Highly Ammonia Sensing Using Direct *In Situ* Electro-Deposited Polypyrrole-Dodecylbenzene Sulfonic Acid Film on ITO Coated Flexible Substrates

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Abstract: Air quality monitoring is of major concern as it is directly linked to public health. It requires the development of high sensitive devices with fast response towards hazardous gas and volatile compounds. Such performances depend on the nature and quality of deposition of the sensing layer. Herein, adherent polypyrrole-dodecylbenzene sulfonic acid (PPy–DBSA) films were deposited on a *N*-(*3-trimethoxysilylpropyl) pyrrole modified ITO coated polyethylene teraphtalate (PET) flexible substrate by facile direct electrochemical oxidation of pyrrole in an aqueous solution of sulfonic acid. The obtained PPy-DBSA films were subjected to various characterization techniques such as, FTIR, Raman, SEM and conductivity measurements. Chemiresistive gas sensing tests have demonstrated selectivity and sensitivity of films toward ammonia vapors over the other vapors (nitrogen dioxide, carbon dioxide, hydrogen sulfide, acetone, methanol and ethanol) with higher response at 20 ppm, reasonably fast response time of 3 min and reaching detection limit of 3ppm. The response of the sensor can reasonably be related to the strong electrostatic interactions between vapor molecules and the dopant agents within PPy films. In comparison PPy-DBSA films prepared on pristine ITO/PET has exhibited lower response at 20 ppm of ammonia exposure, which highlights the role of surface modification and the contribution from the dopant agent nature for ammonia sensing. Moreover, chemiresistive response performances have been tested in the presence of humidity, under varied temperatures, and finally their behaviors were featured by an impedance spectroscopy in both presence and absence of gas. This work conclusively shows that the sensing performances are not only driven by the molecular interactions between the sensor and the analyte but also by the quality of deposition and adhesion of the former to the transducer. The latter feature can be controlled by appropriate chemical surface modification.

Keywords: polypyrrole/DBSA films, ITO/PET, electropolymerization, flexible chemiresistive gas sensor, ammonia sensing.

1. Introduction

During the last decades, academic and applied studies on volatile organic compounds have progressed at remarkable pace in order to achieve high sensitivity and fast response times of molecular recognition devices. The rationale for this world wide concern lies in the ever growing need for high air quality. Indeed, the quality of ambient air is intimately linked to occupational health care and safety, home automation, biomedical diagnostics, industrial process control, disaster prevention and security.1,2 These issues led to the development of numerous methods of air quality monitoring in terms of composition and detection of hazardous compounds.3 Particularly, the detection of ammonia gas at a very low level of concentration is considered as defiance in the field of gas sensors development. Owing to its potential effects when its concentration exceeds the threshold limit value of 25 ppm, particularly on the human respiratory system, causing severe irritation of the nose and throat, inducing cough, breathing difficulties and tightness in the chest, moreover, it may irritates or burns the eyes, resulting the blindness,4,5 which has pushed the governmental air quality control agencies to tight their standards and to increase their awareness level. This has therefore created needs for fast, reliable, cost effective and highly sensitive systems for the detection of NH3 across industrial, commercial and domestic areas. Hence, various sensors have been investigated including surface acoustic waves sensors (SAW),6,7 quartz crystal microbalance (QCM),8,9 metal oxide sensors,10,11 and so on. Unfortu-
nately, ammonia sensors based on metal oxides are known to be gourmand in terms of energy consuming as they require high temperatures standing in a range higher than 200 °C for their operation, which might negatively affect the sensor response stability. Therefore, researches’ efforts have been extended to the investigation of sorbent materials, particularly polymers thin films and their composites, which can satisfy good sensing requirements. Among the various tested polymer categories, inherently conductive polymer-based chemiresistive gas sensor have shown promises applications. Polypyrrole is widely sought-after, due to its excellent stability under environmental conditions, good conductivity and biocompatibility. It was one of the polymers widely used in alcohols and other organic vapors sensing.

