Chemiresistive sensors based on Dodecyl benzene Sulfonic acid doped Polypyrrole and Reduced Graphene Oxide for nitrogen oxides

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Abstract. A new series of polypyrrole doped with n-dodecylbenzene sulphonic acid /reduced graphene oxide (PPy-DBSA/rGO) nanocomposite was electrodeposited on Indium tin oxide coated Polyethylene terephthalate (ITO/PET) flexible substrate by electrochemical route using the chronoamperometric technique. As-prepared for testing of chemiresistive properties against the detection of nitrogen dioxide (NO$_2$) vapors at room temperature. The sensitivity and reactivity of the composite toward NO$_2$ was evaluated. The recorded morphological and structural data confirmed that the PPy-DBSA/rGO forms a homogeneous nanocomposite. The optimal NO$_2$ sensing properties have been revealed by the PPy-DBSA/rGO in terms of response (43%), response time (30.25 s), the detection limit (1ppm), and reproducibility. Furthermore, Results showed that the doped by sulfonic acid improved both the sensitivity and the reactivity of our produced nanocomposite toward NO$_2$. Due to the strong interactions between the NO$_2$ gas molecules and the rGO was dramatically enhanced the electronic properties of these nanocomposites. These striking characteristics of the newly developed nanocomposites make them very suitable to be used as NO$_2$ gas sensor.

Keywords. reduced graphene oxide, graphene nanoplatelets,Polypyrrole, NO2 sensing, nanocomposite.

1. Introduction

Nitrogen dioxide gas (NO$_2$) is one of the hazardous environmental pollutants that is caused by the breakdown of ester energetic elements, causing dangerous autoignition under certain conditions [1]. In addition, the rapid sensing of NO$_2$ vapors at a ppm level is strongly recommended to alleviate all of the aforementioned issues and expected disasters [1]. This gas is known for its high toxicity for human health and environment especially when it is contacting oxygen or water, where it can be to provoke respiratory infections that leads to susceptible death [2]. The necessity for detection of this gas at low concentrations grew due to rigorous environmental regulations and the requirement to control emissions from various activities [1].

Metal oxides based NO$_2$ sensors family are widely investigated, where they showed a good stability, altering oxygen stoichiometry, and develop a polarity on its surface in the presence of target gases [3]. However, due to their high operating temperature, the intrinsic resistance drift of MO-based sensors has limited their practical use. therefore, conductive polymers doped with organic surfactants have recently been developed to replace these conventional inorganic semiconductors due to their room temperature sensing ability, high selectivity, improved stability and short response time characteristics [4]. For example, filled and pure conductive polymers of polyaniline, polyphenylene, polythiophene and PEDOT have been widely used for the chemical detection of various hazardous gases.
Polypyrrole (PPy) is getting prominence because of its easy production, excellent electrical conductivity, good reduction-oxidation characteristic, and long ambient life [5]. The morphology, surface area, and electrical properties of PPy can be controlled using different dopants [6,7] such as camphor sulphonic acid (CSA) and dodecylbenzene sulfonic acid (DBSA) to improve the solubility of polymers with high conductivity. To develop novel gas sensors with lower detection limits, faster response times, and higher sensitivity.

However, carbon-based nano-fillers, particularly graphene, is widely used to reinforce PPy conductive polymer doped with sulfonic acid owing to its outstanding feature [7]. Suitable for increasing gas sensing properties. One step synthesis of PPy-graphene nanocomposite doped with DBSA: (i) the exfoliation of reduce graphene oxide with DBSA, when formed electrolyte solution (ii) electrochemically deposition of PPy and graphene loaded with dopant during the electro polymerization reaction. On the other hand, several procedures were adopted for producing PPy-Graphene films nanocomposite, including the in-situ chemical approaches, drop- coating, spin-coating, and dip coating [8]. However, graphene segregation in the polymer matrix is a significant complaint. Thus, the dispersion state of graphene in organic solutions can be promoted by exfoliation using various surfactants such as n-dodecylbenzene sulphonic acid [9]. This exfoliation of reduce graphene oxide in PPy matrix can also have enhanced sensing characteristics of PPy sensors by increasing the surface area and the performance sensorial proprieties. To the aimed to contribute, no previous research has been conducted to investigate the potential of polypyrrole-reduced graphene oxide doped with DBSA nanocomposites as a NO₂ chemiresistive sensor.

