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Ambient Chemiresistive Sensing of Hydrogen Peroxide Based on PEDOT:PSS/PEDOT Film

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Abstract: Compared with other gas-phase analytes, the coexistence and competing effect of moisture component has long faced great difficulty and technical challenge for the reliable detection of chemically oxidizing active H_2O_2 vapor (HPV). Recently, our group designed and prepared a chemiresistive sensor based on conductive films of poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and PEDOT:PSS/PEDOT to achieve direct detection of HPV at ppm level. Specially, the hydrophobic PEDOT layer was polymerized on the surface of the PEDOT:PSS film by electrochemical method to attenuate the adverse effect of moisture within HPV on the stability and detection performance of the sensing film of PEDOT:PSS/PEDOT.

Keywords: chemiresistive sensor; hydrogen peroxide; PEDOT:PSS; PEDOT; gas detection

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1. Introduction

Hydrogen peroxide (H_2O_2) is a colorless and transparent aqueous solution with a weak odor. It is widely used as an environmentally friendly and efficient oxidation and disinfection agent with many domestic, industrial and environmental applications [1]. HPV is a volatile matter of hydrogen peroxide, which has two components: oxidative H_2O_2 and moisture. However, in view of the differences in diffusion degree and exposure time, the strong oxidizing properties of H_2O_2 may still cause corrosion and irritation to human skin, eyes and mucous membranes, and the oxidative stress generated by free radicals after H_2O_2 entered the human body may lead to cellular damage and disease, accelerate the aging of the human body and cause respiratory diseases, inflammatory diseases, cancers, and so on. The threshold value of the H_2O_2 is a limit of 1.0 ppm and the short-term exposure (15 min) limit is 2.0 ppm, which is stipulated by the American Conference of Governmental Industrial Hygienists (ACGIH) [2]. Moreover, its oxidative function depends on the coexisting moisture but moisture will inevitably affect its accurate detection. Therefore, compared with other gas-phase analytes, the reliable detection of HPV faced great difficulties.

In view of the preparation of gas sensors, the detection sensitivity and response speed of analyte were often improved by adjusting the microstructure and porosity of gas-sensitive films. Constructing a composite material system with controlled structural morphology was an effective way to improve sensor response [3]. The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) film polymerized by electrochemical mean has certain porosity, which can improve the adsorption capacity of gas molecules, thereby improving the performance of sensor [4]. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) has the advantages of excellent film processing under wide selectable range of film formation techniques, high tolerance for the choice of substrate, high film conductivity, and easier compositing with other materials, etc. [5]. And it has been investigated for the detection of H_2O_2 in liquid phase systems by electrochemical methods [6], in our work, PEDOT:PSS film was evenly coated on the ITO conductive glass substrate with the commercially purchased aqueous dispersion (CLEVIOS™ PH1000) through a desktop coater, and the properties of the film were controlled by spin coating conditions, parameters and drying conditions index. PEDOT:PSS/PEDOT composite films were prepared on the basis of above-prepared PEDOT:PSS films, which were used as working electrodes, by building a three-electrode electrochemical experimental apparatus and using an electrochemical workstation to electropolymerize EDOT monomer by the chronoelectric method. For comparison, PEDOT film was also prepared by electrochemically polymerizing EDOT under the same electrolyte systems. Finally, the resistance signal response of these films to HPV was tested and analyzed contrastively.

2. Results and Discussion

In order to evaluate the sensing response of these PEDOTs-based sensing films to HPV, a self-made test device system (**Figure 1**) was built [6]. PEDOT:PSS film was successfully used as a chemiresistive probe for HPV sensing, which can meet the concentration and response time of the H_2O_2 threshold limit.

