃ molecules and Cu⁺ ions. When CuBr-coated quartz-crystal microbalance (QCM), a typical gravimetric transducer, was exposed to NH₃, the device displayed a decrease rather than an increase in total mass. This was an unusual phenomenon. In situ diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) was employed to examine the reasons of this total mass decrease. Probing of species formed on the CuBr surface revealed that a complex form between the Cu⁺ ions and the O₂ molecules in air existed. Consequently, O₂ gas with a higher molecular weight than NH₃ was substituted by NH₃ gas, inducing the decrease in mass. The band at 1123 cm⁻¹ of the DRIFT spectrum of CuBr corresponding to the complex formed between O₂ molecules and Cu⁺ ions was identified. The intensity of this band which decreased with the formation of NH₃ complex was also observed. The observation was a result of the substitution process for O₂ adsorption instead of NH₃.



INTRODUCTION

Copper(I) bromide (CuBr) was considered to be a favorable ammonia (NH₃) gas sensing material because of the strong interaction between copper(I) ions (Cu⁺) and NH₃ gas molecules.^{1–4} This could be a basis for the development of a NH₃ gas sensor in comparison to usual, especially metal oxide semiconductor devices.¹ However, the NH₃ gas sensing mechanism of CuBr remained unclear because of its inherent characteristic of mixed ionic–electronic conducting. Diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) was an increasingly popular technique in catalysis research, and the formation of surface species study for it permitted in situ observation of the reaction in powder or granular form.^{5–7} Therefore, the investigation of the NH₃ sensing mechanism of CuBr could be carried out through in situ DRIFTS.

Furthermore, it was assumed that the complex interaction between Cu⁺ ions and NH₃ molecules was the reason of NH₃ response of CuBr based sensor.⁸ A mass change, particularly a mass increase, could be observed, if NH₃ molecules were adsorbed on the surface of CuBr. A quartz-crystal microbalance (QCM) was a typical gravimetric transducer for bio/chemical sensing that transformed the mass change of a foreign layer of an analyte into a frequency change of the QCM.^{9–12} When a solid film was immobilized on the QCM surface, the change in resonance frequency (ΔF) would be proportional to the mass change

(Δm) on the QCM surface, and this phenomenon was described and governed by the Sauerbrey equation.⁹ Therefore, the QCM device could be used to characterize the mass change of CuBr before and after the CuBr adsorbing NH₃ molecules.

However, in this study, the unexpected results were observed for a CuBr coated QCM device for NH₃ response. The increase in frequency of the QCM device, corresponding to the mass decrease, was found when NH₃ gas was injected into the test chamber. On the other hand, the frequency decrease was detected, when other sensing material-coated QCM devices, such as ZnO nanowires, were used to detect NH₃.¹³ Thus, the NH₃ gas sensing mechanism of CuBr may be more complicated. In situ DRIFTS was employed to examine the reasons for this mass decrease after adsorption of NH₃ gas molecules. Our primary goal was to determine the species causing this unexpected phenomenon and to understand the complicated interaction of the CuBr and NH₃ gas molecules. The combination of the QCM device and DRIFTS technique would result in the development of a better NH₃ gas sensor and provide an opportunity to investigate the NH₃ gas sensing mechanism.

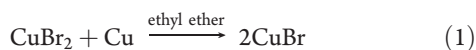
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EXPERIMENTAL SECTION

