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Highly sensitive H_2S sensors based on ultrathin organic single-crystal microplate transistors

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ABSTRACT

Based on ultrathin dinaphtho[3,4-d:3′,4′-d′]benzo[1,2-b:4,5-b′]dithiophene (Ph5T2) single-crystal microplates, the highly sensitive organic field-effect H_2S sensors are realized at room temperature. The response is as high as 1.2×10^6% in 50 ppm H_2S. This value is extremely high for H_2S sensors, and is three orders of magnitude higher than that of the most reported semiconductor gas sensors. The response/recovery time is respectively as low as 2 min and 1 min in 50 ppm H_2S. The detect limitation is as low as 0.5 ppm. The ultrathin single-crystal microplates provide direct and efficient ways for the analytes' activities within the conducting channel, and therefore mainly account for the improved sensing performance. The excellent sensing performance of ultrathin Ph5T2 single-crystal microplate transistors reveals the capacity of developing highly sensitive room-temperature sensors.

1. Introduction

Hydrogen sulfide (H_2S) is one of the most toxic gases in industrial pollution. According to the safety standards established by American Conference of Government Industrial Hygienists, the threshold limit of H_2S is 10 ppm [1]. When the H_2S concentration is higher than 100 ppm, it can lead to losing consciousness or even death. Currently, only a few efforts have been made to develop the semiconductor H_2S sensors. A detailed performance list for the reported semiconductor H_2S sensors is shown in Table S1. The previously reported semiconductor H_2S sensors demonstrated the response at 70–900%, and most of them suffered from a slow response/recovery time of over 10 min. Undoubtedly, higher sensitivity and faster response/recovery rate will significantly increase the credibility and fidelity of sensors [2,3]. Therefore, it is necessary to develop high-sensitivity and fast-response sensors for H_2S detection to protect human lives and environmental safety.

Until now, the H_2S semiconductor sensors are mainly focused on inorganic metal oxide, such as ZnO, WO_3, SnO_2 and In_2O_3. In contrast, the organic sensors show the promising potential in flexible and portable electronics because of their obvious advantages in low cost and light weight [4–8]. As far as we know, there are mainly two groups to study the organic H_2S semiconductor sensors. Tai' group used pristine CuPc thin film as sensitive layer to prepare field-effect gas sensor, which showed the response at 95% and the response/recovery time of about 1 min and 23 min in 200 ppm H_2S [9]. The sensors with field-effect configuration can dramatically enhanced the response by modulation of the gate electrode in the subthreshold regime [10–12]. Aswal' group used gold to modify CoPc film to enhance the response of resistance devices with the response as high as 424% in 10 ppm H_2S [13]. The surface modify of semiconductor can effectively increase the adsorption sites, and further improve the response of sensors.

In this communication, we adopted a new method to improve the response of sensors. Using ultrathin dinaphtho[3,4-d:3′,4′-d′]benzo[1,2-b:4,5-b′]dithiophene (Ph5T2) single-crystal microplates as the sensitive layer and combining with field-effect configuration, the highly sensitive H_2S sensors are realized at room temperature. Ph5T2 gas sensing properties have been studied for the first time. The response is as high as 1.2×10^6% in 50 ppm H_2S. The detect limitation is down to sub-ppm levels (0.5 ppm) with high response (128%). Ultrathin active layer enables the conducting channel to be effectively exposed to analyte molecules, and thus can accelerate the interaction between the conducting channel and analytes [3,14–19]. The excellent sensing performance of our ultrathin

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Ph5T2 transistors shows the capacity of developing highly sensitive semiconductor sensors at room temperature.

2. Experimental section

Based on ultrathin Ph5T2 microplates, organic field-effect transistors (OFETs) with bottom-gate top-contact configurations were fabricated by the "gold film stamping" method [20]. Ph5T2 single crystal microplates were fabricated by physical vapor transport method as previously described [21]. The PMMA in anisole was spin-coated onto the surface of the Si substrate as the dielectric. PMMA was spin coated at 4000 rpm for approximately 40 s followed by thermal annealing at 100 °C for 5 min. The thickness of PMMA insulation layer is ~300 nm. Dielectric capacitance is generally ~10 nFcm^{-2}. Then the ultrathin Ph5T2 microplates and the Au films were successively transferred on the PMMA/Si substrate with the mechanical probe. The field-effect and the gas response properties of the devices were recorded with a Keithley 4200 SCS in a homemade stainless steel chamber at room temperature. Pure dry N_2 and H_2S were accurately controlled by gas flow meters (Beijing Sevenstar Electronics Company, D07-19B), and introduced to the chamber through stainless tube. SEM images were obtained on a Philip XL30 instrument. AFM measurements were carried out on a SPA400HV instrument with a SPI 3800 controller (Seiko Instruments).

3. Results and discussion

Selection of appropriate organic semiconductor is crucial for obtaining high-performance gas sensors. In our experiments, Ph5T2 is selected as the active layer to detect toxic gas due to its excellent field-effect performance and good air stability [21,22]. In addition, its single crystals are plate-like and possess ultrathin crystal thickness (<20 nm), which enables the conducting channel of OFETs to be effectively exposed to analyte molecules. According to the previous reports, Li et al. used a structured ultrathin organic thin film of dialkyl tetrathiapentacene (DTBDT-C6) to realize high-performance field-effect ammonia sensors with the sensitivity of 1000 under the concentration of 100 ppm [3]. Yang et al. compared the gas sensing characteristics of 4 molecular layer (ML) and 50 ML cobalt phthalocyanine (CoPc) transistors, and found that the 4 ML devices show faster response times, higher base line stabilities, and sensitivity enhancements for organic analytes [14]. Therefore, using Ph5T2 ultrathin single crystals as sensitive layer probably realize the high-performance gas sensors.

