Highly sensitive, reproducible, selective and stable CSA-polypyrrole NO$_2$ sensor

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ABSTRACT

Camphor sulfonic acid (CSA) doped polypyrrole (PPy) thin film sensors were prepared by spin coating method on glass substrates. Structure and morphology of the CSA doped in PPy films were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM), respectively, which proved that there is a strong synergetic interaction between the CSA and PPy. The prepared gas sensors were tested for different concentrations of nitrogen dioxide gas at room temperature conditions by sensing the changes in surface resistivity of the films with respect to time and the results compared with the data on pure PPy sensor. The CSA doped PPy sensor exhibited better sensitivity, selectivity and stability to NO$_2$ when compared with PPy alone. It was revealed that 30% CSA doped PPy sensor operating at room temperature could detect NO$_2$ gas at low concentration (10 ppm) with high selectivity ($Q = 13\%$ compared to H$_2$S) and high sensitivity ($S = 52\%$), with better stability (73%). Plausible NO$_2$ sensing mechanism of the CSA doped PPy sensor is discussed. Also, the synergetic interaction between CSA-PPy and NO$_2$ is carried out using impedance spectroscopy and the results are explored.

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1. Introduction

Conducting polymers have had the attention of researchers for about two decades. A lot of interest is shown due to their relatively large conductivity, light weight and flexibility. These features make them more desirable than metals in certain applications. Much of the past research on conducting polymers has concentrated in the bulk material [1–3].

Polypyrrole (PPy), Polyaniline (PANi), Polythiophene (PTh) and their derivatives are conducting polymers, which have been widely investigated as an active layer for the development of room temperature gas sensors. The sensors made of conducting polymers have improved characteristics like high sensitivities and short response time at room temperature. As a result, a lot of attention is paid to the sensors fabricated from conducting polymers [4].

However, a major disadvantage of the conducting polymer based sensors is their lack in specificity i.e. they sense all the gases. This is because conducting polymers are doped/undoped by redox reactions; therefore, their doping level can be altered by transferring electrons from or to the gas. Electron–acceptor (oxidizing) gases, such as NO$_2$, Cl$_2$ etc., can remove electrons from the aromatic rings of conducting polymers. When this occurs at a p-type conducting polymer (e.g. PPy), the doping level as well as the electric conductance of the conducting polymer is enhanced. An opposite process will occur when detecting an electro-donating (reducing) gas e.g. H$_2$S, NH$_3$, CH$_4$ and CO. Thus, a major challenge in conducting polymers based sensors is to enhance their specificity. Fortunately, the structural properties of conducting polymers can be modified conveniently by adding metals, [5] metal-oxides, [6,7] organic molecules, [8] or carbon nanotubes, [9] which in many cases improve the specificity.

Among various conducting polymers, polypyrrole has an edge due to its chemical stability against atmospheric conditions and ease of synthesis by electrochemical and chemical methods [10,11]. Surface charge characteristics of polypyrrole can easily be modified by changing the dopant species in the material during synthesis [12] and it exhibit interesting electrical properties such as their ability to oxidize and reduce at specific electrochemical potential. PPy has shown capability in sensing technology and used as a sensors for air borne volatile organic compounds referred to as electric nose, especially for detection of alcohols, NO$_2$, etc. and has shown interesting NH$_3$ and NO$_2$ gas sensing properties at room temperature [13,14].

An important draw back with polypyrrole is its limited mechanical strength. In case of conducting polymer the intrinsic redox reactions it can undergo, results in different electrical properties that vary easily with doping, making it suitable for gas sensing application [15,16] as well as doping with various acids influences the gas sensing properties by changing the chemical and structural nature of polymer and also creating more active sites [17,18].

Potential dopants for polypyrrole include β-naphthalene sulfonic acid (NSA), camphor sulfonic acid (CSA), and dodecylbenzene sulfonic acid (DBSA), etc. [19]. Among those different dopants camphor sulfonic acid (CSA) have enhanced chemical stability and thermal degradation properties and have performed as better materials than the polypyrrole itself.

In present paper, we have successfully prepared camphor sulfonic acid (CSA) doped polypyrrole material using different weight percentages of camphor sulfonic acid (10–50%) dispersed in polypyrrole. Films of CSA doped polypyrrole were fabricated by spin coating technique on a glass substrate and the effect of varying concentrations of camphor sulfonic acid on the structure and morphology was explored using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) technique, respectively, as well as their gas sensing performance was studied for NH_3, H_2S, CH_3OH, C_2H_5OH and NO_2 gases at room temperature. For a comparison, thin films of PPy were also prepared separately and evaluated along with the CSA doped polypyrrole films for sensing NO_2 gas at room temperature. We report our findings in this paper and discuss a plausible mechanism for the formation and electronic behavior of such material. To the best of our knowledge, no attempt has been made to form a NO_2 gas sensor based on CSA doped PPy thin films and this is the first ever attempt made to study CSA doped polypyrrole thin films for the application of NO_2 gas sensor operating at room temperature.

