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Abstract

Ferriprotoporphyrin IX chloride (haemin)-functionalized Al-doped zinc oxide (ZnO) is used for nitric oxide (NO) sensing at room temperature. The devices show high selectivity to NO against CO_2 and O_2. There is no such selectivity without haemin. Porous ZnO film made by a polystyrene sphere template is used to provide a high surface area. In comparison with non-porous ZnO film with low surface area, both the sensitivity and the response speed of the sensor made by porous ZnO are clearly improved. NO concentration down to 1 ppm can be detected. The response time is 20 s. The sensor is reversible after purging with pure nitrogen for about 100 s. Such a device is able to detect real-time variation of NO which is a vital physiological signalling molecule.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nitric oxide (NO) is a key signalling molecule in the cardiovascular system. NO controls the relaxation of vascular smooth muscle, the inhibition of platelet aggregation and immune regulation [1]. It has been reported that less than 1 μM of NO generated in endothelium cells suffices to influence the blood pressure [2]. Hence NO sensor is extremely valuable for physiological studies. In addition to aqueous NO, it is important to detect the gas phase NO in the breath of patients for asthma attack prevention [3]. Study of NO gas released from the heart is also known to be important for medical research. It is therefore highly desirable to develop a real-time, chemically selective, solid-state and low-cost NO gas sensor operated at room temperature. NO gas sensor using GaAs as the active semiconductor has been reported [4]. The high cost of the compound semiconductor fabrication, however, makes it unlikely to be disposable as usually required for biochemical sensors. Transition metal oxide semiconductor is one of the earliest discovered gas-sensing semiconductors [5]. Some gas

sensors based on ZnO nanorods, SnO_2 nanowires and In_2O_3 nanowires have been fabricated [6–8]. These nanorod sensors have good response and recovery characteristics due to their ultrahigh surface to volume ratio, but they are not convenient for low-cost production. Other works on ZnO gas sensor are based on the low-cost solution process. However, most ZnO sensors are sensitive to different gases and not selective for a particular target gas [9, 10]. Temperature is carefully controlled to achieve selectivity for certain gas at certain temperature [11]. So far there is no report on a highly selective NO sensor based on solution-processed semiconductors.

In this work we develop a NO gas sensor using solution-processed aluminium-doped ZnO film surface-functionalized by the probe molecule haemin which has a particularly strong affinity to NO [12]. ZnO films can be naturally functionalized by haemin with the reaction between hydroxyl group (–OH) on the ZnO surface and carboxyl group (–COOH) of haemin. In order to increase the surface area the ZnO film is made porous by a template technique where films with three-dimensional periodic submicrometre spherical voids are arranged in a close-packed structure [13]. ZnO films are doped with Al by a

sol–gel method [14] with the advantages of surface evenness and fabrication simplicity.

The promises of the combination of ZnO and haemin can be understood from the electronic structure point of view. The conduction band of ZnO is mainly composed of the 4s orbitals of zinc. The n-doping and therefore the conductance of ZnO is highly sensitive of the surface conditions including oxygen deficiency and other defects. On the other hand, there is a iron ion at the centre of the haemin molecule with partially filled 3d orbital which is almost resonant in energy to the nearly empty 4s orbitals in ZnO. It is well known that iron ions have a few oxidation states very close in energy. There is therefore an easy electron transfer between the 4s orbitals in the n-doped ZnO and the iron 3d orbitals in haemin when they are in proximity. The electron affinity of haemin can be modulated by NO attachment because NO has a unpaired electron and an electron withdrawing tendency. The enhanced electron affinity of the iron ion by NO favours electron transfer from ZnO to haemin. Such characteristics of ZnO manifests as a reduced conductance ultimately caused by NO attachment.

We demonstrate that the conductance of the aluminium-doped ZnO functionalized by haemin has high sensitivity to NO down to the ppm level. There is a rapid response to the change in the NO concentration in a few seconds. The device is therefore able to achieve real-time detection of NO variation occurring within a small time scale at room temperature. The sensor has a high selectivity against other common gases in air including CO_2 and O_2. There is no such selectivity for devices made with bare ZnO without haemin as expected.

