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Experimental Study on PEDOT: PSS Conductive Polymer and N-doped Graphene Quantum Dots for H_2O_2 Sensing

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Abstract

The detection of hydrogen peroxide (H_2O_2) is considered important in various fields. This work described a resistive H_2O_2 sensor without using an enzyme, based on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and N-doped graphene quantum dots (N-GQDs) composite on a transparent and flexible substrate. Using the drop-cast method, the uniform film was deposited onto interdigitated aluminum electrodes. The mechanism of H_2O_2 detection and reason for the use of GQDs have been explained. On exposure to 9 M H_2O_2, the sensing response obtained was 27.54%.

Keywords : *PEDOT:PSS, N-GQDs,* H_2O_2

1. Introduction

Sensors are applied in many fields including environmental control, industrial production, food process control and medicine [1], [2]. Recently, conductive polymers have been used for the fabrication of various sensors, for example detection of hydrogen peroxide (H_2O_2) uusually produced in enzymatic reactions [3]. H_2O_2 is not only produced in this way but also as a mediator in food, pharmaceutical, industrial, environmental analyses and other fields [4]. H_2O_2 detection is used to assess the safety and quality of pharmaceutical and cosmetic formulations [5]. Many methods have been used for H_2O_2 determination such as spectrometry [6], chemiluminescence [7], and electrochemical technique based on horseradish peroxidase (HRP) enzyme [8]. Since materials used for immobilization of enzymes may prevent electron transfer [9], thus in this study, a H_2O_2 sensor was designed that does not use enzyme and its immobilization. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is one of the conductive polymers that has been investigated for use as chemical and biological sensors [10], [11], [12]. Graphene composites with conductive polymers could enhance

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sensing properties due to superior conductivity, high stability and good biocompatibility [4]. To make the use of graphene easier in nanodevices, an offer is the conversion of two-dimensional (2D) graphene to 0D graphene quantum dots (GQDs) [13]. The dispersion of GQDs in common solvents is one of its advantages in various solution-processable applications [14]. GQDs are considered due to low cost [15], low toxicity and environmental compatibility [16]. Nitrogen substitution in the GQDs lattice produces more active sites which can be used in various fields including sensors [17].
This study is the first to assess the use of PEDOT:PSS and N-doped GQDs (N-GQDs) composite, as a resistive H_2O_2 sensor. In fact, this sensor shows the presence of H_2O_2 by film resistance change.

2. Experimental

In this study, N-GQDs were synthesized by hydrothermal processing. The details of synthesis of the N-GQDs is explained in a previous publication by the authors [18]. The PEDOT:PSS aqueous solution (1.3 wt% dispersed in H_2O, conductive grade) was purchased from Sigma-Aldrich. The N-GQD solution was combined with 50 wt% PEDOT:PSS solution and a homogeneous dispersion was obtained after stirring for 2 h. this dispersion was considered as the sensing film.
Polyethylene terephthalate (PET) was used as a flexible substrate. Aluminum interdigitated electrodes with a width of 200 µm were deposited on the substrate. Thereafter, 6 µL N-GQDs/PEDOT:PSS composite was drop casted on the electrodes. After drying in the oven, the sensing film thickness was about 3 µm. Finally, the sensor was placed in the test chamber and its resistance was measured. A schematic picture of the fabricated sensor is shown in Fig. 1.

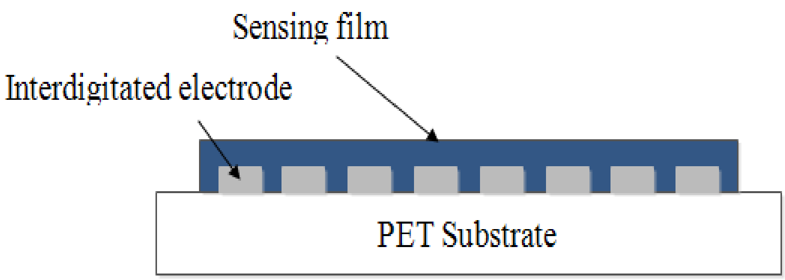

Fig. 1 : Schematic picture of the sensor structure.

3. Results and Discussion

Fourier transform infrared spectroscopy (FT-IR) of N-GQDs/PEDOT:PSS is shown in Fig. 2. The bands at 3452.6, 1638.23 and 1261.9 cm^{-1} are attributed to the stretching and bending vibration of -OH groups, C=C stretching and C-O-C stretching vibration, respectively. The π-electrons exist in both N-GQDs and PEDOT:PSS. This suggests the presence of $\pi - \pi$ interactions between them [16, 19].