Ph5T2 single-crystal microplates were grown by a physical vapor transport technique. Its molecular structure is shown in Fig. 1a, which comprises of seven fused rings, two α-position fused naphthyl terminals and a benzene-thiophene alternating central unit. Fig. 1b and c respectively are the scanning electron microscopy (SEM) image and atomic force microscopy (AFM) image of typical Ph5T2 single-crystal microplates. As shown in Fig. 1b, the Ph5T2 single-crystal microplate shows regular hexagon shape and uniform color. The lateral size of ultrathin microplates ranges from several micrometers to tens of micrometers. The AFM results show that the thickness of the microplates less than 20 nm. The thinnest crystal is 9.05 nm thick as shown in Fig. S1. The molecular length of Ph5T2 is 1.805 nm [22], which suggests that the ultrathin microplates consist of only a few to a dozen of molecule layers.

Based on ultrathin Ph5T2 single-crystal microplates, OFETs were prepared on PMMA/Si substrates by the "gold film stamping" method [20]. The detail preparation process of Ph5T2 field-effect transistors (FETs) is in the experimental section. Fig. 2a and b respectively show the schematic and SEM image of the device. As known to all, the excellent stability of devices is a basic premise for

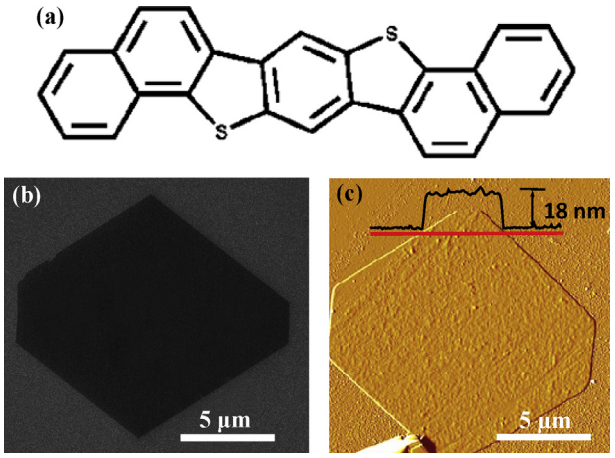

Fig. 1. (a) The molecular structure of Ph5T2. (b, c) Typical SEM and AFM image of ultrathin Ph5T2 microplates.

their practical applications as sensors [11]. Fig. 2c and d are the multi-measured transfer curves of a Ph5T2 device in air and N_2, respectively. The multi-measured results show the excellent stability with completely overlapped transfer curves either in air or N_2. In addition, all the fabricated transistors exhibit well-defined field-effect behavior and the clear p-type characteristics. According to transfer curves, we calculated the field-effect performance of devices in the saturation regime. The mobility and ON/OFF current ratio range for 15 individual transistors are 0.018–0.43 cm^2 V^{-1} s^{-1} and 10^6 to 10^7 at room temperature in air, respectively.

The schematic diagram of the gas detecting is shown in Fig. 3. The chip with Ph5T2 single-crystal transistor was put in the stainless testing chamber. Its leading wires were connected to the Keithley 4200-SCS semiconductor characterization system. The whole testing system is connected with stainless tube in order to maintain its seal characteristic. Before the gas detection, dry N_2 (99.999%) was introduced to the chamber through the stainless tube over one hour to remove the air. In order to ensure the stability of the Ph5T2 device, its field-effect performance was first measured in N_2 about half an hour. Then, different concentration of H_2S was introduced to the chamber and diluted with N_2. The flow rate of N_2 and H_2S was accurately controlled by mass flow meters.

The gas sensing properties of ultrathin Ph5T2 microplates FETs for a certain concentration of H_2S gas (50 ppm) were tested at room temperature in dark. Fig. 4a shows a schematic image of a field-effect sensor based on the ultrathin Ph5T2 microplate and the adsorption of H_2S gas on microplate surface in ambient N_2 environment. Fig. 4b and c displays the typical transfer curves of the device for 50 ppm H_2S gas. Field-effect sensors over resistor sensors are the current modulation by the extra gate electrode which can dramatically enhance the sensitivity in the subthreshold regime. In order to clearly observe the change of the source-drain current (I_{SD}) in the subthreshold regime, the vertical axis of transfer curve becomes logarithmic coordinates (Fig. 4c). After exposure to 50 ppm H_2S gas, I_{SD} rapidly decreases over three orders of magnitude. As known to all, H_2S is a reductive gas. Thus H_2S molecule can act as a π-electron donor at the process of charge transfer interaction [23]. Ph5T2 is a p-type organic semiconductor and its conducting carrier is a hole. When H_2S molecules adsorb on the active layer of Ph5T2, they inject electrons to Ph5T2 semiconductor. The donated electrons combine with hole in Ph5T2 and trap carriers resulting in the decrease of carrier density and I_{SD}. Turning off the H_2S stream and using a 365 nm UV irradiation for 10 s results in a quick recovery of I_{SD} to the initial range. The band gap of Ph5T2 is 3.04 eV and it is a