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A Room-temperature Hydrogen Gas Sensor Using Palladium-decorated Single-Walled Carbon Nanotube/Si Heterojunction

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We report a room-temperature (RT) hydrogen gas (H_2) sensor based on palladium-decorated single-walled carbon nanotube/Si (Pd-SWNTs/Si) heterojunction. The current-voltage (I-V) curves of the Pd-SWNTs/Si heterojunction in different concentrations of H_2 were measured. The experimental results reveal that the Pd-SWNTs/Si heterojunction exhibits high H_2 response. After exposure to 0.02 %, 0.05 %, and 0.1 % H_2 for 10 min, the resistance of the heterojunction increases dramatically. The response is 122 %, 269 % and 457 %, respectively. A simple interfacial theory is used to understand the gas sensitivity results. This approach is a step toward future CNTs-based gas sensors for practical application.

Keywords: gas sensor, carbon nanotube, heterojunction.

1. INTRODUCTION

Due to its high efficiency, renewable properties, and for being environmentally friendly, hydrogen gas (H_2) provides an enormous potential solution to the current and future energy supply and environmental challenge [1]. However, H_2 is a colorless and odorless gas, with a wide explosive concentration range (4 – 75 %) at standard atmospheric pressure. Therefore, to ensure the safety of its generation, transport and storage, an H_2 sensor that can detect and monitor H_2 leakage is required [2]. Various metal-oxide semiconductors, such as SnO_2 [3], have been selected to fabricate H_2 sensors, which require better performance at high temperatures, resulting in high power consumption and difficulty in integration. So, it is essential to select suitable materials for fabricating H_2 sensors for detecting the content of hydrogen at room temperature (RT) in the development of a hydrogen energy industry [4].

Carbon nanotubes (CNTs) have attracted significant interests as a promising chemical sensing material because of their inherent properties such as its extremely small size, high strength, high electrical and thermal conductivity, and high specific surface area [5]. Recent studies show that CNTs-based gas sensor can effectively detect polar molecules at RT, such as ammonia gas (NH_3) and nitrogen dioxide (NO_2) because the electrical conductivity of CNTs changes drastically upon exposure to these gases [6, 7]. However, CNTs are insensitive to most nonpolar molecules including H_2. Pd is considered to be an attractive H_2 sensing material because of its superior H_2 solubility at RT. In recent years, Pd as catalyst decorated on CNTs (Pd-CNTs) for H_2 sensor have been reported, and most of them are Pd-CNTs resistance-type [8]. A typical Pd-CNTs resistance-type consists of one or several pairs of electrodes that make electrical contact with the Pd-CNTs film. A change in the electrical resistance of the Pd-CNTs film upon exposure to H_2 is measured as the output signal [9]. The advantages of resistance-type H_2 sensor include low power consumption and simple operation. However, the gas response of Pd-CNTs resistance-type H_2 sensors is not high enough for excellent gas sensors.

In this paper, we fabricated Pd nanoparticles decorated single-walled carbon nanotube/Si (Pd-SWNTs/Si) heterojunction H_2 sensor. It is found that H_2 molecules have a dramatic effect on the current-voltage (I-V) characteristics of the Pd-SWNTs/Si heterojunction at RT. Upon exposure to 0.02 %, 0.05 % and 0.1 % H_2 at RT, the interface resistance of the heterojunction is found to dramatically increase to about 122 %, 269 % and 457 %. The results show that the heterojunction has very high H_2 gas response than that of CNT-based resistance-type H_2 sensors reported previously.

2. MATERIALS AND EXPERIMENTS

Carboxylic acid functionalized SWNTs (Length: 30 μm, -COOH content: 2.73 wt., purity: > 90 %) were purchased from the Xian Feng Nano Company and used without further purification. Palladium chloride ($PdCl_2$, purity: > 99.9 %) was purchased from Aladdin Inc. The mixed cellulose esters (MCE) filter membranes were purchased from Whatman Inc.

Pd-SWNTs was prepared according to a method reported previously [10, 11]. Typically, 6 mg of carboxylic acid functionalized SWNTs and 20 mg $PdCl_2$ were added to 20 ml of deionized water and sonicated for 60 min. Subsequently, 5 ml of aqueous solution of sodium borohydride ($NaBH_4$) (0.01 M) was added dropwise to the mixture as a reductant for $PdCl_2$ for 20 min to obtain Pd-SWNTs. Then, the aqueous suspension of the as-prepared Pd-SWNTs solution was magnetically stirred for two hours after adding 475 ml deionized water. Lastly, a few drops of Triton X-100 surfactant were added to disperse further Pd-SWNTs into deionized water.