Synthesis. The preparation of CuBr was achieved through an antiproportionation reaction between Cu^{2+} ions and metal Cu powder in the existence of anhydrous ethyl ether (see eq 1). In a typical synthesis, 0.054 g of CuBr_2 powder (Alfa Aesar) was immersed in 20 mL of anhydrous ethyl ether (Shanghai Chemical Industrial Co. Ltd.). Then, 0.012 g of metal Cu powder (Shanghai Chemical Industrial Co. Ltd.) was added, mixed uniformly with CuBr_2 powder using a clean glass bar. The mixture was allowed to react for about 60 min at room temperature. Anhydrous ethyl ether should be added again when the powders are nearly exposed to air. The reaction was completed when metal Cu powder totally disappeared. Finally, white CuBr product could be obtained after rinsing with absolute ethanol several times until the brownish-black color of CuBr_2 residue was removed, and it was dried at 60 °C under vacuum for 2 h. In this preparation process, the amount of CuBr_2 should be excessive because any surplus CuBr_2 could be removed with ethanol. To confirm the substitution process between Cu^+ ion complexes, CuCl was synthesized for comparison with CuBr. In the synthesis procedure of CuCl , 0.7 g of CuCl_2 powder (Alfa Aesar) was immersed in 25 mL of deionized water. After the dissolution of CuCl_2 , 25 mL of HCl and 0.6 g of Cu powder were added. The resulting solution was heated at 80 °C, until a brown suspended solution was obtained. Then, yellow solution was separate from the mixture using a decantation method. The separated yellow solution was then poured into a mixture of 300 mL of water and 15 mL of anhydrous ethyl ether. The formation of CuCl could be seen by the appearance of white precipitate. The following steps are same to that of CuBr.



Characterization. Morphologies and sizes of the CuBr microparticles were evaluated by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F, 15 kV). The structure of the product was identified by powder X-ray diffraction (XRD) analysis using a D/max 2550 V diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) (Rigaku, Tokyo, Japan), and the XRD data were collected at a scanning rate of 0.02 deg s^{-1} for 2θ in a range from 10 to 70°.

Detection of NH_3 Gas Responses with a Chemiresistor Sensor. The final product of CuBr was mixed and ground with ethanol in an agate mortar forming a paste, which was then coated on an alumina tube-like substrate on which a pair of Au electrodes had been previously deposited by a thin film technique followed by drying at 60 °C under vacuum for 2 h. A stationary state gas distribution method was used for the test of gas sensing properties. In the measuring electric circuit, a load resistor (10 M Ω) was connected in series with a gas sensor. The circuit voltage was 10 V, and output voltage (V_{out}) was the terminal voltage of the load resistor. The resistance of a sensor in air or test gas was measured by monitoring V_{out} . The test was operated in a measuring system of HW-30A (Hanwei Electronics Co. Ltd., P.R. China). Detecting gases, such as NH_3 , were injected into the chamber and mixed with dry air. The measurement chamber was swept with compressed dry air at gas flow rate of 2.0 L min^{-1} for 5 min before injecting the detecting gases. The gas response of the sensor in this paper was defined as $S = R_g/R_a$, where R_a and R_g were the resistance in air and in a test gas, respectively.

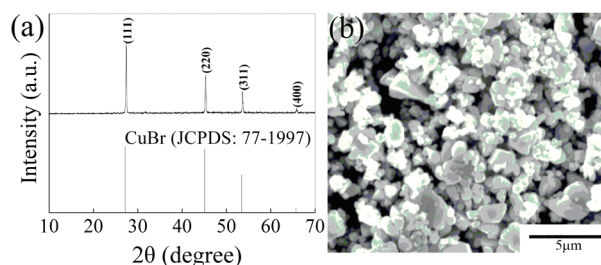


Figure 1. Characterization of CuBr particles: (a) XRD pattern, (b) FE-SEM image.

Detection of NH_3 Gas Responses with a QCM Sensor. The AT-cut 10 MHz quartz P/Z crystal (Beijing Chenjing Electronic Co., China) (1.25 cm diameter, silver electrodes) was used to fabricate the device. The electronic control equipment consisted of a self-constructed frequency oscillator, a 6 V DC regulated power supply, and a frequency counter (53131A Universal Counter, Agilent) with an accuracy of 1 Hz. The frequency signal was acquired by a personal computer via a 16 bit digital-to-analogue conversion and was monitored as a function of time. The silver electrodes of the quartz crystals showed a smooth, metallic surface having good reflection of light. They were cleaned ultrasonically in acetone for 10 min and then immersed into ethanol for 10 min. Finally, the surface was thoroughly rinsed with deionized water and gently blow-dried under a flow of nitrogen gas. The as-prepared CuBr powder (5 mg) was dispersed ultrasonically into 10 mL of ethanol forming an aqueous suspension, then used as the sensing material and deposited on the QCM sensing electrode by the drop-coating method. The characterization of NH_3 gas response of CuBr particles was performed through a static gas distribution, and the gas delivery system was identical to that of detection with a chemiresistor sensor.