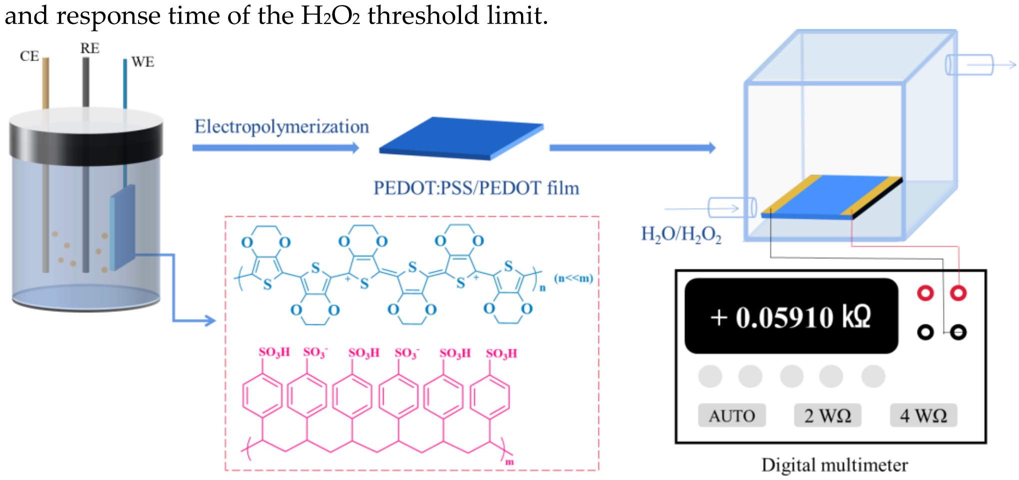

Figure 1. Schematic diagram of the device used to evaluate the HPV sensor.

In comparison, PEDOT films have certain hydrophobicity and satisfied porous morphology, and thus the effect of moisture on the structure and HPV response of the gas-sensitive film can be attenuated, and the sensing performance of the gas-sensitive film for HPV can be improved. After exposure to HPV, the resistance of the PEDOT film continued to increase with exposure time, and the value of the change in PEDOT film resistance decreased with decreasing HPV concentration (**Figure 2a**). For the response to HPV at a concentration of 1.9 ppm, the resistance of the PEDOT:PSS film reached the first peak in 12 min, which was able to meet the safety threshold (2.0 ppm, 15 min) (**Figure 2b**). Compared to the PEDOT:PSS film, the PEDOT:PSS/PEDOT composite film showed an approximately 97% improvement in resistance response to HPV at the same concentration (**Figure 2c**). In contrast, the effect of HPV at a low concentration of 1.0 ppm on the resistance value of the PEDOT:PSS/PEDOT composite film of HPV adsorption and resistance response ($\Delta R/R_0$) were in an unsaturated state for a given detection time (50 min, 0.72), but still exhibited a nearly 89% higher resistance response compared to the PEDOT:PSS film (50 min, 0.38) (**Figure 2d**). Due to the simultaneous existence of PEDOT:PSS and PEDOT, although the resistance signals of PEDOT:PSS film were still affected by moisture, the PEDOT layer on its surface can partly protect it from interference and provide increased contact area and diffusion channel to enhance the adsorption rate of HPV and correspondingly improve the signal response.