Herein, we present a one-step synthesis of PPy-DBSA/reduced graphene oxide nanocomposite materials. Then, a comparison with electrochemically-polymerized PPy-DBSA/rGO nanocomposites films of NO₂ sensing has been made. In addition, the composites were also characterized by Raman, SEM, chronoaamperometry, and conductivity. Finally, several analysis approaches were used to determine the sensor's sensitivity, reaction time, reproducibility and the effect of humidity.

2. Experimental section

2.1 Materials
Pyrrrole (Sigma-Aldrich, purity>98%) was distilled under reduced pressure, and then it was stocked at 4 °C in the dark before synthesis. Organic solvents used as received, and deionized (DI) water was also used. rGO was synthesized by ourselves in the laboratory, dodecylbenzene sulfonic acid (DBSA) was purchased from Sigma Aldrich. All electrochemical measurements were performed using an Autolab 101 type device.

2.2 Methods
Electronic microscopy micrographs were taken on Scanning Electron Microscope (FEI-Quanta 600). Raman spectroscopy was carried out using (Horiba Labram HR evolution), excitation was at 633 nm from He-Ne Laser at room temperature. The four-point probe technique measured the electrical conductivity of films (with a typical probe separation of 1 mm) using the Jandel RM3000 apparatus.

2.3 Electrochemical polymerization
Typically, the PPy-DBSA / rGO processed films were electrochemically deposited on indium tin oxide ITO substrates at room temperature. Using potentiostat- galvanostat type VMP3 -AUTOLAB. They were using constant potential amperometry in a three-electrode electrochemical cell. The electrochemical deposition was done at a potential of 2.5 V with 0.01 mol L⁻¹ DBSA, 0.01 mol. L⁻¹ pyrrole, and 0.5 g. L⁻¹ of the reduce graphene oxide. In a configuration with three electrodes where the ITO substrate constitutes the working electrode, a reference electrode is Ag/AgCl, and a counter electrode is a platinum (Pt). In order to prepare the electrolyte used in the electrochemical cell in order to deposit the PPy-DBSA/rGO film, a dispersion of reduce graphene oxide in acetonitrile was ultrasonicated for 15 min, then appropriate amount of pyrrole was added and stirred well to form a colloidal solution, followed by sonication for 15 min. After that, one volume of dodecylbenzene sulfonic acid DBSA was dissolved in this solution with magnetic stirring. The addition of reduce graphene oxide were also made. After electrodeposition of the PPy-DBSA/rGO layer on the ITO/PET, the films were rinsed with DI water and dried under azote and ambient temperature. Cyclic voltammetry (CV) was
performed in 0.1 M (C_{16}H_{36}BF_{2}N) and 0.01 M acetonitrile solutions at various potential windows and scan rates 100 mV/s.

2.4 Chemiresistive sensor system set up
All sensing tests were conducted out on a handmade platform that we had previously described in ours works [10]. The nitrogen dioxide vapors were extracted from fuming nitric acid and injected using a Hamilton Microsyringe through a small hole on the test cell. Flexible polymer nanocomposite mounted on a movable piston and inserted into a 60 mL polyethylene tube. A four-point probe attached to a device of type Jandel RM3000 is mounted on the top of the tube for dynamic electrical conductivity measurement. Samples are inserted using a microliter syringe through a tiny hole (contact point). The environmental humidity was made purely by evaporating distilled water that was attached directly to the test compartment. Electrical conductivity measurements were taken at temperatures between 25 and 30 °C. The precise concentrations of vapors released were determined using our earlier work [11]. The response % was calculated using the following equation:

$$S=\frac{|R_g-R_a|}{R_a}*100\%$$  

When $R_g$ is the response value of sensor thin layers under measuring gas, and $R_a$ is the response value of fresh air.

