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Flexible Perylene Tetracarboxylic Diimide–Poly (3,4−Ethylenedioxythiophene) (PTCDIs@PEDOT) Films with Interpenetrating P−N Heterojunction and Their Gas Sensing Use †

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Abstract: Through the selection of N-type organic semiconductor molecules and the method of supramolecular self-assembly at the solvent phase interface, a perylene tetracarboxylic diimide (PTCDIs) nanofiber film with loose and porous morphology was constructed via in situ deposition on the surface of ITO conductive glass. Then, the P-type organic semiconducting polymer poly(3,4−ethylenedioxythiophene) (PEDOT) was grown in the fiber interweaving network of this film via quantitative electrochemical polymerization, thus preparing a PTCDIs@PEDOT composite film with N−P heterojunction architecture. The composite film has a nanometer-sized N−P heterojunction interpenetrating network structure, which is beneficial for full exposure to and contact of hydrogen peroxide vapor (HPV). The response time is 5.76 min, the recovery time is 5.53 min, and the response to 1.0 ppm concentration of HPV is 1.76. The PTCDIs@PEDOT film has good moisture resistance and improved sensitivity and signal response for gas-phase H_2O_2 detection.

Keywords: P−N heterojunction; PEDOT; PTCDI; gas detection; chemosensor

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1. Introduction

Chemiresistive sensors are widely used in chemical sensing applications. In particular, electrical-signal-based devices with nanostructured semiconductors as sensitive materials have the characteristics of high selectivity and sensitivity for the detection of gas-phase analytes, and have been widely used in the fields of environmental analysis and safety monitoring [1]. Their gas-sensitive performances mainly depend on the composition, type, and shape of the composite materials, and their photoelectricity and other properties. Compared to inorganic or other organic semiconductors, the P-type conducting polymer poly(3,4−ethylenedioxythiophene) (PEDOT) and its water-based machinable composite poly(3,4−ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) have the advantages of good optical thin-film transparency, chemical stability, high conductivity, and biocompatibility, which is one of the focuses of current research in this field [2].

Hydrogen peroxide (aqueous solution of H_2O_2) is widely used as an environmentally friendly and efficient oxidant and disinfectant. Its detection is very important for biological health, environmental safety, the food industry, and other fields. However, due to the coexistence of moisture and oxidation capability, the detection of its gas phase (HPV) has been facing great difficulties. In recent years, our research group has constructed a series of thin-film sensors based on PEDOT, PEDOT:PSS, and their combination with ammonium titanyl oxalate (ATO) to achieve chemical-resistive sensitization detection

of HPV [3,4]. The P−N type heterojunction architectures usually promote the optical absorption and photoelectric response of semiconductor composites, and are therefore widely used in the design of optical, chemosensitive, and other sensing materials [1,5]. Perylene tetracarboxylic diimides (PTCDIs), as typical N-type organic semiconductor materials, have many advantages such as multiple structures and outstanding optical and fiber-based conductive properties, so they are widely used in the fields of fluorescence, colorimetric, and photoelectric sensing to detect liquid- and gas-phase analytes [5–7]. In our research, PTCDI nanofiber films with loose porous morphology were constructed on the surface of ITO conductive glass using a side-chain structure design [8]. Then, PEDOT was grown in the interwoven network via quantitative electrochemical polymerization, and a series of PTCDIs@PEDOT composite films with a P−N heterojunction interpenetrating network architecture were prepared (Figure 1a) [9], and the chemiresistive response to HPV relying on the selected PTCDI molecule was studied.

