Highly Sensitive Thin Film Sensor Based on Worm-like Carbon Nanofibers for Detection of Ammonia in Workplace

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A thin film sensor was fabricated using the mixture of worm-like carbon nanofibers (WCNF), which were synthesized using aluminium supported iron catalysts via chemical vapour deposition, and glass dust in proportion of 3 : 2, combined by drops of terpineol. The morphology of the catalyst, the worm-like carbon nanofibers and the film surface were investigated with the help of TEM and SEM. Low single-potential signal was employed to investigate gas sensitivity of the sensor to the deleterious ammonia, in atmospheric pressure at room temperature. The results suggest that the sensor has high sensitivity at low concentration (0.175—0.35 mg/m^3), perfect reproducibility, and a fast response time (0.05 s) and restoration time (1 min).

Keywords   worm-like carbon nanofibers, thin film sensor, sensitivity, ammonia, chemical vapour deposition

Introduction

With the increasing aspiration for the best quality of environment, the quality of environment has been a hot focus of public concern, especially the quality of room and workspace environment. Deleterious gases are threatening the daily life of us, such as NH_3, SO_2, NO_x and O_3. These gases have been regarded as the most complicated and difficult pollutant, due to their characteristics that gas sources and compounds are not only very diverse, but their detection and evaluation are also difficult and subjective. As well as we know, NH_3 is a well-known deleterious pollutant, and the detection of NH_3 is an important task in many technological fields, such as industrial processes, clinical diagnosis, and environmental monitoring, especially the detection of low concentration ammonia.

Choice of suitable sensing materials is the key step for the detection system. Different organic and inorganic materials are used as sensing elements, such as polyaniline,[1,2] ZnO,[3] tellurium[4] and In_2O_3.[5] In spite of the various advantages of organic and inorganic material based gas sensors, some fundamental problems persist, such as the high operating temperatures, low sensitivity, poor selectivity and reliability. Recently, carbon nanotubes[6] have attracted great attention due to their extraordinary properties, such as large surface-to-volume ratio, electronic properties and chemical stability. So, the carbon nanotube based gas sensors have

been employed to detect a variety gases, such as N_2, CO_x, and NO_x.[7-13] Until now, there are only a few researches on single and multi-wall carbon nanotube-based sensors for the detection of NH_3.[14-16] The drawback of these sensors based on carbon nanotubes is the slow and incomplete recovery that has been conceded. In this study, we want to develop a reliable sensor presenting the following properties: ability to detect a small amount (less than 0.7 mg/m^3) of ammonia in a known atmosphere with a relatively short response time (less than 1 s), a relatively short restoration time (less than 1 min) and low power consumption (1 mW). In order to accomplish this purpose, the carbon nanofibers are employed as the sensitive material to detect ammonia, due to their inherent properties like small size of diameter, 1—100 nm, and good electrical and mechanical properties.

In this paper, the worm-like carbon nanofibers, which have been synthesized by Yen,[7,8] were synthesized through the chemical vapour deposition in an economical method. The thin film was prepared using the mixture of WCNF, glass dust and terpineol in a proper proportion, and the low single-potential signal was selected to test the sensor properties, such as its sensitivity, reproducibility, and response and restoration time. This may be the first try to use the carbon nanofibers as the sensitive material detecting the deleterious gases.

Experimental

Preparation of iron catalyst

The preparation procedure of the iron catalyst was as follows. Initially, 10 mL of 0.01 mol/L $Fe(NO_3)_3$ were mixed with 10 mL of distilled water and the mixture was stirred for 20 min. The mixed solution was added into 80 mL boiled distilled water, and stirred for 20 min using the glass stick slowly. Then, the reddish brown solution of $Fe(OH)_3$ was prepared, and cooled down to room temperature. Adjust the PH value of the solution to a point of 4.2, with 1% HCl and 1% NH_4OH. Subsequently, 10 mL of $Fe(OH)_3$ solution were taken out into a container, and was dispersed by 10 mL of 0.01 mol/L hexadecyl trimethyl ammonium bromide surface active agent. The dispersed $Fe(OH)_3$ suspension was prepared by sonicating treatment in an ultrasonic device (42 kHz), which was deposited on a aluminium sheet by a micro-sprayer and dried at room temperature overnight. Finally, the thin film on the aluminium substrate was annealed using a CVD device at the temperature of 873 K reached in steps of 10 K/min with protection of N_2. During this process, the $Fe(OH)_3$ was converted to Fe_2O_3 through dehydration. After that Fe_2O_3 was deoxidized using the reducing agent of H_2, and was converted to Fe atom.

