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Co-porphyrin–functionalized CVD graphene ammonia sensor with high selectivity to hydrogen.

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Abstract

Recently low-power, small gas sensors have been strongly demanded to realize "super smart society". In particular, ammonia sensors are expected to be key devices for breath diagnosis as well as livestock farming. However, it is difficult for ammonia sensors to obtain high selectivity against hydrogen, since conventional metal-oxide gas sensors respond to any reducing gases. In this study, Co-porphyrin–functionalized graphene sensors were fabricated, and it is shown that the sensors respond not to hydrogen but to ammonia because of the selective metal-ligand bond of Co with ammonia. The sensor successfully detected sub-ppm ammonia, while it showed no response to 400-ppm hydrogen.

1. Introduction

Low-power, small gas sensors, which detect low-weight molecules selectively in complex gas mixture, should be essential components enabling "super smart society". Among these gas sensors, sensors which can selectively recognize low-concentration ammonia (NH_3), are strongly demanded because of potential applications such as breath diagnosis and livestock farming. It is reported that exhaled breath of patients with end-stage renal failure contain mean NH_3 concentration of 4.88 ppm [1], whereas NH_3 with concentration of less than 1 ppm is contained in exhaled breath of healthy person. To measure NH_3 in exhaled breath, we need to have a gas sensor that is not affected by hydrogen (H_2), since the dynamic range of hydrogen in breath is very large; hydrogen concentration in breath ranges from a few ppm to hundreds ppm [2]. Conventional ammonia sensors utilize a sensing mechanism based on redox reaction of platinum or palladium [3,4]. Therefore, these gas sensors inevitably suffer from low selectivity between NH_3 and H_2. To overcome this low-selectivity issue, NH_3 sensors, which utilize a metal-ligand bond of Co with ammonia as a sensing mechanism, were fabricated and demonstrated.

In this work, 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt (II) (CoOEP)- functionalized Chemical Vapor Deposition (CVD) graphene substrates were used. We demonstrated the superiority of CoOEP functionalized graphene sensor in terms of sensitivity and selectivity over non-functionalized, pristine graphene sensors.

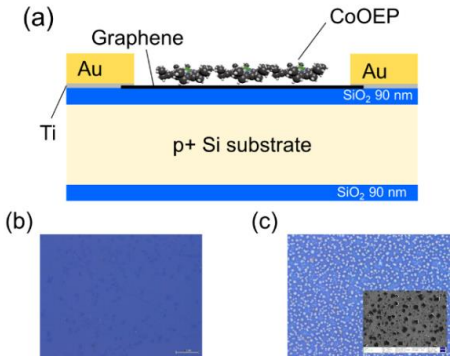

Fig. 1: (a) A cross-sectional schematic of CoOEP –functionalized graphene sensor. Optical images of graphene before CoOEP functionalization (b) and after CoOEP functionalization (c). A SEM image CoOEP functionalized graphene is shown in the inset of (c).

2. Device Fabrication

A CVD graphene on thermally oxidized Si substrate was purchased from Graphene Platform [5]. The oxide thickness was 90 nm. After cleaning in acetone and 2-propanol, electrodes were formed by electron-beam deposition of Ti/Au with a shadow mask. A schematic diagram of the device structure is shown in Fig. 1(a). To functionalize the CVD

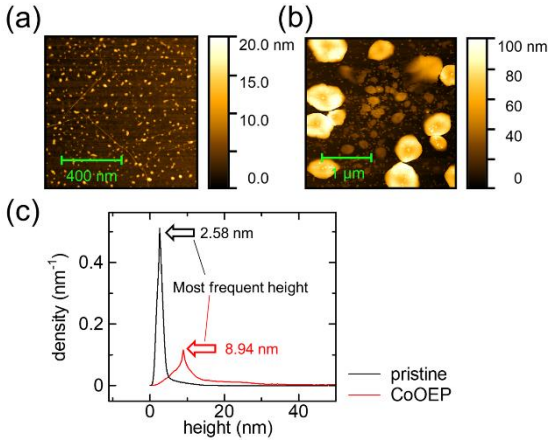

Fig. 2: (a) AFM image of pristine graphene. (b) AFM image of CoOEP – functionalized graphene. (c) Comparison of height distribution before and after functionalization.

graphene, CoOEP saturated chloroform solution was spin-coated onto the graphene. Optical microscope images of the graphene before and after CoOEP functionalization are shown in Figs. 1(b), (c).