In situ DRIFTS Experiments. In situ DRIFTS experiments were conducted in a self-constructed reaction cell, adapted in a Bruker Vertex 70v FT-IR spectrometer. A special design of the cell with the capacity of 500 mL allowed the diffusion of NH_3 and other gases to the surface of CuBr for adsorption and interaction.

RESULTS AND DISCUSSION

The as-synthesized CuBr used in this study was characterized by XRD and FE-SEM first. Figure 1a showed the XRD pattern of as-synthesized CuBr particles, contributing to a cubic structure with lattice constants of $a = b = c = 0.5684 \text{ nm}$. All of the diffraction peaks in Figure 1a could be well-indexed to the standard pattern of CuBr (JCPDS No. 77-1997). No characteristic bands were observed for CuBr_2 or Cu. FE-SEM observation (see Figure 1b) revealed that the as-synthesized white powder consisted of CuBr particles with diameters of $0.5\text{--}1.5 \text{ }\mu\text{m}$.

The NH_3 gas sensing performance of a chemiresistor sensor fabricated with CuBr particles was characterized. The dynamic response of the sensor to 5 ppm NH_3 is shown in Figure 2a. One notices that the resistance of the chemiresistor increased six times after the sensor exposed to 5 ppm of NH_3 gas. The time necessary to reach 90% of the equilibrium value after the gas switching off was about 100 s. Seven other typical reducing gases acting as interference gases were selected to investigate the selectivity of the sensor at room temperature. The concentration of the NH_3 gas was 5 ppm, while the concentration of each of the other gases was 50 ppm. The gas sensor based on the CuBr sample showed

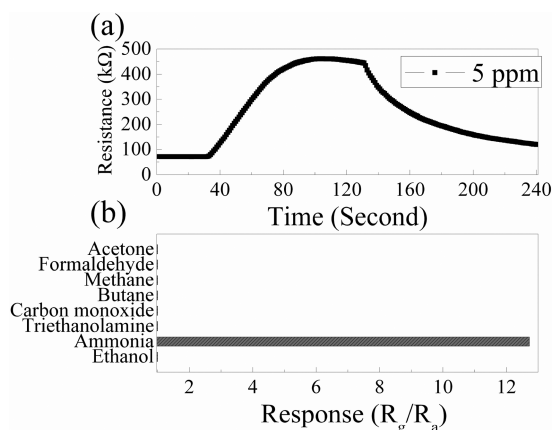


Figure 2. NH_3 gas sensing performance of CuBr particles fabricated with a chemiresistor sensor.

good selectivity to NH_3 with little interference against other gases (see Figure 2b).

The aqueous suspension of CuBr was coated on the QCM sensing surface and used to detect NH_3 gas. Different amounts of standard NH_3 gas were diluted into dry air to obtain the desired concentrations. Figure 3 showed the frequency change of the CuBr coated QCM device upon exposure to different concentrations of NH_3 gas. The frequency increase was observed with multiple injections of NH_3 gas. About 700 Hz of frequency increase was clearly visible, when a concentration of 10 ppm NH_3 was injected into the test chamber (see Figure 3a,b). The device also demonstrated a stepwise increase in frequency corresponding to an increase in the concentration of NH_3 gas, which revealed the reproductive capacity of CuBr device to detect NH_3 gas. However, the presence of high concentration of NH_3 gas in the test chamber led to a lower signal, possibly as a result of the formation of saturated adsorption of NH_3 gas at the concentration of about 100 ppm as shown in Figure 3a. The steady-state frequency of CuBr desorbed from NH_3 was higher than the starting frequency of CuBr in air (see Figure 3a,b). Since the complex reaction efficiency of the Cu^+ ion with NH_3 gas was high, the complex of Cu^+ ion with NH_3 may be accumulated at high NH_3 concentration inducing the difficult recovery of CuBr to its initial state. The increased frequency signal was not observed by introducing other gases, such as $\text{CH}_3\text{CH}_2\text{OH}$, CH_3COCH_3 , HCHO , and CH_4 .