Synthesis of worm-like carbon nanofibers

Initially, the iron catalysts on the substrate were placed in a horizontal quartz tube furnace, which was kept at the atmospheric pressure all the time. The furnace temperature was then raised to the synthesis temperature of 873 K at a rate of 10 K/min, for the WCNF synthesis with protection of N_2. Subsequently, the gaseous C_2H_2 (20 mL/min) diluted with 200 mL/min N_2 was decomposed in the furnace for 15 min. After the WCNF synthesis, the furnace temperature was cooled down to room temperature. The deposits on the substrate were dissolved in 1 mol/L NaOH solution to make the deposits apart from the substrate. The resulting solution was centrifuged in an ultracentrifuge (Beckman Coulter-Allegra^{TM}64R Centrifuge) for 20 min at 8000 r/min and 290 K in order to gain purified deposits. Some dark materials were kept down in the centrifugal pipe, and then 15 mL of C_2H_5OH were added in the pipe as the solvent to disperse the dark materials. The resulting solution was sonicated in an ultrasonic device (42 kHz) to disperse mixture suspension for 20 min, which was purified by the centrifugal device again. The high purity deposits were dealt with the same method for 5 times, and then dried in an oven at a temperature of 333 K to gain the powder for further experiments. In this study, the synthesis process was according to our previous work,[19] such as the reactive temperature, the flow rate of gases and the reaction time.

Preparation and detection processes of thin film sensor

The sensitive material was prepared using 37 mg of deposits, 24.7 mg of glass dust and some drops of terpineol in a vessel, and the mixture was deposited on the china substrate (80 mm×30 mm×10 mm) forming a thin film. The thin film was heated at a temperature of 1073 K at a rate of 20 K/min with the protection of N_2, and cooled down to room temperature. Then, the thin film sensor based on WCNF was fabricated.

Low single-potential signal was used in the detection of NH_3 as the input signal of the thin film sensor, 1 V, and the surface temperature of the thin film was kept at the temperature of 393 K heated by the resistance on the opposite surface of the china substrate. During the experiment, the room temperature was 290 K and the humidity was 66%. We have developed a simple apparatus to monitor the ammonia sensing by the thin film sensor at room temperature. The detection process in details was as follows: First a 2.5 L airproof apparatus was opened in order to make the air the same inside and outside of the apparatus. Second, the sensor element was put into the apparatus connected through the electrical wires to the exterior controlled device, which was heated for 10 min at the beginning to provide constant working temperature. Subsequently, the single-potential signal was transmitted to the thin film to detect the changes of the film resistance when WCNF reacted with the air in the apparatus. Finally, ammonia was injected into the apparatus, and the film resistance changes and the response time were detected automatically. Increasing the concentration of the ammonia, all the changes were noted again by the current-time (*I-T*) curves. Moreover, during the same detection process, different *I-T* curve was noted at different time to monitor reproducibility of this sensor. Then the sensor element was removed from the apparatus and kept in ammonia-free atmosphere to monitor the conductivity recovery.

Ammonia-air mixture was taken from the top space of the bottle containing ammonia solution. The ammonia concentration in the mixture was estimated by trapping a known volume in ice-cold dilute hydrochloric acid solution that was titrated with standardized sodium hydroxide. The minus of the current only shows the opposite orientation of the current. In this study, all the detections of ammonia were under the same simulated environment as the true scene where NH_3 was leaked and detected.

Characterization

The morphology of the iron catalyst was shown by the scanning electron microscope (SEM, JEM-200CX, Japan) coated with gold grains using a Bal-Tec MD 020 instrument (80 s and 30 μA).