2. Experimental details

2.1. Synthesis of polypyrrole

Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer pyrrole. Analytical grade ammonium per-sulphate APS, was used as oxidizing agent. The chemical polymerization was carried out in a beaker by mixing 0.1 M aqueous solution of pyrrole and 0.1 M of APS in 1:1 ratio by volume. The polymerization was carried out for a period of 3 h. After termination of the polymerization process, the precipitate obtained was filtered. The product was washed successively by methanol followed by distilled water [14].

2.2. Preparation of CSA doped polypyrrole

Camphor sulfonic acid (CSA) doped polypyrrole were prepared by solid state synthesis route using different weight percentages of camphor sulfonic acid (10–50%) dispersed in polypyrrole. matrix. Thin films of the CSA doped polypyrrole were prepared on glass substrate by using spin coating technique at 3000 rpm for 40 s and dried on hot plate at 100 °C for 10 min.

2.3. Characterization techniques

X-ray diffraction (XRD) studies were carried out using X-ray diffractometer (Model: PW-3710, Holland) using CuKα radiation ($\lambda = 1.5406$ Å) in 2θ range of 10°–80°. Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 100) of solid powder samples dispersed in potassium bromide (KBr) and compressed into pellets in frequency range of 400–4000 cm^{-1} was used for chemical structural analysis [20]. The surface morphology of the samples were carried out using scanning electron microscopy (SEM, Model: JEOL JSM 6360) operating at 20 kV. UV–vis spectra of PPy, and CSA doped PPy were recorded on a Simandzu-100 UV–Vis spectrophotometer. Two probe technique was used for the purpose of electrical dc conductivity measurements of PPy, and CSA (10–50%) doped ppy. Ambios XP-1 surface profilometer was used to measure thicknesses of the sample films. It is observed that thickness of PPy
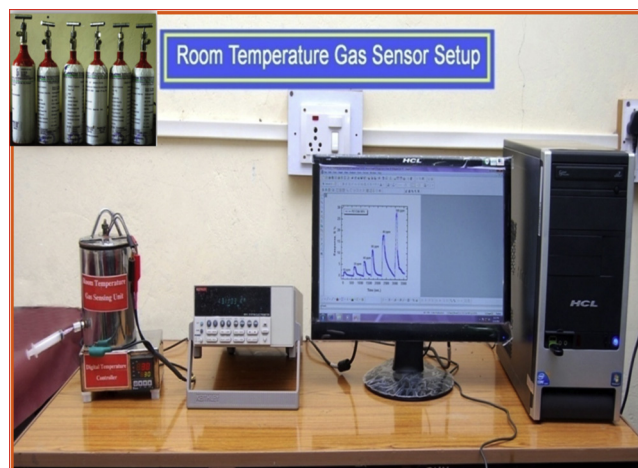

Fig. 1. Experimental set up for gas sensing measurement.

film (0.920 μm) decreases from 0.746 μm (10%) to 0.232 μm (50%) as content of CSA increases from 10 to 50%.

The gas sensing behavior was investigated by using custom fabricated room temperature gas sensing measurement unit. In order to measure the gas response, the resistance of the films was measured in air ambient and in gas atmosphere. For resistance measurement, silver electrodes (1 mm wide and 10 mm apart from each other) are drawn on sensing materials for the contacts. The experimental set up for gas sensing measurement is shown in Fig. 1. The resistance variation of the sensor films was measured using a Keithley 6514 System Electrometer, which was controlled by a computer. For monitoring the response of the films to various gases, the films were mounted in 250 cc air tight container and the known gas (NO_2, NH_3, H_2S, C_2H_5OH and CH_3OH) of particular concentration was injected through a syringe. All the gas sensitivity measurements were carried out at room temperature. The definition of gas sensitivity S (%) was the ratio of $R_a - R_g/R_a \times 100$ in which R_a and R_g represented the resistance of the sensor in clear air and testing gas, respectively.

Impedance spectroscopy measurement of the CSA-PPy samples were carried out using Wayne Kerr precision impedance analyzer (model: 6500 B) in the frequency range 20 Hz–10 MHz.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction (XRD) pattern of pure polypyrrole and 10–50% camphor sulfonic acid doped polypyrrole are shown in Fig. 2. The X-ray diffraction pattern of pure PPy shown in Fig. 2(a), which has a broad peak at $2\theta = 20°–30°$ indicating the amorphous behavior of the polymer [21]. The broad peak results from the scattering of X-rays from PPy chain. Figure (b–f) shows the X-ray diffraction pattern of 10–50% camphor sulfonic acid doped polypyrrole, respectively. The X-ray diffraction peak at $2\theta = 11.44°$, 13.82°, 15.40°, 16.35°, 17.41°, 18.87°, 19.50° in the diffraction pattern of CSA (10–50%) doped polypyrrole are belongs to CSA and their strength is found to be increasing with increasing wt% of CSA in polypyrrole and they are more significant in the 40 wt% and 50 wt% CSA doping patterns [18,22,23]. All XRD patterns of CSA doping has broad peaks at lower diffraction angles approximately at $2\theta = 20°–30°$. This broadening of peaks can be ascribed to the scattering of the bare PPy chains at the interplaner spacing [24]. This result indicates that the presence of CSA has no influence on the broadening peak of polypyrrole.