We detected the repeatable response of the CuBr-coated QCM sensor to NH_3 . The frequency-change signals showed the same value for each detection of 20 ppm NH_3 , suggesting that the responses of the CuBr-coated QCM sensor to NH_3 had a good repeatability (see Figure 3c). The humidity interference of the CuBr-coated QCM sensor was also studied (see Figure 3d). The controlled humidity environments were achieved by using saturated aqueous solutions of different salts of MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, NaCl , KCl , and CuSO_4 in a closed glass vessel at ambient temperature, which yielded 33%, 56%, 75%, 85%, and 97% relative humidity, respectively.¹⁴ The frequency increased at the humidity of 33% and 51%, whereas the frequency decrease was observed at the humidity of 85% and 97%. For molecules with low molecular masses such as ammonia and water, both molecules had similar chemical properties, complex interaction with Cu^+ ion, and a rather similar volume and shape.¹⁵ The frequency increase signal at low humidity could be attributed to the same response mechanism as NH_3 gas. While the frequency decreased at high

humidity may be because of a large amount of H_2O molecules adsorbed on the surface of the CuBr-coated QCM sensor. The humidity only had a relatively large effect on NH_3 responses under high humidity or when the humidity has a large fluctuation. If the detection was carried out under low humidity ($\text{RH} < 30\%$), the interference of water molecule would be negligible. However, the detection to NH_3 gas would be carried out in dry air for the calibration of responses, especially for the detection of low NH_3 gas concentration.

According to the relation between the mass changes Δm (g) and the frequency shifts Δf (Hz) (shown as eq 2), the increased frequency indicated the decrease in mass on the QCM sensing electrode.

$$\Delta F = -2.3 \times 10^6 F_0^2 \frac{\Delta m}{A} \quad (2)$$

To explore the reason of this unexpected phenomenon, DRIFT spectroscopy was utilized for the in situ identification of the species formed on the surface CuBr under exposure to various gases. First, in situ DRIFT spectra of CuBr powder adsorbed with 10 ppm NH_3 for 2 s were obtained, and desorption for different times in clean air was performed (Figure 4). Three obvious bands at 3327, 1599, and 1230 cm^{-1} were detected, when the sample was exposed to NH_3 . It also could be observed that the band at 3327 cm^{-1} disappeared rapidly with the subtraction of NH_3 . However, the bands at 1599 and 1230 cm^{-1} decreased slowly with the time, which faded away gradually until after 6 min, indicating the strong interaction of NH_3 and the Cu^+ ion (Figure 4).

We also found the intensity of the band at 1123 cm^{-1} to decrease with the formation of NH_3 complex (Figure 5). Moreover, the signal intensity recovery at this band was observed after the subtraction of NH_3 gas. The intensity change of the band at 1123 cm^{-1} with the introduction and subtraction of NH_3 may be the reason for the unexpected phenomenon for a used CuBr-coated QCM device to detect NH_3 . The decrease in intensity of the band at 1123 cm^{-1} after introducing NH_3 could be ascribed to the partial substitution of some other higher molecular weight gases with NH_3 molecules.

Air is known as being mainly composed of N_2 and O_2 . Besides the two gases, CO_2 and H_2O also account for a considerable proportion in the air and most probably may have a complex interaction with the Cu^+ ion. The coordination and infrared spectra of $\text{Cu}^+(\text{H}_2\text{O})_n$ had been reported in previous research, which showed the bands at 3035 and 3340 cm^{-1} in the spectrum of $\text{Cu}^+(\text{H}_2\text{O})_3$ and the bands at 3060 and 3340 cm^{-1} in the spectrum of $\text{Cu}^+(\text{H}_2\text{O})_4$, respectively.¹⁶ Sárkány detected the DRIFT spectra of the Cu^+ ion coordinated with the CO_2 complex in the region of 2200–2100 cm^{-1} .¹⁷ Accordingly, the decrease of the band at 1123 cm^{-1} did not relate to the coordination between the Cu^+ ion and H_2O or CO_2 . However, few studies on the complex interaction of O_2 or N_2 with mobile Cu^+ ions in CuBr solid have been reported; in particular, their DRIFT spectra were scarcely investigated.