The deposits were confirmed and analyzed by the scanning electron microscope and the transmission electron microscope (TEM, JEM-100SX, JEOL, Japan).

The morphology of the thin film on the substrate was studied making use of the scanning electron microscope.

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Result and discussion

Morphology of iron catalyst

Figure 1 shows the morphology of Fe atoms with size of 15 nm, with uniform morphology and ideal dispersion. During this synthesis process, the hexadecyl trimethyl ammonium bromide played a crucial role in the dispersion of $Fe(NO_3)_3$, avoiding the reunion of them and providing a possibility for the ideal dispersion of Fe atoms. Furthermore, Fe ions in $Fe(NO_3)_3$ solution combined well with aluminium substrate avoiding the recombination during the processes in which $Fe(OH)_3$ was converted to Fe_2O_3 when heated in the furnace, and finally Fe_2O_3 was converted to Fe atoms through the deoxidization with the help of H_2. Finally, the ideal dispersed catalysts were prepared for the synthesis of carbon nanofibers.
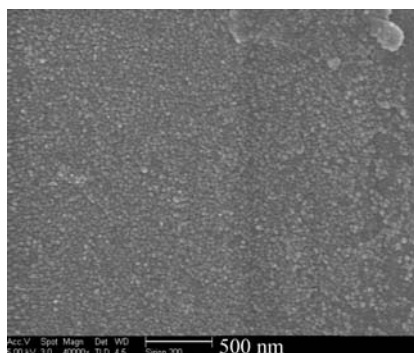
Figure 1 SEM image for the Fe catalysts on the aluminium substrate synthesized through a sol-gel method.
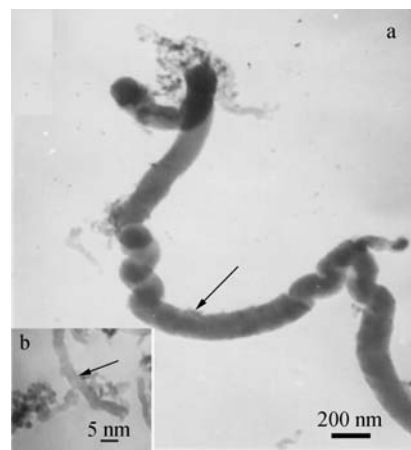
Synthesis of worm-like carbon nanofibers

Using the ideal dispersed catalysts, the deposits were produced via the CVD method heating at 873 K, at the atmospheric pressure. This is a simple device with only the temperature and gas control. The deposits contain lots of lovely carbon materials as shown in Figure 2, and two kinds of the materials exist with different morphologies and sizes at diameter of 200 and 5 nm. The morphology of larger one looks like a worm, with a
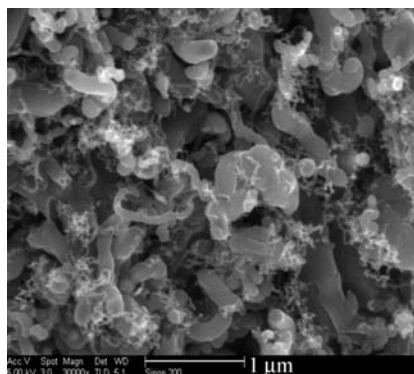
Figure 2 SEM image for the carbon nanofibers and carbon nanotubes synthesized using the aluminium supported Fe catalysts via the chemical vapour deposition at the temperature of 873 K.

bigger head and a fatten body. Figure 3a shows that the larger material was solid carbon nanofibers with length of 5×10^{-3} mm, and Figure 3b shows that the smaller material was hollow carbon nanotubes. In fact, the worm-like morphology of the carbon nanofibers was conducted by the faster adsorption rate between the catalysts and the carbon species than the synthesis rate of the carbon nanofibers.

Figure 3 TEM image for carbon nanofibers (a) and carbon nanotubes (b).