The size and morphology of CoOEP was characterized by AFM. The top views of AFM are shown in Figs 2(a) and (b). A comparison of the height distribution before and after functionalization is shown in Fig. 2(c). The height distribution peak shift after functionalization indicates that CoOEP was functionalized to graphene, which induces the surface roughness.

3. Results and Discussion

Fig.3 (a) shows the typical time dependence of sensor response to target gas. The sensor response was defined as

$$(\text{Sensor Response}) = \frac{R - R_0}{R_0} = \frac{\Delta R}{R_0}, \qquad (1)$$

where R was the time dependent resistance and R_0 was the initial resistance at the time when the device started to be exposed to the target gas.

Fig.3 (b) shows the comparison of sensor responses to 2-ppm NH_3 between the CoOEP–functionalized graphene and a pristine graphene. The sensor response of CoOEP-functionalized graphene was approximately six times greater than that of the pristine graphene. The improvement of the sensor response originates from a difference in binding energy to NH_3 between functionalized and pristine graphene films. The calculated binding energy of a pristine graphene to NH_3 is 0.11 eV [6], whereas that of Co porphyrin is 0.21 eV [7]. The larger binding energy resulted in a greater adsorption of NH_3 to CoOEP- functionalized graphene, and thus the sensor response was improved.

Fig.3 (c) shows time-dependent sensor responses of CoOEP-functionalized for various NH_3 concentrations ranging from 0.04 ppm to 0.79 ppm. The concentration of NH_3

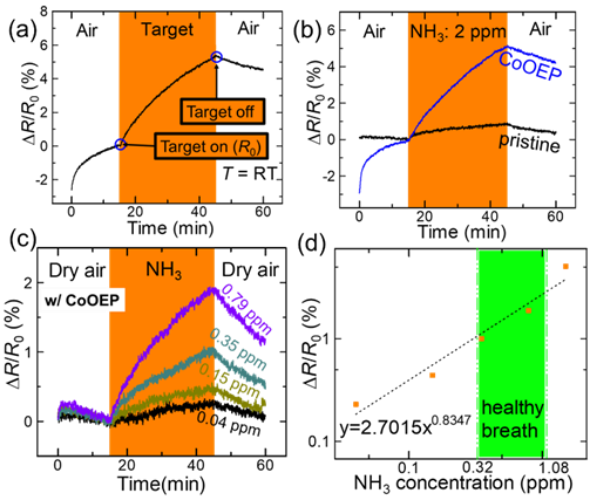

Fig. 3: (a) Typical gas sensing response. (b) A comparison of gas sensing properties. (c) NH_3 concentration dependence of the sensor response. (d) Relationship between the sensor response and NH_3 concentration.

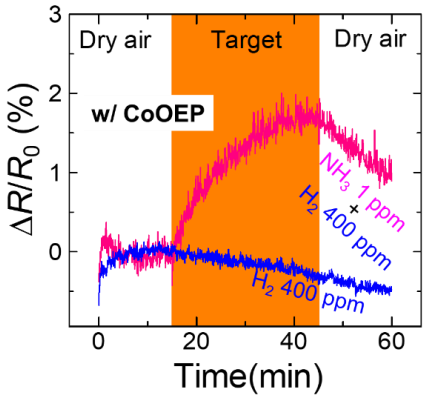

Fig. 4: Selectivity of the CoOEP – functionalized graphene device to NH_3 against H_2.

was determined from gas chromatography. Even at the lowest NH_3 concentration of 0.04 ppm, a clear sensor response of 0.23 % was observed.

Fig.3 (d) shows the NH_3 concentration dependence of the sensor responses. The relationship is fitted by the function: $2.7x^{0.835}$, where x is the NH_3 concentration in ppm unit. Exhaled breath of healthy human contains NH_3 with concentrations ranging from 0.32 to 1.08 ppm [8]. Thus, our sensor showed enough sensitive to NH_3 for breath ammonia detection.

However, human breath contains several hundred ppm H_2; H_2 can be disturbing gas for accurate detection of NH_3, because both H_2 and NH_3 are reductive. Fig.4 shows the selectivity of the CoOEP–functionalized graphene sensor. Our sensor did not show any response to H_2. Even under atmosphere where H_2 concentration was four hundred times greater than NH_3 concentration, our sensor successfully recognized low-concentration NH_3.

4. Conclusion

In summary, the CoOEP–functionalized graphene sensor fabricated in this work successfully recognized low-concentration (1 ppm) ammonia without any response to 400-ppm H_2, which is enabled by selective metal-ligand bond of Co to ammonia. The sensor can operate with extremely low power and will play an important role in “super smart society”.

Acknowledgements

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