2. Experimental

Zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot H_2O$] and aluminium nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] are chosen as the starting materials. 2-propanol and ethanolamine are used as solvent and stabilizer, respectively. Zinc acetate dihydrate and aluminium nitrate nonahydrate are first dissolved in a mixture of 2-propanol and ethanolamine solution at room temperature. The dopant level is maintained at 1% and the concentration of zinc acetate is 1 M. The solution is stirred for 2 h to yield a clear and homogeneous solution, which serves as the precursor solution. For the preparation of porous Al-doped ZnO films, dispersed polystyrene (PS) spheres of 200 ± 10 nm diameters are first spin-coated on cleaned glass substrates and preheated at 115 °C for 5 min on a hotplate to remove residual solvents and obtain a self-assembled arrangement. And then the porous and non-porous devices are fabricated in the same processes with or without the PS spheres, respectively. First, the precursor solution is spin-coated onto the substrates at 3000 rpm for 30 s. The gel layers are then preheated at 100 °C for 5 min on a hotplate to evaporate the solvent and remove organic residuals. Second, these films are annealed at 450 °C in air to remove the PS spheres for the porous devices. The thickness for all samples is about 320–350 nm. Aluminium source–drain contacts are thermally evaporated on top of the porous and non-porous Al-doped ZnO surface using a shadow mask with the drain/source electrodes of 50 μm channel length and 2 mm width. These devices are surface-functionalized by
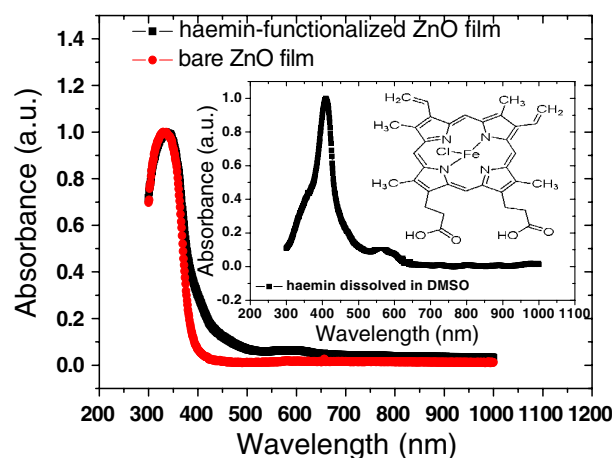

Figure 1. The absorption spectrum of the bare and haemin-functionalized ZnO samples. Inset shows the absorption spectrum of haemin dissolved in DMSO.

submerging them into a 1 mM haemin solution for 1 h. The solvent is dimethyl sulfoxide (DMSO). Finally, these samples are thoroughly washed by DMSO and de-ionized water, in sequence, and then dried in air at 110 °C. Sample is then loaded into the gas-sensing chamber as soon as possible. The life time of the haemin-functionalized sensor is about 3 h when it is exposed to air. All the materials and solvents are purchased from Aldrich.

Chemical bonding between haemin and ZnO is analyzed by ultraviolet (UV) absorbance. Surface morphology of the porous and non-porous ZnO film is examined by a JSM-7401F field emission scanning electron microscope. Electrical sensing characteristics of these devices are examined by a gas-sensing system. Various NO concentration is obtained by uniformly mixing various amount of NO (from a cylinder contains 1000 ppm NO) with high pure nitrogen (N_2) in a small mixing chamber. The amounts of NO and N_2 sending into the mixing chamber are separately controlled by mass flow controllers (MFCs). The gas inlet pipe ended with a nozzle inside the measuring chamber is just above the sample, and the distance between the nozzle and sample is no longer than 10 mm. NO at certain concentration spurt from the nozzle is therefore dominates the gas environment surround sample. The volume of the measuring chamber will not affect the NO concentration surround sample. A constant voltage of 1 V is applied to the sensor, and current is measured by a Keithley 2400 source meter. High purity nitrogen gas continuously passes into the gas-sensing chamber and maintain a constant flow rate of 1 SLM (standard litre per minute) during gas-sensing measurement.