The thin film sensor

Yen and co-workers spared no effort on the synthesis of WCNF and its application to field emitter.[17,18] In this study, the main goal of our work is to find an economical method to synthesize the material and study its gas sensitivity. Scanning electron microscopy (SEM) micrograph as shown in Figure 4 suggests that the mixture of WCNF and the glass dust was dispersed well on the substrate. All the WCNF species were connected with each other, not reunited together but connected the beginnings and ends forming a network, and the interspaces among WCNF were filled with the glass dust, forming a thin film together on the substrate with thickness of 200 nm with only one layer.
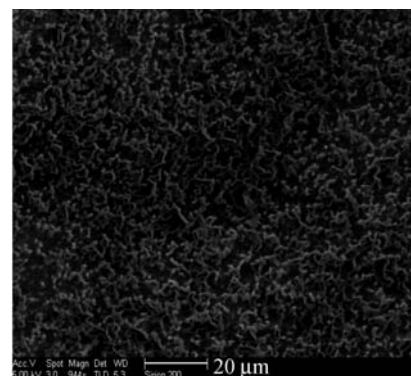

Figure 4 SEM image for the thin film surface based on worm-like carbon nanofibers.

When the sensor was exposed to air, the WCNF will react with O_2 and H_2O via both chemisorption and phy-

sisorption, and then the resistance of the film will change correspondingly. When the film works in air, adding the single-potential signal at the temperature of 393 K, the resistance of it is 47 kΩ, proving that WCNF is a semiconductor.

Ammonia sensing Characteristics

In this study, the low voltage testing method was selected, and the voltage of the film was changed from 0 to 1 V immediately when the signal was transmitted. The sensitivity of the sensor to different concentrations of ammonia, in the range of 0.175—0.35 mg/m^3, was tested using this signal, at 0.1 s interval with 100 sampling points. And the *I-T* characteristics of this film to different concentration ammonia are shown in Figure 5. These three curves show the resistance changes with different concentrations of NH$_3$, suggesting that the resistance increases with increasing the amount of ammonia. The gradient curve reflects the changes of resistance along with the signal changes from 0 to 1 V, and the film resistance keeps almost the same at the constant voltage of 1 V. Furthermore, it is shown that the current decreases with the increase of the ammonia concentration, which has an obvious change from 0.245 to 0.35 mg/m^3 of ammonia especially, suggesting that the film has highly sensitive response to ammonia with the increase of the concentration. In fact, there is no *I-T* curve existing below the concentration of 0.175 mg/m^3.
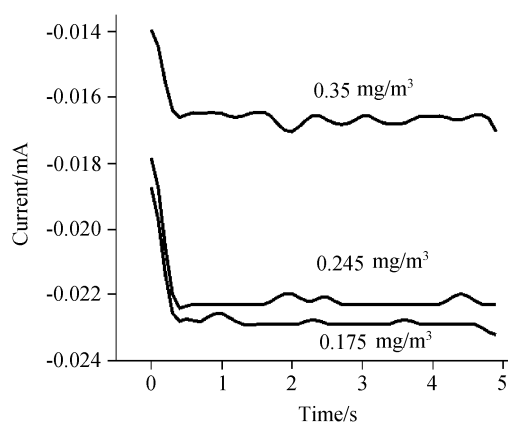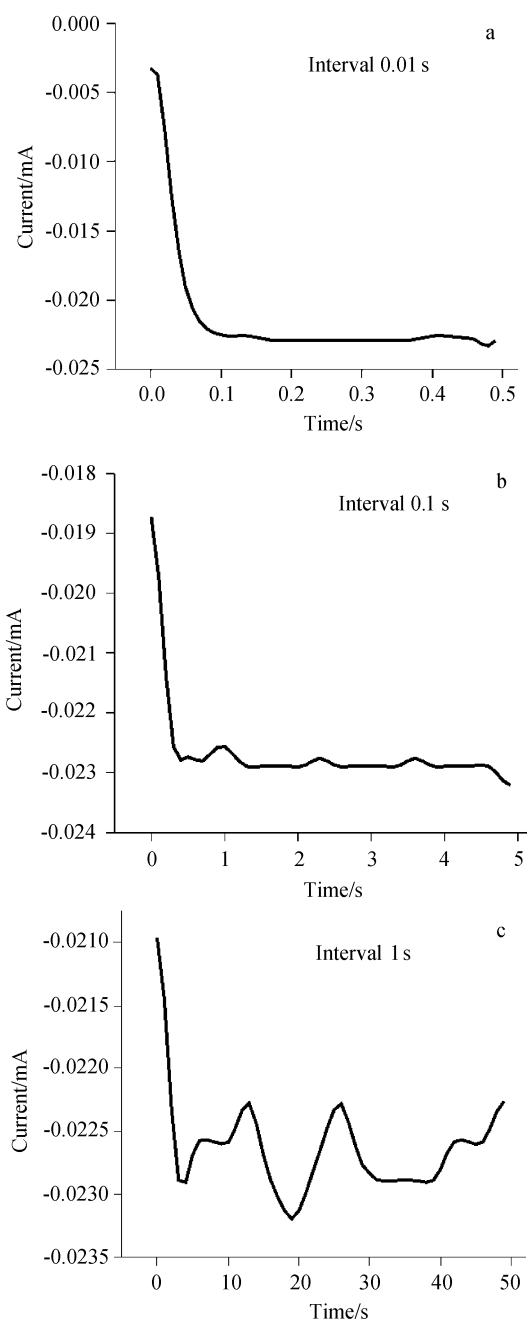