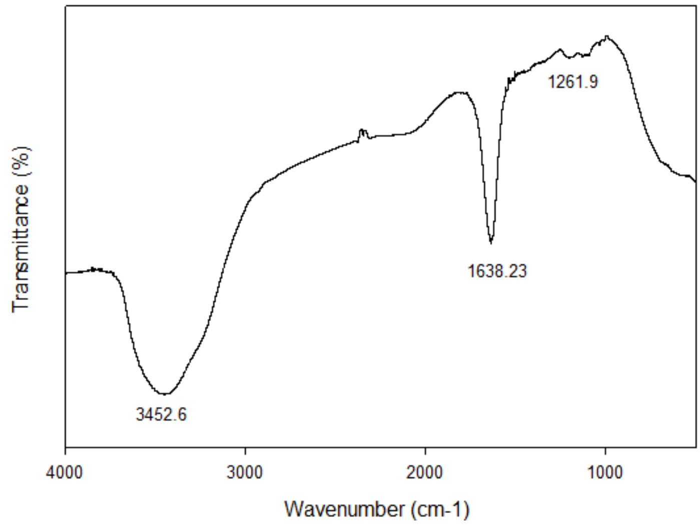

Fig. 2 : FTIR spectra of N-GQDs/PEDOT:PSS.

Upon exposure to 9 M H_2O_2, the N-GQDs/PEDOT:PSS sensor resistance increased from 2.07 to 2.64 kΩ. PEDOT:PSS was reported as a resistive humidity sensor by Taccola et al. [20], who observed that the resistivity of PEDOT:PSS increased exposure to moisture, it relates to the swelling of the polymer (PSS) by absorption of water. Graphene/PEDOT:PSS as an ammonia detector has also been reported, and it has been shown that the swelling process occurs in the presence of this gas [19]. Swelling causes a reduction in connection between PEDOT chains (acting the role of conduction in PEDOT:PSS), reduces electron hopping and increases sensor resistance [19], [20]. Also, alcohols (e.g. methanol, ethanol and etc.) prevented the electrical connection between the PEDOT islands [21], [22].

All the gases and vapors contained above are the same, in terms of containing hydrogen. Therefore, one proposed mechanism of H_2O_2 detection is the separation of conductive pathways (including N-GQDs and PEDOT) as a result of the placement of H_2O_2

molecules between them as a screen (Fig. 3). Therefore, the resistance of the sensing film increases.

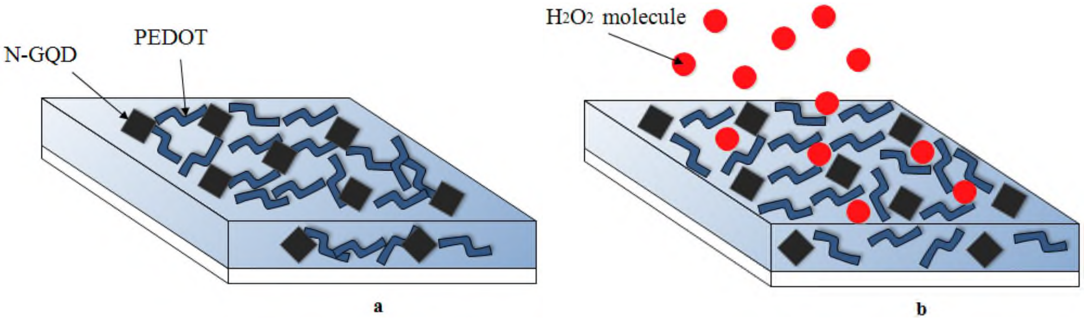

Fig. 3 : Schematic picture of the sensor
(a) before and (b) after exposure to H_2O_2.

It is known that hydrogen is a reducing gas and donates electrons to the sensing film during adsorption. The electrons recombine with the holes and increase the resistance of a p-type semiconductor [23], [24]. Since H_2O_2 contains hydrogen, it is expected that a reduction/oxidation reaction occurs between PEDOT:PSS and H_2O_2. It can be another possible mechanism for H_2O_2 sensing which is in accordance with the reaction given in Eq. (1) [25]:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (1)$$

Since the sensing film is a p-type material, the carrier concentration decreases when the electrons of H_2O_2 analyte interact with the holes of sensing film. Therefore, the electrical resistance increases.

Graphene has a large surface area and thus, enhances the sensing response of the sensor [26] which is calculated with the equation:

$$\text{Sensing response\%} = \frac{(R_{H_2O_2} - R_{air})}{R_{air}} \times 100 \quad (2)$$

where R_{air} and $R_{H_2O_2}$ are the sensor resistance in pure air and in the presence of H_2O_2, respectively. The sensing response of the N-GQDs/PEDOT:PSS sensor was obtained as 27.54%, on exposure to 9 M H_2O_2. The advantages of this sensor include good sensing response, low cost and simplicity of manufacturing process and measurement.

Moreover, the larger surface area of graphene causes the reaction to be faster and easier between the sensing film and analyte, so the response time decreases [27]. The response time obtained was 480 s for the N-GQDs/PEDOT:PSS sensor and it is expected to decrease as the sensing film thickness decreases [28].

4. Conclusions

In summary, this study describes a H_2O_2 sensor without using enzyme. The sensor was fabricated by PEDOT:PSS conductive polymer and N-GQDs. It showed a response of 27.54% upon exposure to 9 M H_2O_2 for 480 s. The advantages of this sensor include good sensing response, easy fabrication, flexibility, low cost and biocompatibility. In addition, reduction reaction and swelling process were explained as possible mechanisms for H_2O_2 sensing.

5. References

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