3. Results and discussion

The absorption spectra of the bare and haemin-functionalized ZnO sample are shown in figure 1 and the absorption spectrum of haemin dissolved in DMSO is shown in the inset of figure 1. The spectrum of haemin shows two peaks at 407 and 562 nm. The spectrum of haemin-functionalized ZnO sample shows a distinct increase at 400–650 nm compared with bare ZnO
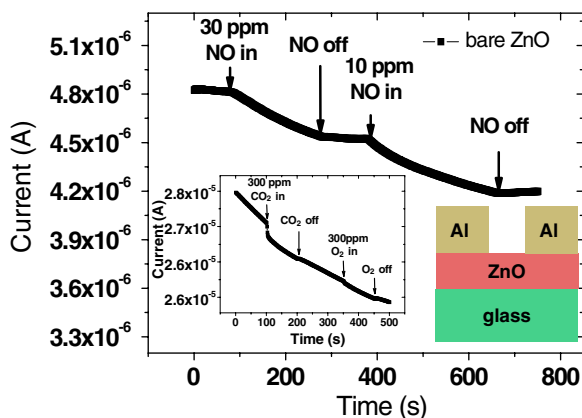
Figure 2. Current of the bare sensor as a function of time exposed to different NO concentrations. Inset shows schematic device structure of a bare ZnO sensor and current of the bare sensor as a function of time exposed to varied gases.

samples. By comparing the shape of haemin-functionalized ZnO and haemin absorption spectra, the increased absorption is consistent with that of haemin. These observations show that the carboxyl group (–COOH) of haemin is chemically bound to the hydroxyl group (–OH) on the ZnO surface.

Electrical current of the bare sensor device as a function of time exposed to different NO concentrations is shown in figure 2. Schematic device structure of a bare ZnO sensor is shown. The current continuously decreases with time during an exposure of 30 ppm NO for 200 s or 10 ppm NO for 280 s. The $\Delta I/I_0$ can be chosen as the sensing response, where $\Delta I = I - I_0$. Here, I and I_0 represent the current values after and before the exposure to gas. The relative responses of bare sensors are 5.8% at 30 ppm NO for 200 s and 7.3 % at 10 ppm NO for 280 s. No saturated current can be obtained for the bare ZnO sensors, and the relative responses also show no correlation with the NO concentrations. In addition, the current of the bare sensor has almost no change after removing NO. The response and recovery of the current is due to the slow adsorption and desorption of nitric oxide molecules on the ZnO surface. The inset of figure 2 shows current of the bare sensor as a function of time exposed to other gases. A similarly low sensitivity for 300 ppm O_2 and CO_2 is obtained. The relative responses of bare sensors are 2.9% at 300 ppm CO_2 and 1.5% at 300 ppm O_2. The slightly higher response to NO may be due to stronger electron transfer from ZnO to NO. However, the difference of response between NO and other gases is not large enough to distinguish NO among all the gases. In other words bare ZnO device is not a selective NO sensor.

Response of haemin-functionalized non-porous Al-doped ZnO sensors at different NO concentrations is shown in figure 3(*a*), and response of porous haemin-functionalized ZnO sensors is shown in figure 3(*b*). The devices are exposed to several cycles of NO concentration variation up to 30 ppm. SEM images of non-porous and porous films are also shown in the upper right corner of figures 3(*a*) and (*b*), respectively. In sharp contrast to the bare devices, the current of haemin-functionalized sensors change significantly with NO concentrations from 1 ppm to 30 ppm and saturates rapidly in a few seconds. The relative current response is 13% at
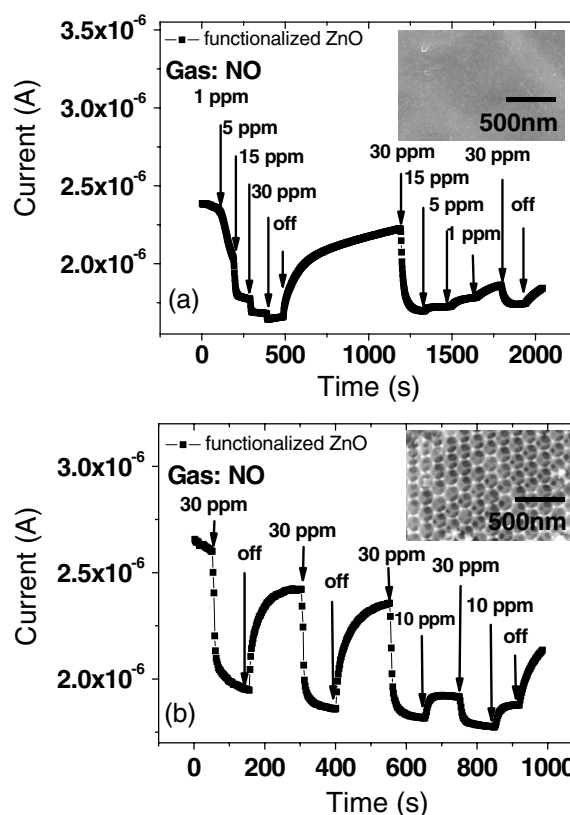