Moreover, attempts have been extensively broadened to the combination of polypyrrole with metals such as PPy-Ag, PPy-Au, PPy-Pt, PPy-Pd, and PPy-Cu. Even though there are several studies which have dealt with conducting polymers and their composites as sensing materials, their poor mechanical features are still slowing down their widespread utilization, and hence, works have focused on the incorporation of surfactant anions as dopants and/or plast-dopants. Therefore, in recent years, there has been an increasing demand for the preparation of flexible conducting polymers films, which can be further transferred into flexible devices. In particular, a significant interest toward flexible conducting polypyrrole films, and thence, several methods have been adopted for their fabrication, such as the interfacial polymerization which permits an easy grow up with highly flexible freestanding films. However, they suffer from poor mechanical strength, and therefore have limited use in practical devices. To overcome this drawback, alternative simple procedures based on deposition of polypyrrole thin films on flexible substrates such as PET, PMMA, polyimide, ITO-coated PEN, and PET, by chemical polymerization, photo-polymerization, electro-polymerization, plasma polymerization and irradiation methods. Although, all of these synthetic techniques are commonly used in laboratory, the electrochemical pathway offers several advantages over the other methods, the distinct advantages being firstly in the in situ production of material with no further intermediated synthetic steps, secondly, the great deal lies in the in situ collection of information during the polymerization process, allowing the properties study of the generated polymer in each step before continuing the production of polymer. Moreover, it gives uniform polymer layer in terms of film thickness and morphology on a wide range of substrates including flexible polymer sheets. Unfortunately, quality of conducting polymers films on the plastic substrates is hampered by the poor adhesion as there is no chemical bonding between the substrate surface and the conducting polymer. Therefore, it is imperative to modify the plastic substrates using appropriate coupling agents. In this regard, several coupling agents are reported in the literature, such as silanes, thiols, and diazonium.

In this work we portray for the first time, the features rising from the combination of non-electroactive molecule dodecylbenzene sulfonic acid (DBSA) as dopant and flexible substrates for the preparation of polypyrrole thin layer by direct in situ electropolymerization, and its application to an online organic vapors sensing, through highlighting the influence of the dopant nature on the electrostatic interactions between vapor analyte and PPy films. Actually, polypyrrole/DBSA films were electro-deposited on indium-tin-oxide coated polyethylene terephthalate (ITO/PET) substrate; the preparation process consists of three steps: (i) Activation and creation of an OH terminated ITO/PET surface; (ii) covalent grafting of N-(3-trimethoxysilylpropyl) pyrrole onto the OH-terminated ITO/PET surface by self-assembly; (iii) polypyrrole thin layer formation through the direct electrochemical oxidation of pyrrole in an aqueous solution of dodecylbenzene sulfonic acid and its electro-deposition on the top silanized ITO/PET substrates.

2. Experiment

2.1. Materials

PPy (Sigma-Aldrich, purity>98%) was subjected to distillation under reduced pressure in order to remove impurities, then it was refrigerated at 4 °C in the dark prior to synthesis. Dodecylbenzene sulfonic acid (Sigma-Aldrich, purity>98%) was used as received. The organic solvents used were of analytical, and deionized (DI) water was used for washing and solution preparation. The ITO (thickness, 150 nm; sheet resistance, 30-50 Ω/ square)-coated PET substrates (thickness, 25 μm) were purchased from Sigma-Aldrich. These sheets were cut into a 20 mm × 10 mm size using a cutter to conduct the surface treatment experiments. N-(3-Trimethoxysilylpropyl) pyrrole (purity 98%), used for the surface modification of ITO/PET, was procured from Fluorochrome. Prior to the surface modification process, ITO-coated PET substrates were ultrasonically washed using chloroform, DI water, and ethanol for 30 min, then dried for 4 h at 70 °C in an oven.

2.2. Surface modification of ITO/PET substrate by grafting of N-(3-Trimethoxysilylpropyl) pyrrole

Surface modification process was achieved as described in. Briefly, ITO-coated PET substrates were ultrasonically washed using dichloromethane, acetone and dionized water, then the surface was hydroxylated by dipping in the potassium hydroxide (KOH) containing dimethyl sulphoxide (DMSO) solution (4 mg KOH dissolved in 30 mL DMSO). The sheets were left to react with KOH for 30 min, then thoroughly washed in distilled water and dried.

The hydroxylated sheets were then dipped in a N-(3-trimethoxysilylpropyl) pyrrole solution (115 mg in 25 mL of ethanol and 1 mL of acetic acid) and left to react for 48 h. After that, the substrates were thoroughly cleaned using ethanol and dried for 2 h at 70 °C in an oven.

2.3. Preparation of polypyrrole-DBSA coatings on silanized ITO/BOPET

The electro-polymerization of pyrrole on silanized ITO/BOPET sheets forming the working electrode with surface area of 2 cm², was carried out at room temperature in a one-compartment