To confirm the species formed with Cu^+ ion in CuBr, the DRIFT spectra of CuBr exposed to O_2 and N_2 were further observed, respectively. Figure 6a showed the spectra of the sample exposed to O_2 and air and desorption from O_2 . When O_2 was introduced to the sample, the bands at 1300, 1192, and 1123 cm^{-1} appeared rapidly. Among the three bands, the band at 1123 cm^{-1} was also found in the spectrum of CuBr exposed to air. This band remained relatively constant after subtraction of

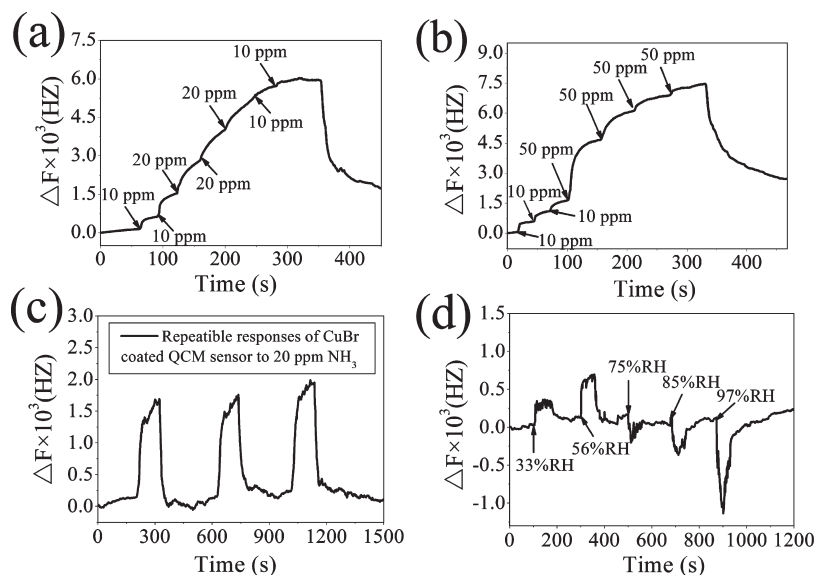


Figure 3. Responses of the CuBr-coated QCM device to NH_3 and humidity interference. (a–b) Frequency-time trend recorded during multiple injections of different concentrations of NH_3 gas (all labeled concentrations are supplemental injections of NH_3 gas); (c) repeatable responses to 20 ppm NH_3 ; (d) humidity interference detection.

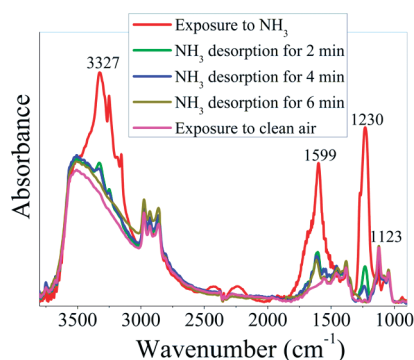
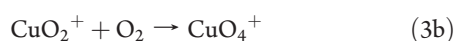
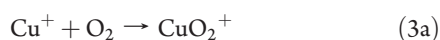


Figure 4. In situ DRIFT spectra of CuBr particles exposed to NH_3 , followed by desorption for different times.

O_2 , which could be attributed to the formation of coordinated O_2 on CuBr with Cu^+ ion. The bands at 1300 and 1192 cm^{-1} disappeared after removing of O_2 , indicating the adsorption of O_2 on CuBr particles. Among Cu^+ ion complex species, $\text{O}_2 \rightarrow \text{Cu}^+$ complex was known to exist, and experimental and theoretical studies on the complex of $\text{O}_2 \rightarrow \text{Cu}^+$ had been well-established.^{17,18} Moreover, the room-temperature kinetics and reaction efficiencies between Cu^+ ions and molecular oxygen had been reported by Bohme and his group.¹⁹ The product of CuO_2^+ was formed by direct addition of O_2 to Cu^+ . Sequential O_2 addition was observed, producing the bimolecular product of CuO_4^+ (see eq 3). The reaction efficiency of Cu^+ ions toward molecular oxygen was $3.8 \times 10^{-4}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ for CuO_2^+ and $7.2 \times 10^{-4}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ for CuO_4^+ , respectively.¹⁹



Contrarily, the DRIFT spectra of the sample exposed to pure N_2 showed no increase in intensity at the band of 1123 cm^{-1} , and