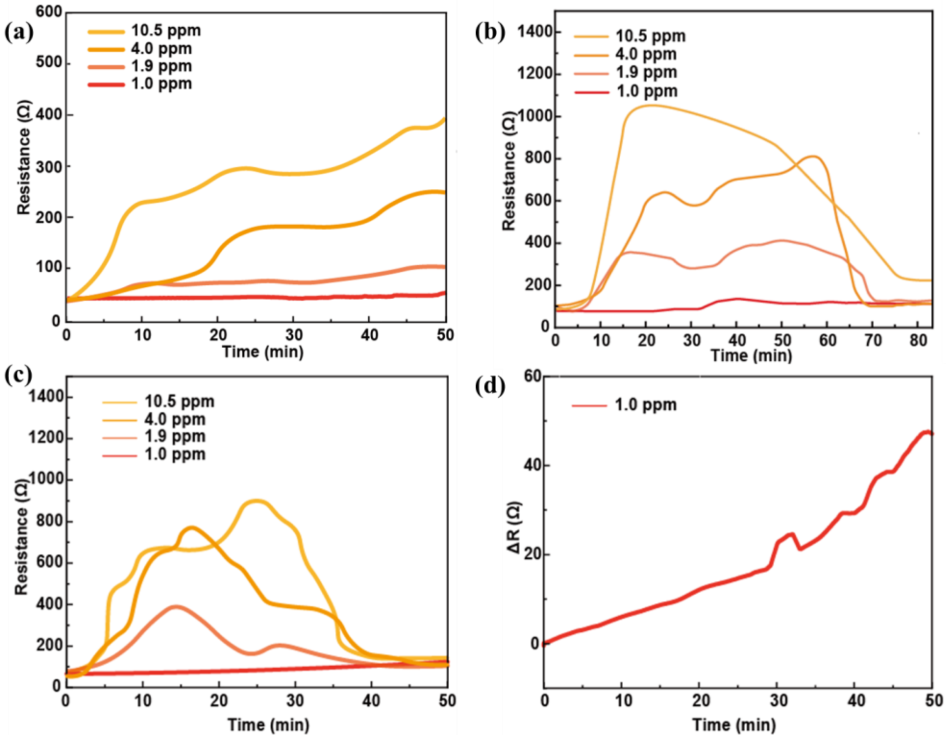

Figure 2. (a) Resistance-time curve of PEDOT film to different concentrations of HPV; (b) Resistance-time curve of PEDOT:PSS film to different concentrations of HPV; (c) Resistance-time curve of PEDOT:PSS/PEDOT (30 mC) composite film to different concentrations of HPV and (d) Resistance change-time curve of PEDOT:PSS/PEDOT (30 mC) composite film to 1.0 ppm HPV.

3. Conclusions

In summary, PEDOT:PSS/PEDOT films were prepared by quantitative deposition via electrochemical polymerization, and the effect of surface loading of PEDOT was systematically investigated on the electrical properties, moisture stability and response of PEDOT:PSS, as well as the resistive signal response to HPV. The results demonstrated the effectiveness and availability of all-organic semiconductor films for nonenzymatic sensing of chemically active gases or even under high moisture environment. In the future, the rich structural design and processing methods of PEDOTs-based materials can be used to regulate and optimize the composite systems themselves and their sensing performance from various aspects. Moreover, it is also worth developing PEDOTs-based sensing systems with dual or multiple signal responses to enhance the accuracy and reliability for HPV detection.

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References

1. Berger, D.; Gundermann, G.; Sinha, A.; Moroi, M.; Goyal, N.; Tsai, A. Review of aerosolized hydrogen peroxide, vaporized hydrogen peroxide, and hydrogen peroxide gas plasma in the decontamination of filtering facepiece respirators. *Am. J. Infect. Control*, **2022**, *50*, 203–213.
2. Dewey, H.M.; Jones, J.M.; Keating, M.R.; Budhathoki-Uprety, J. Increased use of disinfectants during the COVID-19 pandemic and its potential impacts on health and safety. *ACS Chem. Health Saf.*, **2022**, *29*, 27–38.
3. Chen, S.; Slattum, P.; Wang, C.Y.; Zang, L. Self-assembly of perylene imide molecules into 1D nanostructures: Methods, morphologies, and applications. *Chem. Rev.*, **2015**, *115*, 11967–11998.
4. Dunst, K.; Karczewski, J.; Jasi ´nski, P. Nitrogen dioxide sensing properties of PEDOT polymer films. *Sens. Actuators B Chem.*, **2017**, *247*, 108–113.
5. Gao, N.; Yu, J.Y.; Tian, Q.Y.; Shi, J.; Zhang, M.; Chen, S.; Zang, L. Application of PEDOT:PSS and its composites in electrochemical and electronic chemosensors. *Chemosensors*, **2021**, *9*, 79.
6. Xie, X.W.; Gao, N.; Zhu, L.; Hunter, M.; Chen, S.; Zang, L. PEDOT:PSS/PEDOT film chemiresistive sensors for hydrogen peroxide vapor detection under ambient conditions. *Chemosensors*, **2023**, *11*, 124.