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The Pd-SWNTs/Si heterojunctions were obtained by a filtration and transfer printing method [12]. Typically, 10 ml of the as-prepared Pd-SWNTs solution was vacuum filtered through a mixed cellulose ester membrane and then a thin Pd-SWNTs film was attached on it. Both p-type and n-type Si wafers were used as substrates for transfer printing of the Pd-SWNTs films. The mixed cellulose ester membranes with Pd-SWNTs films on them were placed on the Si substrates. Then, a compressive force was applied on the mixed cellulose ester membranes during baking in an oven at 80 °C for two hours to stabilize the adhesion of the Pd-SWNTs film to the substrates. Finally, the mixed cellulose ester membranes were dissolved by acetone, thus the Pd-SWNTs/Si heterojunction were fabricated.

3. EXPERIMENTAL RESULTS

Fig. 1 shows the typical scanning electron microscopy (SEM) image of the as-prepared Pd-SWNTs film on Si substrate. As seen, the film is networks constituted by randomly oriented Pd-SWNTs bundles.

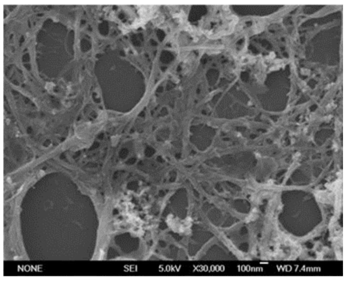


Fig. 1. SEM image of Pd decorated SWNTs film on Si substrate

The I-V curves of the Pd-SWNTs/p-Si and Pd-SWNTs/n-Si heterojunctions in the air are shown in Fig. 2. All H_2 sensing experiments were investigated by exposing the heterojunctions to various concentrations H_2. The gas concentration was obtained by injecting a required quantity of H_2 gas into a homemade test chamber with the air. The I-V characteristics of the Pd-SWNTs/Si heterojunctions were measured by using the two-probe method with a Keithley 2400 sourcemeter.

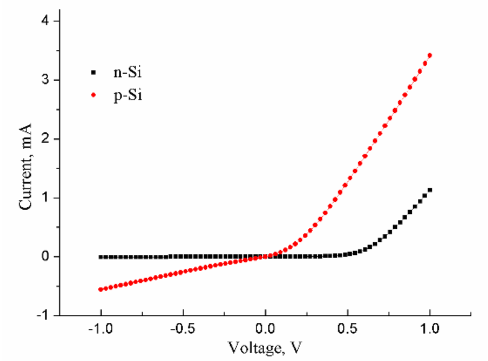
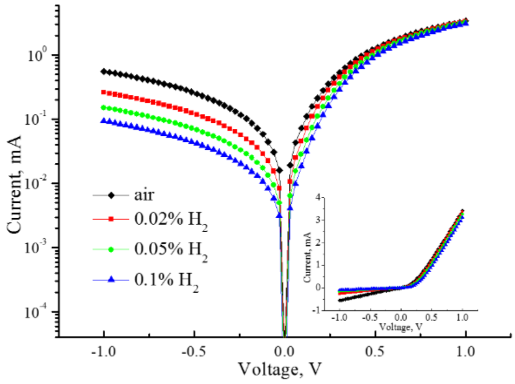


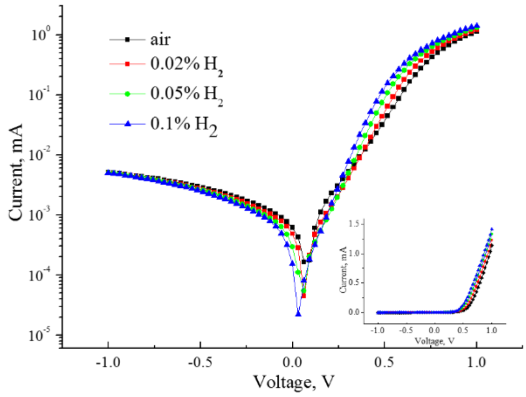
Fig. 2. The I-V curves of the Pd-SWNTs/n-Si and Pd-SWNTs/p-Si heterojunction in the air

As can be seen, the I-V curve of the Pd-SWNTs/n-Si heterojunction in the air shows a good rectifying behavior [13]. As can be seen, by contrast, the I-V curve of the Pd-SWNTs/p-Si heterojunction in the air shows a poor rectifying behavior with a big leakage current under reverse bias voltage [14]. The current rectification ratio at a bias voltage of ± 1 V of the Pd-SWCNT/n-Si heterojunction in the air is about 220 while the current rectification ratio of the Pd-SWCNT/n-Si heterojunction is only 6.