Figure 3. (*a*) Response of haemin-functionalized ZnO sensors at different NO concentrations. (*b*) Response of porous haemin-functionalized ZnO sensors exposed to several cycles of NO concentrations (30 ppm and 10 ppm). Corresponding SEM images of non-porous and porous films are shown in the upper right corner of figure 3(*a*) and (*b*), respectively.

1 ppm, 22% at 5 ppm, 26% at 15 ppm and 30 % at 30 ppm. It takes about 700 s for the device to recover to their initial current after turning off NO. Such gas detection mechanism is attributed to the electron transfer between haemin molecule and ZnO. As NO molecules are captured by haemin, the electron affinity of haemin increases resulting in electron transfer from the conduction band of ZnO to haemin iron level. In addition, the desorption of NO from haemin is much easier than that from bare ZnO, implying it is easier to refresh the sensor with haemin-functionalization. Compared with bare ZnO sensors, haemin-functionalized ZnO sensors improve the sensitivity to NO by the factor of 10 and obtain faster response time. Figure 3(*b*) shows a porous haemin-functionalized ZnO sensors with regularly arranged voids. In comparison with figure 3(*a*) both the sensitivity and response speed are clearly improved. The recovery of porous sensor is in only 100 s. It is much faster than that of non-porous sensor. The current cannot return to its original value when the NO gas was removed. There is a continuous trend towards low conductance values probably due to NO adsorption on the ZnO surface without haemin modification. The performance of porous sensors is improved because of the increase in the surface to volume ratio which allows the gas molecule to diffuse in and out through the void network instead of only through the small grain boundary clefts of non-porous films. In addition, the relative response of non-porous sensors is reduced to 26% and 23% from 30%
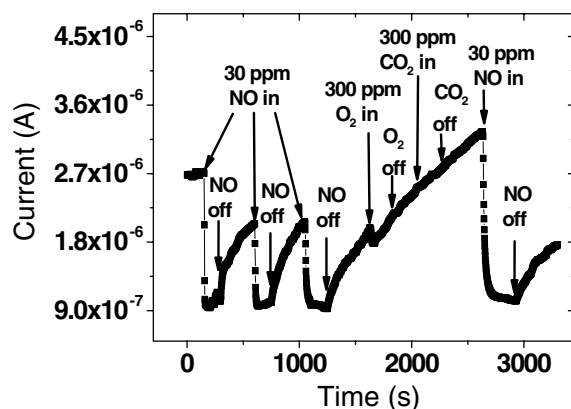
Figure 4. Detection of various gases including several cycles of 30 ppm NO, 300 ppm O_2 and CO_2 for the porous haemin-functionalized ZnO sensors.

in the second and third cycle of 30 ppm NO but maintained at 27% for porous sensors for all cycles. This confirms the higher reversibility and stability of the porous haemin-functionalized ZnO sensors than non-porous sensors.

The selectivity porous haemin-functionalized ZnO sensor is studied for detection of various gases including 30 ppm of NO, 300 ppm of O_2 and 300 ppm of CO_2, as shown in figure 4. It is observed that the sensors are by far most sensitive to NO among these gases. After exposure to 300 ppm CO_2 and O_2 little response is measured. The current continually increases, probably due to the purge effect on haemin sites which were deactivated by some adsorbed chemicals. The response and recovery characteristics are still reproducible when exposed to another cycle of 30 ppm NO. The sensors show high selectivity for NO and can easily distinguish the NO target among common gases in air such as CO_2 and O_2.

4. Conclusion

In conclusion, a zinc oxide semiconductor sensor is developed to detect the gas phase NO, which is a key signalling molecule to control blood pressure and the immune system. The surface of the zinc oxide is chemically functionalized by a probe molecule haemin which enables high selectivity against other common gases in air and breath, high sensitivity down to ppm level, rapid response in a few seconds, and reversibility upon NO removal. Such real-time selective NO sensor will be a vital tool for a wide range of biomedical research and medical diagnosis.

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