2.5 Synthesis of PPY-DBSA/rGO thin films
Figures 2 show the evolution of the chronoamperogram recorded on ITO / BOPET electrodes. The electropolymerization time is 30 s, and the imposed potential is 2.5 V.

![Figure 1. Photography of PPy-DBSA/rGO films electrodeposited on ITO/BOPET.](image1)

![Figure 2. Chronoamperogram of an aqueous solution of 10^{-1} M pyrrole, 10^{-1} M DBSA, and 1g of rGO, on an ITO electrode (Ag / AgCl reference electrode, Pt against electrode).](image2)
3. Results and Discussion

3.1 Spectroscopic characterization

Typical Raman spectra of composites are shown in Fig. 3. They show bands demonstrating the characteristic peaks observed on the PPy-DBSA at 1350 cm\(^{-1}\) and 1572 cm\(^{-1}\), which correspond to the elongation of the C = C bond of the polymer chain. Regarding pure PPy, the bands were observed in 1388 cm\(^{-1}\) and 1574 cm\(^{-1}\) due to ring mode stretch and the C=C backbone stretching of PPy. The nanocomposite decrease in the \(I_D/I_G\) value showed that the disorder graphene is less in the composite and manifested in the G-band peak from 1572 cm\(^{-1}\) to 1566 cm\(^{-1}\).

![Raman spectra for the PPy, PPy-DBSA, and PPy-DBSA/rGO](image)

**Figure 3.** Raman spectra for the PPy, PPy-DBSA, and PPy-DBSA/rGO.

3.2 SEM Characterization

Figure 4 demonstrates PPy-DBSA/rGO nanocomposite morphology. On the surface of reduced graphene oxide nanosheets, PPy has a wrinkled shape generating a mesh structure. This morphological characteristic provides a broad adsorption surface contact and enhances the adsorption of NO2 molecules.

![SEM images of PPy-DBSA/rGO films grown on surface ITO/PET.](image)

**Figure 4.** SEM images of PPy-DBSA/rGO films grown on surface ITO/PET.
3.3 Reproducibility and response time of thin films of PPy-DBSA/rGO

The reproducibility test for the PPy-DBSA/rGO thin-film based NO2 sensor was evaluated by plotting the response curve in dynamic mode after exposure of the film to different concentrations of nitrogen oxide ranging from 1ppm up to 20ppm, as shown in Fig. 5. The response and recovery time showed in Fig. 6 were estimated 30.25 s and 75 s respectively.

![Figure 5. Reproducibility test of thin film Sensor PPy-DBSA/rGO](image)

![Figure 6. Response and recovery time of thin film PPy-DBSA/rGO](image)

3.4 Effect of relative humidity on the sensor response

The injection of 2-ppm of NO2 gas was carried out under a humid atmosphere to scrutinize the effect of humidity on the sensor performance. A hygrometer (Omega type HH314A) was used to indicate the relative humidity (RH) generated by injecting water vapor in the test chamber at rates ranging from 20% to 80%, as illustrated in Fig. 6. Under a humidity rate higher than 50%, a substantial humidity impact on sensor efficiency was detected. This result may be due to the inhibition of the active sites by -OH groups, when they are bridged with -COOH entities in surfactant agent through a hydrogen bond.
4. Conclusion

A newly flexible nanocomposite-based nitrogen dioxide chemisensor was developed from polypyrrole filled with graphene doped with DBSA using electro polymerization technique. The addition of DBSA and reduce graphene oxide enhanced the electrical conductivity of as-prepared nanocomposite. Results showed that the produced PPy-DBSA/rGO sensor demonstrated improved NO$_2$ sensing properties including response time (30.25 s), the detection limit (2ppm), and reproducibility. Furthermore, Results showed that the rGO exfoliated by n-dodecylbenzene sulfonic acid improved both the sensitivity and the reactivity of our produced nanocomposite toward NO$_2$. Higher NO$_2$ response was detected for this nanocomposite in comparison to several studied gases such as NO, NH$_3$, H$_2$S, and CO$_2$. Furthermore, its sensitivity remained considerable under varied temperature and humidity, indicating its good function ability under harsh environment film. confirmed that this sensor displayed a resistor–like type.

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