Figure 5 Current-time characteristics for different concentration ammonia.

When the sensor was exposed to air, the O$_2$ and H$_2$O will react with WCNF and the Fermi level of the WCNF is changed resulting in the resistance changes of the film. There are two kinds of adsorption on the surface of the sensor during the ammonia detection process, ie, chemisorption and physisorption. In the chemisorption between NH$_3$ and the WCNF, electrons are sent to the WCNF from NH$_3$ and the number of cavities existing in the WCNF decreases according with coming of foreign electrons. Also, the NH$_3$ is adsorbed on the surface through the Van Der Waals' forces in the physisorption. And the NH$_3$ will combine with H$_2$O existing on the surface of the film, and the formed NH$_4$OH escapes

from the surface rapidly resulting in the increase of the resistance. Just as shown in Figure 5, from the black curve we know that the current of this film is 23×10^{-3} mA, and the corresponding resistance is 43 kΩ; from the blue one it is known that the corresponding resistance has increased to 70 kΩ rapidly. Compared with the resistance in the air (40 kΩ), it is reasonable to conclude that the sensor has high sensitivity to NH$_3$.

Furthermore, the sensor has flash response to NH$_3$ as shown in Figure 6, using the single-potential signal, 100 sampling points and different time intervals. These *I-T* curves are the reflection of resistance changes during different reactive intervals. From the top curve, it is

Figure 6 Current-time characteristics for different intervals during a whole detection process: 0.01 s (a), 0.1 s (b), and 1 s (c).

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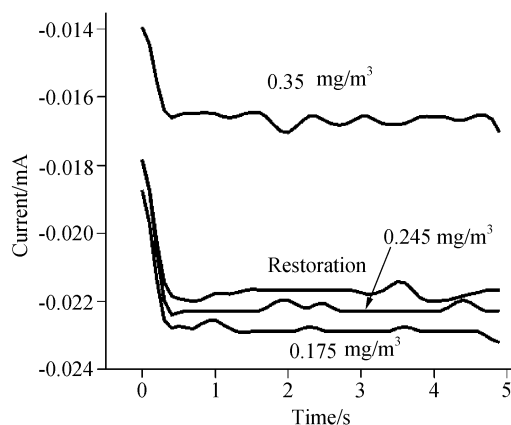*Chin. J. Chem.*, 2008 Vol. 26 No. 4   **653**