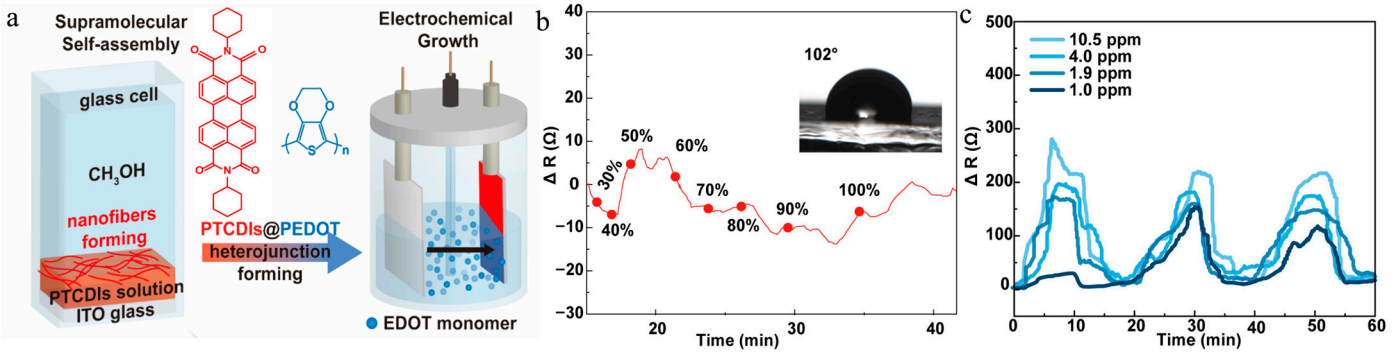

Figure 1. (**a**) Schematic diagram of preparation process of PTCDIs@PEDOT composite film [9]; (**b**) resistance change−time curve of PTCDI@PEDOT heterojunction composite film under increasing ambient humidity (30% RH~100% RH). Inset: surface water contact angle test image of PTCDI@PEDOT heterojunction composite film; (**c**) three-cycle response−recovery curve of PTCDI@PEDOT heterojunction composite film.

2. Experimental

In general, the preparation of the PTCDIs@PEDOT composite film was divided into three stages [9]: (1) selection and synthesis of PTCDIs molecules; (2) a suitable solution-phase supramolecular self-assembly system was designed to prepare porous films with one-dimensional nanofibers of PTCDIs on the surface of an ITO glass electrode; and (3) the PTCDIs@PEDOT films were prepared by using the above thin-film electrode as the working electrode, designing a three-electrode electrochemical reaction system, adjusting the electropolymerization parameters, and realizing the electropolymerization of EDOT.

In view of the need to meet the solution-phase self-assembly and the formation of a stable and orderly one-dimensional nanofiber structure, in this work, one alkane group (cyclohexyl) was selected as the side-chain group of the asymmetric PTCDI molecule. On the surface of ITO conductive glass, pre-configured PTCDI dissolved in $CHCl_3/CH_2Cl_2$ solution was dropped and spread freely, and then CH_3OH was added dropwise to the surface. Finally, the supramolecular self-assembly and mass-transfer processes were driven by the formation of solvent exchange on the surface, and a one-dimensional nanofibrous film of PTCDI was deposited in situ on its surface. The PTCDI@PEDOT composite film was prepared via electrochemical polymerization using a PTCDI nanofiber membrane electrode as the working electrode, Ag/AgCl as the reference electrode, platinum sheet (1.5 cm × 1.5 cm) as the counter electrode, ACN−Bu_4NPF_6 (0.1 M) as the electrolyte, and a concentration of the monomer EDOT (5 mM).

3. Results and Discussion

The structure, morphology, heterojunction interface, and optical, electrical, and electrochemical properties of the composite films were studied in detail using scanning electron microscopy, fluorescence microscopy, UV-vis and FT−IR spectroscopy, and electrical, electrochemical, and spectroelectrochemical methods. Compared to other derivatives [8,9], it was found that the difference in molecular structure has an important impact on the solubility, self−assembly behavior, and aggregate morphology of the selected PTCDI molecules, but its impact on spectroscopy and electrochemical, photoelectric, and other properties is not obvious. PTCDI with cyclohexyl side chains could be dissolved in CH_2Cl_2 solution, and cooperated with PEDOT to form a composite film with a good nanosize and P−N heterojunction interpenetrating network structure, which can be used for HPV detection. Before using the film to detect HPV, its resistance change in an environment of continuously increasing humidity was tested. As shown in Figure 1b, when the humidity in the air chamber changes from 30% RH to 100% RH, the resistance change of the composite film does not exceed ±10 Ω, showing good resistance to moisture during the test. The water contact angle test (Figure 1b inset) shows that the as-prepared composite film (102°) has great surface-wetting resistance. It does not only have good surface wettability, which can partially counteract the interference of moisture on the response of H_2O_2, but it can also ensure the stability of the material during long-term use. The composite film can achieve a detection limit of HPV as low as 1.0 ppm, a response time within 5.76 min, and a recovery time within 5.53 min (Figure 1c). These results may come from the stability of the composite film, the P/N heterojunction structure effect, the porous architecture supported by PTCDI nanofibers, and the unique conductive mechanism of PEDOT.

4. Conclusions

In summary, a special PTCDI@PEDOT porous film with an all-organic P−N type heterojunction architecture has been constructed and was demonstrated to be an effective HPV-sensing material employing a chemiresistive signal. When the indoor humidity rose, the resistance change in the composite film did not exceed 10 Ω, and it was also responsive to HPV concentrations as low as 1 ppm. This research breaks the technical bottleneck of HPV detection, proposes a new strategy for constructing organic semiconductor heterostructures, and expands the application of PEDOT and PTCDIs in the field of chemosensors, which will provide materials, theory, and application bases for further research in the future.

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