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Facile chemical bath deposition method for interconnected nanofibrous polythiophene thin films and their use for highly efficient room temperature NO_2 sensor application

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ABSTRACT

Interconnected nanofibrous polythiophene (INPTh) film was deposited on the glass substrate through a simple chemical bath deposition method. The influence of monomer concentration on INPTh film properties as well as on NO_2 sensing properties of the film was studied. The morphological and structural studies were carried out using FTIR spectroscopy, FE-SEM microscope, and AFM analysis. The FTIR spectra confirmed the formation of PTH structure. The interconnected nanofibrous surface morphology was observed in FE-SEM images. The roughness of the film and thickness (225 nm–442 nm) was found to increase with monomer concentration up to 0.5 M, after that, both decreased at 0.6 M monomer concentration. The highest selectivity of PTh thin film towards NO_2 was observed than the other gases like H_2S, SO_2, NH_3, CO and LPG. The influence of film morphology and thickness on gas sensing properties was observed, which was varied with monomer concentration. The film deposited at 0.5 M monomer concentration showed the highest NO_2 gas response of 47.58% at room temperature. Present results revealed that monomer concentration was also one of the deposition parameters for tuning the morphological as well as gas sensing properties of the chemical bath deposited PTh film.

1. Introduction

Use of organic fuels and other chemicals have become an essential part of the social as well as industrial life. They produce an enormous amount of harmful, toxic, flammable exhaust pollutant gases like NO_x, H_2S, NH_3, Cl_2, etc. in the atmosphere [1,2]. These toxic gases (NO_x ($x = 1, 2$), N_2O_4, etc.) are one of the major exhausted pollutants from the society needs like a vehicle and domestic and industrial exhaust. Direct inhalation of NO_2 can irritate the lungs and lower resistance to respiratory infections. The excess Nitrogen oxide pollution in the air can significantly contribute to the acid rain, photochemical smog (atmospheric reactions that produce ground-level ozone) and eutrophication in coastal waters of the Chesapeake Bay. These processes have adverse effects on both terrestrial and aquatic ecosystems. Due to increase in awareness about the pollution, hygiene, and health care, gas sensors have received considerable attention for their developed. Especially, detection of harmful toxic and flammable exhaust gases at ppm level has become a subject of growing importance for industrial health, safety, and environmental monitoring both at home and workplaces. In last two-three decades, the development of the gas sensor devices has been focused on detection of such toxic and harmful gases. The metal oxide gas sensors based on SnO_2, ZnO, TiO_2, and WO_3, etc. are suffering from the high operating temperature, low sensitivity, and selectivity [3–6], which places the limitations on its practical use in the development of sensor devices. Therefore, the current research in the field of gas sensor devices has been focused on the development of sensors for the detection of hazardous, toxic and flammable gases, which have the character-

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istics of high sensitivity, good selectivity, rapid response, and low cost.

Recently, organic conducting polymers (OCP) such as Polyaniline (PANI), Polypyrrole (PPy), and Polythiophene (PTh) are found to be an attractive alternative to the metal oxide gas sensors due to their high sensitivity at room temperature[7–10]. Among these polymers, polythiophene and its derivatives, which have received much attention due to their unique properties like flexibility, good environmental stability, and high electrical conductivity, simple and ease polymerization technique and low cost for the development of various applications. Polythiophene powder and thin films have been prepared by different synthesis techniques, such as chemical oxidative polymerization [9], spin coating [11], vacuum evaporation [12], inkjet printing [13], successive ionic layer adsorption and reaction (SILAR) [14], sol-gel method [15], Langmuir-Blodgett (LB) technique [16], and chemical bath deposition technique [17,18], etc. Polythiophene has also been used for variety of applications like organic light emitting diode [19], gas sensor [9], organic field effect transistor [20], supercapacitor [14], solar cells [21], biosensor [22], microwave shielding [23], photoconductive and photovoltaic devices, and optical modulator devices [24], etc. Furthermore, polythiophene and its derivatives are attractive polymers for sensing application owing to its good environmental and thermal stability, and high electrical conductivity. Polythiophene has identified as one of the sensors materials for different detection of ammonia, trimethylamine, acetone, alcohol and toluene gases at room temperature [10]. Moreover, their surface morphological modification has improved gas sensing properties [25]. Navale et al. [9] report on the 9% sensing of 10 ppm NO_2 gas for the spin-coated polythiophene thin films. To our knowledge, there are no reports on the NO_2 gas sensing application by chemical bath deposited polythiophene thin films.

In the present work, we report the deposition of high surface area interconnected nanofibers of polythiophene on glass substrates utilizing simple chemical bath deposition technique. The effect of thiophene monomer concentration on the film thickness and morphology as well as NO_2 sensing properties has been investigated.