known that the basic shape has formed rapidly in 0.05 s after the signal is added on the film which has little changes with the increase of the interval. However, with the increase of detection time, the curves undulate like a wave more obviously. In fact, these changes were conducted by the repeating adsorption and desorption of NH_3 in the apparatus. At the beginning, NH_3 reacts with the H_2O to form the NH_4OH, which is released from the film surface rapidly; and then the released NH_4OH can not escape into the outward environment and decomposes into NH_3 and H_2O; subsequently, these decomposed materials and the undecomposed NH_4OH react again with the film.
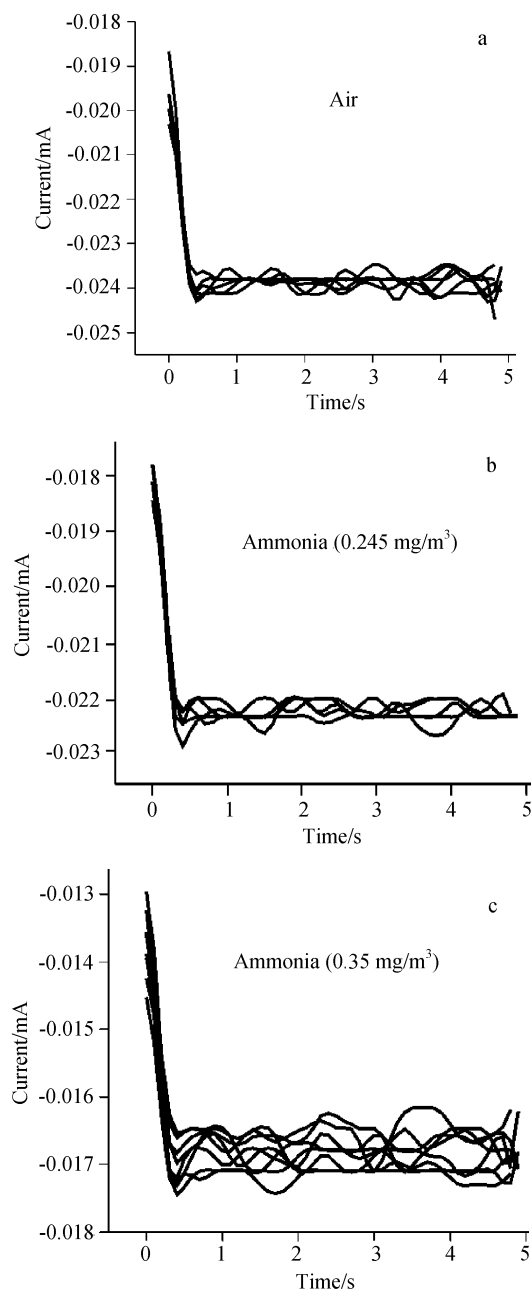
The reproducibility characteristics of this sensor are shown in Figure 7. From these three curves it is known that the sensor based on the WCNF has good reproducibility, not only in air but also in the air filled with low concentration ammonia. The top figure in Figure 7 shows that the current of the film has only 0.35×10^{-3} mA fluctuation at a constant voltage, which was kept during its six discontinuous tests. The middle one in Figure 7 shows that the film current has a 0.34×10^{-3} mA fluctuation in the air filled with 0.245 mg/m^3 ammonia. Comparing the last one in Figure 7 with the others, it can be concluded that the film resistance has a bigger fluctuation in the air filled with 0.35 mg/m^3 ammonia, 0.5×10^{-3} mA, resulting from the repeating adsorption and desorption of more NH_4OH. However, fluctuation of curves can not reflect the reproducibility of the sensor, which can only be reflected by the changes of different curves in different period during the same detection process. So, from Figure 7 we can know that during the same detection process, all the curves have the same changes with the same basic current and the same fluctuation.

When the sensor is exposed to the air again, it will restore to the original level gradually. As shown in Figure 8, the blue curve stands for the restoration curve when the sensor is exposed to the air for 5 s, and other ones are the adsorption curves of the sensor in the air mixed with ammonia. The restoration test was conducted under the same parameters as those in the sensitive experiments. But there are few fluctuations existing compared with above curves. The reason for this is that when the NH_4OH is released in the open environment, it is difficult for the sensor to adsorb the ammonia again avoiding repeating processes of adsorption and desorption on the film surface. Waiting for 1 min, the sensor has restored to the previous state in the pure air. So it is known that this sensor has fast restoration characteristic. As shown in Figure 9, this sensor owns best sensitivity

Figure 7 Current-time characteristics for reproducibility of the thin film sensor in different environment: pure air (a), the air with 0.245 mg/m^3 ammonia (b), and the air with 0.35 mg/m^3 ammonia (c).