The semi-logarithm plots for the I-V curves of the Pd-SWNTs/p-Si and Pd-SWNTs/n-Si heterojunctions in the air, 0.02 %, 0.05 %, and 0.1 % H_2 are shown in Fig. 3.



a



b

Fig. 3. Semi-logarithm plots of measured I-V curves of: a – the Pd-SWNTs/p-Si; b – Pd-SWNTS/n-Si heterojunctions in the air, 0.02 %, 0.05 % and 0.1 % H_2. The insets show the I-V curves of the corresponding heterojunction

The insets show the I-V curves of the corresponding heterojunctions. As can be seen in Fig. 3 a, it is found that H_2 has an obvious effect on the I-V curves of the Pd-SWNTs/p-Si heterojunction. When the Pd-SWNTs/p-Si heterojunction is exposed to H_2, the currents decrease with increasing H_2 concentration. Relatively, the change of the reverse current is higher than that of the forward current, leading a better rectifying behavior. The current rectification ratio at ± 1 V is 13, 21 and 33 when the Pd-SWNTs/p-Si heterojunction is exposed to 0.02 %, 0.05 %, and 0.1 % H_2, respectively, at RT. Differently from the case of the Pd-SWNTs/p-Si heterojunction, as can be seen in Fig. 3 b, the reverse current decreases when the Pd-SWNTs/n-Si heterojunction is exposed to H_2 while the forward current does not always increase or decrease with increasing H_2 concentration. These phenomena could be understood by the interfacial effects between Pd-SWNT film and Si substrate. When the Pd-SWNTs/Si heterojunction are exposed to H_2, Pd nanoparticle absorbs H_2 molecules, which will lower the work function of Pd nanoparticle, leading to the enhanced Fermi level of Pd-SWNTs film. For the Pd-SWNTs/n-Si (p-Si) heterojunction, the energy difference between Fermi levels of the n-Si (p-Si) and the Pd-SWNTs will decrease (increase). Thus, the potential barrier height between the Pd-

SWNTs film and the n-Si (p-Si) substrate will decrease (increase) [13, 14]. According to the reference [15], this leads to the increase (decrease) of the currents. At the same time, the electrons from Pd nanoparticles trap and neutralize the hole-carries in SWNTs, which increases the resistance of Pd-SWNTs film and the series resistance of the Pd-SWNTs/p-Si heterojunction [16]. That is, when the Pd-SWNTs/p-Si heterojunction is exposed to H_2, the change of barrier height leads to a decrease in the current, and so does the change of series resistance, which is always synergistic in the case of Pd-SWNTs/p-Si heterojunction. However, it is always adverse in the case of the Pd-SWNTs/n-Si heterojunction. When the Pd-SWNTs/n-Si heterojunction is exposed to H_2, the change of barrier height leads to an increase in the current, but the change of series resistance leads to a decrease in the current [16]. The current of the Pd-SWNTs$_2$/n-Si heterojunction will increase if the effect of barrier height is dominant. Meanwhile, the current will decrease if the effect of series resistance is dominant, as shown in Fig. 3 b.

Compared to the Pd-SWNTs/p-Si heterojunction, the currents of the Pd-SWNTs/n-Si heterojunction show smaller changes, indicating the former have a higher H_2 response. So we selected the Pd-SWNTs/p-Si heterojunction to examine further the dynamic sensing performance. The dynamic responses of the Pd-SWNTs/p-Si heterojunction at a reverse bias voltage of – 1 V is shown in Fig. 4. The response is defined as:

$$\Delta R/R_{air} = \left(R_{H_2} - R_{air}\right)/R_{air}, \quad (1)$$

where R_{air} and R_{H_2} are the resistances of the sensor before and after exposure to H_2, respectively. As can be seen in Fig. 4, after exposure to 0.02 %, 0.05 %，and 0.1 % H_2 for 10 min, the resistance of the heterojunction increases dramatically. The response is 122 %, 269 % and 457 %，respectively. The Pd-SWNTs/p-Si heterojunction shows very high H_2 response, which is superior to those of CNT-based resistance-type H_2 sensors reported previously. For example, Aguilar et al. got a response of 40 % to 3.3 % H_2 with Pd-SWNTs at RT and Gong et al. got a response of 115 % to 0.15 % H_2 with SWNTs/SnO_2 nano composites at 200 °C [17, 18].

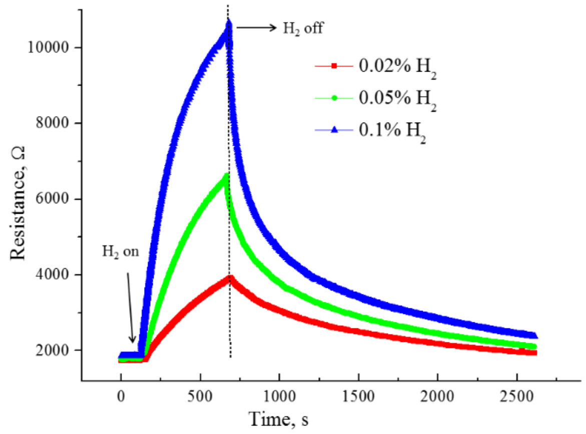


Fig. 4. Dynamic responses to 0.02 %, 0.05 % and 0.1 % H_2 of thePd-SWNTs/p-Si heterojunction at a reverse bias voltage of – 1 V at room temperature

4. CONCLUSIONS

In conclusion, we have developed high response room temperature H_2 gas sensors based on the Pd-SWNTs/Si heterojunction. The response is 122 %, 269 % and 457 % after exposure to 0.02 %, 0.05 %，and 0.1 % H_2 for 10 min, respectively. This will facilitate the development of a new type of sensing platform.

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