Chemiresistive H₂O₂ gas sensors based on graphene decorated with Cu₂O nanowires and a protective PVP layer

Oleksandr Ovsianytskyi^{1,2}, Oleksii Ohiienko³, Yun S. Nam⁴, Oh Young-Jei³, Aleksander Gurlo², Kang B. Lee¹

¹Green City Technology Institute, Korea Institute of Science and Technology, Hwarang-ro 14 gil 5, Seoul 02792, Republic of Korea

² Fachgebiet Keramische Werkstoffe / Chair of Advanced Ceramic Materials, Technische Universitaet Berlin, Berlin 10623, Germany

³ Opto-electronic materials and devices research center, Korea Institute of Science and Technology
Hwarang-ro 14 gil 5, Seoul 02792, Republic of Korea

⁴ Computational Science Center, Korea Institute of Science and Technology Hwarang-ro 14 gil 5, Seoul 02792, Republic of Korea Email: O.Ovsianytskyi@ceramics.tu-berlin.de

Abstract:

In this study, we demonstrate H_2O_2 gas sensing with a single-layer graphene decorated with Cu_2O nanowires (Cu_2ONWs) and a protective PVP layer. Single-layered graphene was grown using chemical vapor deposition (CVD) technique, the Cu_2ONWs were synthesized hydrothermally. The composite has been characterized using AFM, SEM, EDS, XPS and TEM. The average diameter of Cu_2ONWs is 35 nanometers with (111) and (220) crystallographic planes. The functionalization of graphene with Cu_2ONWs nanowires has modified the electronic properties of graphene, achieving a drastic resistivity change in the presence of H_2O_2 gas. This allows for real-time monitoring of low levels (below 1 ppm) of H_2O_2 at ambient temperature with a fast response and recovery time.

Key words: CVD graphene, chemiresistive sensors, H₂O₂ sensing, copper oxide nanowires.

Introduction

Hydrogen peroxide (H_2O_2) is one of the strongest oxidizers known, being used as a disinfectant and a bleaching agent. A concentration of 75 ppm is considered to be immediately dangerous to human life and the safe concentration is typically <1 ppm. Therefore, the detection of low levels of H_2O_2 gas is a crucial issue for the keeping the working personal safe from harmful hydrogen peroxide vapors.

Our goal was to develop an efficient, cost-effective, highly sensitive and selective sensor for real-time monitoring of H_2O_2 gas. We have chosen graphene for this study since it can be produced in large quantities with good repeatability of results, and it is very stable under harsh environments and can effectively work under room temperature.

Recent DFT (Density Functional Theory) calculations revealed that pristine graphene is not suitable for proper H_2O_2 detection, but defects can slightly improve its sensing ability

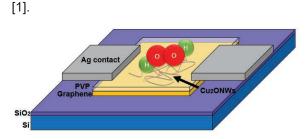


Fig. 1. Schematic representation of the sensor studied in this work

Furthermore, doping with transitional metals can drastically increase graphene sensitivity towards H_2O_2 gas. Particularly, Ag and Cu provide -3.94 and -4.01 eV binding energies with towards hydrogen peroxide, respectively, [2]. Thus, our goal was to develop an effective sensor according to these theoretical investigations.

Experimental

Monolayer graphene was grown using typical CVD route on the 25 μm thick Cu foil which was

chemically cleaned from contaminations and oxides. After the synthesis process, the monolayer graphene was transferred onto Si/SiO₂ substrate.

Cu₂ONWs were hydrothermally synthesized from a mixture of EG with CuCl and NaCl. The resulting precipitation was cleaned several times with acetone and chlorobenzene. Subsequently, Cu₂ONWs were dispersed with IPA and mixed with PVP which is well known for its surface protective applications [3]. Finally, for the preparation of "doped" graphene sensors the Cu₂ONWs-PVP solution was placed onto graphene-Si/SiO₂ substrate using a spin-coating method and baked for 30 min at 80°C.

Results and discussion

We used a common chemiresistive approach to detect gaseous H₂O₂. Thus, the concentrations of our analyte can be quantified by measuring the change of sensor's resistance as a function of time. Fig. 2 represents the reference response of a pristine graphene and a graphene-Cu₂ONWs-PVP composite towards 5 ppm H₂O₂.

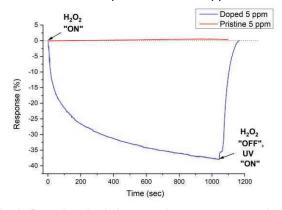


Fig. 2. Doped and pristine sample response towards 5 ppm H_2O_2 gas.

The resistance change of graphene doped with Cu_2ONWs was observed to be -37% after 1000 sec exposure time in comparison to +0.5% of pristine graphene. Our graphene- Cu_2ONWs -PVP composite sensor has shown relatively fast relaxation time (~100-200 sec) under 254 nm UV light illumination. Sensor's response as a function of H_2O_2 concentration is presented in the Fig. 3, with the response measuring time

decreasing for higher concentrations (~1000 sec for 1-5 ppm and ~850 sec for 25 ppm).

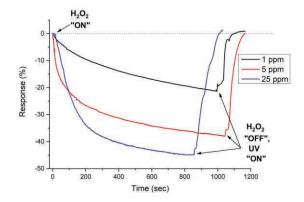


Fig. 3. Sensor's response to different H_2O_2 concentrations.

Conclusion

This study shows that a graphene- $Cu_2ONWs-PVP$ composite can be a suitable choice for sensing gaseous H_2O_2 . The comparison between pristine and doped samples has shown a dramatic increase in the response value. The PVP protective layer prevents access of H_2O from the atmosphere to the surface of the sensor, which can lead to involuntary the formation of hydroxides on the surface of the sensor, as well as averts other contaminations.

References

- [1] G. Luque, M. Rojas, G. Rivas, E. Leiva, The origin of the catalysis of hydrogen peroxide reduction by functionalized graphene surfaces: A density functional theory study, *Electrochimica Acta*, 56 (2010), 523–530, DOI:10.1016/j.electacta.2010.09.016
- [2] D. Düzenli, A Comparative Density Functional Study of Hydrogen Peroxide Adsorption and Activation on the Graphene Surface Doped with N, B, S, Pd, Pt, Au, Ag, and Cu Atoms, *J. Phys. Chem. C*, 120 (2016), 20149–20157, DOI: 10.1021/acs.jpcc.6b06131
- [3] J. Yan, G. Zou, A. Wu, J. Ren, A. Hu, N. Zhou, Polymer-Protected Cu-Ag Mixed NPs for Low-Temperature Bonding Application, *Journal of Elec. Mater.* 41 (2012), 1886, DOI:10.1007/s11664-012-2008-7