Figure 8 Restoration curves of the thin film sensor in the air after 5 s and current-time characteristics of the thin film sensor in the air with different concentration of ammonia: 0.175, 0.245 and 0.35 mg/m^3 (other three curves).

to ammonia, 16.6×10^{-3} mA, compared with those of sulfurated hydrogen and toluene at the concentration of 0.35 mg/m^3, 1.36×10^{-3} mA and 0.565×10^{-3} mA. So it can be concluded that this thin film sensor based on WCNF owns good selectivity to ammonia over sulfurated hydrogen and toluene.
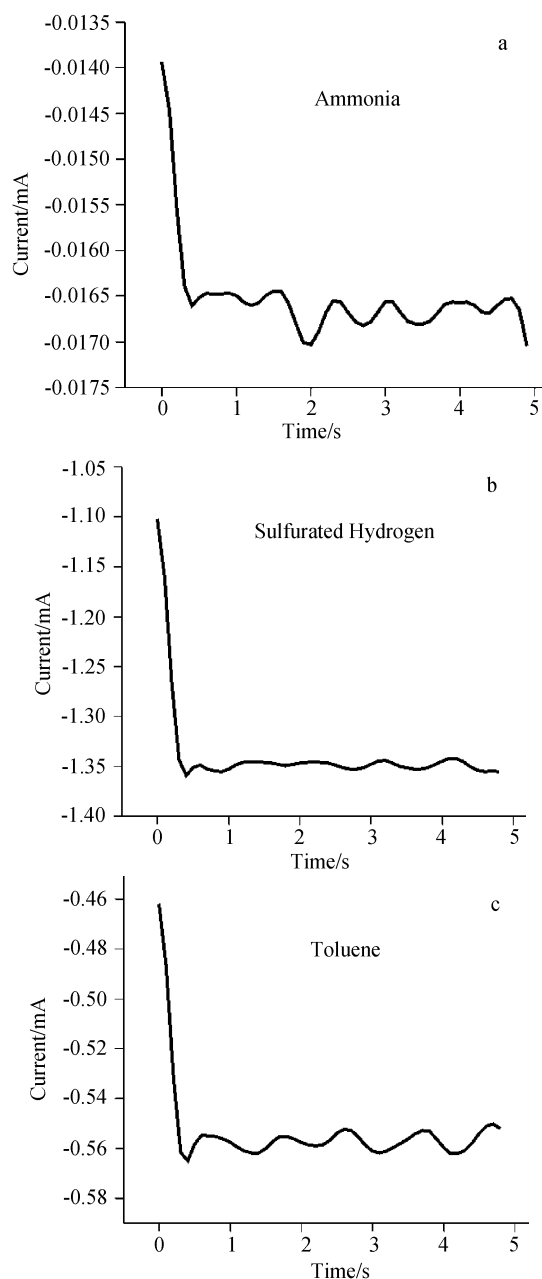
Conclusions

At the beginning of this study, the iron catalysts were synthesized using a sol-gel method, with uniform morphology and diameter of 15 nm. Using these perfect catalysts, the WCNF was synthesized with an economi-

cal method. The thin film sensor based on the WCNF was fabricated to detect ammonia, and the sensitivity, reproducibility, response and restoration characteristics of the sensor were tested using the low single-potential signal in atmospheric pressure at room temperature. Especially, the sensor was tested under the same simulated environment as the actual environment, in which the sensor worked in the air considering the influence of water molecules and oxygen. All the results suggest that the sensor has high sensitivity at low concentration (0.175 mg/m^3), perfect reproducibility, a fast response time (0.05 s) and restoration time (1 min). Although it is the first step for the use of solid carbon nanofibers as the sensitive material to detect deleterious gas, the results show that WCNF is a better candidate for the sensitive material to detect ammonia. Furthermore, we believe that this sensor can be scaled down to length dimensions on the order of micrometers

Figure 9   Current-time characteristics of the thin film sensor to different gases: the air with 0.35 mg/m^3 ammonia (a), the air with 0.35 mg/m^3 sulfurated hydrogen (b), and the air with 0.35 mg/m^3 toluene (c).

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