2. Experimental

2.1. Materials

The interconnected nanofibers of polythiophene were synthesized using AR grade chemicals, such as Thiophene (99%, Aldrich Chem. Ltd.), ferric chloride (98%, Thomas Baker Pvt. Ltd.), methanol (99.5%, Spectrochem Pvt. Ltd.), and chloroform (99.4%, Thomas Baker Pvt. Ltd.). The gas sensing measurements were performed on the NO_2, H_2S, NH_3, CO, SO_2, LPG (M/s Shreya Enterprises Pvt. Ltd.) gases.

2.2. Preparation of polythiophene (PTh) thin film

Interconnected nanofibrous polythiophene thin film was synthesized by chemical bath deposition technique using thiophene as a monomer and ferric chloride as the oxidant, wherein thiophene (AR grade Merck) was purified by distillation before use. Thiophene monomer solution was prepared by dispersing thiophene monomer in chloroform at various concentrations (A-0.3, B-0.4, C-0.5 and D-0.6 M) with continuous stirring for 45 min and 0.4 M ferric chloride was dissolved in chloroform to obtain oxidant solution. The deposition bath was prepared with 25 ml oxidant solution, and 25 ml thiophene monomer solution was dropwise added to oxidant solution with continuous stirring. The ultra-cleaned glass substrates of 2.5 cm × 1.2 cm dimensions were immersed vertically in the bath and kept at room temperature. During the initial deposition course, the glass slides changed its color to brownish, and after two hours finally it became dark brown, which clearly highlights the deposition of INPTh thin films on the glass substrates. The glass substrates coated with INPTh thin films were removed from the bath after 2 h, washed with methanol and chloroform successively for several times to remove unreacted monomer and oxidant from the film, followed by drying in air and preserved in an airtight container. The monomer concentration was varied from 0.3, 0.4, 0.5 and 0.6 M, and the same experiment was repeated to confirm the reproducible formation of INPTh thin films.

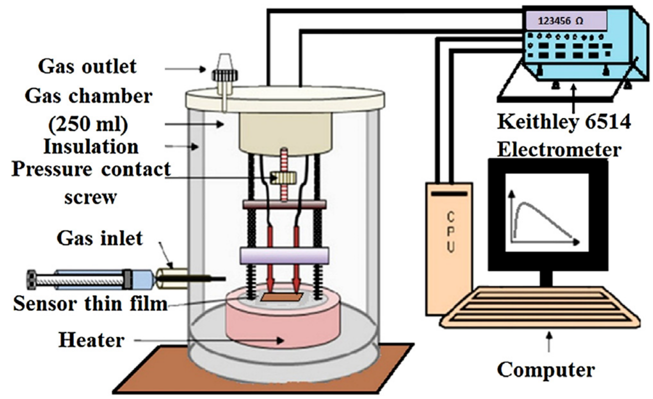

Fig. 1. Schematic of the experimental setup for gas sensing measurement.

2.3. Physicochemical characterization

The chemical structure and functional groups of INPTh thin films were determined using Fourier Transformed Infrared Spectroscopy (JASCO FT/IR-4100 Series) in the range of 500–4000 cm^{-1} wave number. The surface morphological study was carried out using Field Emission Scanning Electron Microscopy (FESEM, MIRA3 LMH) and Atomic Force Microscopy (AFM, INNOVA 1B3 BE) technique. The thickness of the film was measured using a surface profiler (AMBIOS Technology, USA, XP-1). Elemental analysis was carried out using energy dispersive X-ray analysis (EDAX, Oxford Instrument, INCA-X-ACT). The optical properties of INPTh thin film were studied using UV–vis spectrophotometer (UV–1800 Shimadzu, Japan). The gas sensing performance was investigated using custom made gas sensing measurement unit (Fig. 1).

2.4. Gas sensing measurements

Fig. 1 shows the schematic experimental setup of the gas sensor measurement unit. The gas response of the film was measured with variation in the resistance of the film in ambient air and the presence of test gas. For the measurement of resistance, two silver electrodes separated by 10 mm, were deposited on INPTh thin film. The resistance was measured using computer controlled Keithley 6514 electrometer system. For monitoring the gas response of the INPTh thin films for various test gases, the films were mounted in airtight stainless steel container having the volume of 250 cc. The precise concentration of known test gas (NO_2, NH_3, H_2S, SO_2, CO, LPG) was introduced into the chamber by using a syringe. Test gases were commercially acquired from M/s Shreya Enterprises Pvt. Ltd. Mumbai, India. When a steady state was achieved, exposing the sensors to air by opening the lid of the chamber recovery of sensors was recorded. All the gas sensitivity measurements were carried out at room temperature (28 ± 2 °C) with relative humidity (47 ± 2%).