Chemiresistive H$_2$O$_2$ gas sensors based on graphene decorated with Cu$_2$O nanowires and a protective PVP layer

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Abstract:
In this study, we demonstrate H$_2$O$_2$ gas sensing with a single-layer graphene decorated with Cu$_2$O nanowires (Cu$_2$ONWs) and a protective PVP layer. Single-layered graphene was grown using chemical vapor deposition (CVD) technique, the Cu$_2$ONWs were synthesized hydrothermally. The composite has been characterized using AFM, SEM, EDS, XPS and TEM. The average diameter of Cu$_2$ONWs is 35 nanometers with (111) and (220) crystallographic planes. The functionalization of graphene with Cu$_2$ONWs nanowires has modified the electronic properties of graphene, achieving a drastic resistivity change in the presence of H$_2$O$_2$ gas. This allows for real-time monitoring of low levels (below 1 ppm) of H$_2$O$_2$ at ambient temperature with a fast response and recovery time.

Key words: CVD graphene, chemiresistive sensors, H$_2$O$_2$ sensing, copper oxide nanowires.

Introduction
Hydrogen peroxide (H$_2$O$_2$) 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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ detection, but defects can slightly improve its sensing ability [1].

Furthermore, doping with transitional metals can drastically increase graphene sensitivity towards H$_2$O$_2$ 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/SiO\textsubscript{2} substrate.

Cu\textsubscript{2}ONWs were hydrothermally synthesized from a mixture of EG with CuCl and NaCl. The resulting precipitation was cleaned several times with acetone and chlorobenzene. Subsequently, Cu\textsubscript{2}ONWs 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 Cu\textsubscript{2}ONWs-PVP solution was placed onto graphene-Si/SiO\textsubscript{2} substrate using a spin-coating method and baked for 30 min at 80\textdegree C.

**Results and discussion**

We used a common chemiresistive approach to detect gaseous H\textsubscript{2}O\textsubscript{2}. 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-Cu\textsubscript{2}ONWs-PVP composite towards 5 ppm H\textsubscript{2}O\textsubscript{2}.

![Fig. 2. Doped and pristine sample response towards 5 ppm H\textsubscript{2}O\textsubscript{2} gas.](image)

The resistance change of graphene doped with Cu\textsubscript{2}ONWs was observed to be -37\% after 1000 sec exposure time in comparison to +0.5\% of pristine graphene. Our graphene-Cu\textsubscript{2}ONWs-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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} concentrations.](image)

**Conclusion**

This study shows that a graphene-Cu\textsubscript{2}ONWs-PVP composite can be a suitable choice for sensing gaseous H\textsubscript{2}O\textsubscript{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\textsubscript{2}O 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**