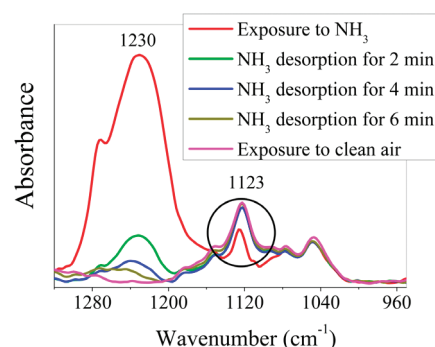


Figure 5. Wavenumber from 1320 to 950 cm^{-1} of DRIFT spectra of CuBr powder exposed to NH_3 and clean air, followed by desorption for different times.

a slight decrease of all bands were observed (see Figure 6b), indicating that there is no substitution between N_2 and the Cu^+ ion.

As additional evidence of the $\text{O}_2 \rightarrow \text{Cu}^+$ coordination formation, the spectrum of CuBr under vacuum was also characterized (see Figure 6c). The bands of CuBr exposed to air and treated with vacuum were highly similar except for the disappearance of bands at 2347 and 2281 cm^{-1} corresponding to the adsorption of CO_2 .^{17,20} The maintenance in intensity of the band at 1123 cm^{-1} further revealed that the interaction between Cu^+ and O_2 was not adsorbed, but rather coordinated.

With the successful observation of the species formed on the surface of CuBr, we also applied CuCl to confirm the hypothesis of the substitution process involving Cu^+ ion complexes. Electrical conductivity measurements of CuCl have verified that it was predominantly an ionic conductor.²¹ The similar phenomena of substitution of O_2 with NH_3 may also be found through in situ DRIFTS experiments. Figure 6d shows the spectra of the CuCl sample exposed to air, NH_3 , and O_2 . Two types of Cu^+ ion complexes were found on the CuCl samples, namely, the O_2 complex and the NH_3 complex. After the exposure of CuCl to O_2 , the bands at 1265 , 1304 , and 1342 cm^{-1} appeared rapidly.

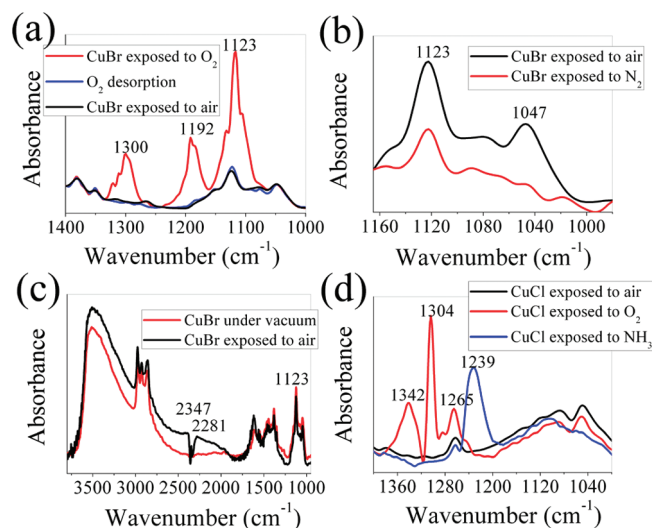


Figure 6. DRIFT spectra of CuBr and CuCl sample: (a) CuBr exposed to O₂ and air and desorbed from O₂; (b) CuBr exposed to N₂ and air; (c) CuBr exposed to air and under vacuum; (d) CuCl exposed to air, O₂, and NH₃.

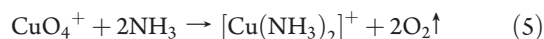
Among the three remarkable bands, the band at 1265 cm⁻¹ also appeared in the spectrum of CuCl exposed to air, which was attributed to the formation of coordinated O₂ with the mobile Cu⁺ ion. The bands at 1239 cm⁻¹ of the DRIFT spectrum of CuCl exposed to NH₃ corresponded to the complex formed between Cu⁺ and NH₃. The band at 1265 cm⁻¹ decreased after CuCl was exposed to NH₃, which was consistent with the spectrum of CuBr exposed to NH₃. Figure 7 shows the responses of the CuCl-coated QCM sensor to different concentrations of NH₃ gas. The frequency increase was also observed when CuCl was exposed to NH₃ gas. Combined with the QCM sensing results and in situ DRIFTS experiments of CuBr and CuCl, the substitution effect of O₂ with NH₃ between Cu⁺ ion complexes could be safely concluded.

Accordingly, the gas sensing process of CuBr exposed to NH₃ gas was deduced on the basis of our experimental results. The overall reaction consisted of three major steps as follows.

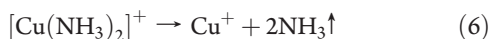
Complex interaction of O₂ with mobile Cu⁺ ion in air:



Partial substitution of O₂ with NH₃ after introducing NH₃:



Desorption of NH₃ from the CuBr:



The reaction process of the Cu⁺ ion with ammonia was studied by using ion beam tandem mass spectrometer.²² The reaction mechanism between Cu⁺ ion and NH₃ was presumed as shown in eq 8. The lifetimes of reaction intermediates and products were measured and calculated by using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.²² According to the dissociation constant of Cu(NH₃)₂⁺ ($K_d(\text{NH}_3) = 3.2 \times 10^9 \text{ cm}^3/\text{s}$) and $[\text{M}^+ \cdots \text{NH}_3]^*$ ($K_d = 4.3 \times 10^7 \text{ s}^{-1}$),²² Cu⁺ ions would be easily dissociated from Cu(NH₃)₂⁺. However, the complex reaction

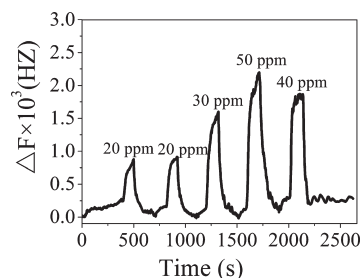
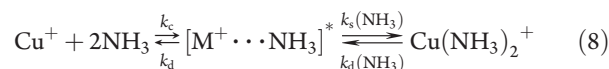


Figure 7. Responses of the CuCl-coated QCM sensor to different concentrations of NH₃ gas.

efficiency of the Cu⁺ ion with NH₃ gas was quite high, and the complexes between Cu⁺ ion and NH₃ would accumulate at high NH₃ concentrations. Moreover, the relative low reaction efficiency of Cu⁺ ions toward molecular oxygen was another reason for the difficult recovery of Cu⁺ complexes to the initial state. This deduced reaction process was in reasonable agreement with the response and recover behavior of CuBr coated QCM device to NH₃ (see Figure 3a,b).



The detailed mechanism leading to the observed NH₃ sensing performance of CuBr particles could be proposed. (1) A complex interaction of O₂ molecules occurred with CuBr in air. The reaction efficiency of the Cu⁺ ion with O₂ was relatively slow, and the copper ion vacancy concentration was rather limited. The electrical conductivity provided by the mobile Cu⁺ ion was correspondingly high. (2) After the NH₃ molecules are introduced on the surface of CuBr, the strong interaction between Cu⁺ and NH₃ molecules enhanced the copper ion vacancy concentration in the space charge region. It was substantiated that the low-temperature conductivity data of CuBr consistently interpreted a change from electron hole conduction below 260 K to Cu⁺ ion conduction above that temperature,²³ although CuBr was a mixed ionic–electronic conducting halide.^{23–25} Thus, the conductivity of CuBr was ionic at room temperature. The enhancement of copper ion vacancy concentration led to a decrease in majority carriers and, thereby, an increase in the resistance.

CONCLUSIONS

QCM characterization of the NH₃ sensing response of CuBr particles revealed an unexpected result of mass decrease after adsorbing NH₃ gas. The DRIFT studies confirmed the O₂ complex species formed on the surface of CuBr. The band at 1123 cm⁻¹ corresponding to the complex of O₂ and Cu⁺ ion was identified. The intensity of this band decreased with the formation of NH₃ complex. We concluded that the main reason for the mass decrease after adsorbing NH₃ was due to the substitution of O₂ with NH₃. The sensor behavior is interpreted as an O₂ complex with the Cu⁺ ion before CuBr was exposed to NH₃ and NH₃ substitution during the following used as the NH₃ gas sensor.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xujiaqiang@shu.edu.cn. Fax: (+86) 21-66134725. Tel.: (+86) 21-66132406.

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