



Ammonia sensing properties of polypyrrole thin films at room temperature

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ABSTRACT

Polypyrrole thin films were synthesized in situ by chemical polymerization. Fourier transform infrared spectroscopy revealed formation of polypyrrole. The morphological studies by scanning electron microscopy showed formation of uniform granular structure with average grain size of 0.6 μm. The film composition was characterized by X-ray photoelectron spectroscopy for chemical composition in polypyrrole film. These films were investigated for their sensing behaviour towards NH₃ and NO at room temperature. It has been observed that these films are selective for NH₃ and the sensitivity exhibited a linear response in range of 4–80 ppm.

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1. Introduction

Ammonia is extensively used in many industries that include chemical industry in nitric acid manufacturing, petrochemical industries, industrial hygiene monitors and in calibration gas mixtures in environmental emission monitors. The other applications of ammonia include manufacture of plastics, explosives, textiles, pesticides, dyes etc. It is also used as refrigerating fluid instead of Freon in some refrigerators. In case of electronics industries it is widely used in formation of silicon nitride (Si₃N₄) and gallium nitride (GaN) by chemical vapor deposition. However ammonia is amongst group of very toxic gases (threshold limit –25 ppm, short term exposure limit –35 ppm) causing hazards to respiratory systems, eyes and skin if exposed. Ammonia is soluble in water wherein it hydrolyzes to ammonium hydroxide, a strong base, causing irritation in upper respiratory tract and eye. Therefore it is necessary to have sensors which can sense ammonia at very low level (~few ppm) operating at room temperature.

In recent years conducting polymers like polypyrrole and polyaniline have been studied as sensing materials essentially due to their operation at room temperature and easy sensor element processing [1–6]. 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 [4,5]. In recent reports, polypyrrole has been reported

for ammonia sensing applications, synthesized by electrochemical [5] and Langmuir–Blodgett technique [7,8]. The later gives selective NH₃ sensor, but the response of sensor and response time (>100 s) of the film are a function of number of monolayers. The response for NH₃ is checked for concentrations in the range 0.01–1% [7,8]. Chemically synthesized polypyrrole films show NH₃ sensing in the range from 100 to 300 ppm at room temperature with response values 4–8% and response time of order of ~4 min [9]. Composite films of electrochemically deposited polypyrrole–PVA (poly vinyl alcohol) are studied for NH₃ sensor application but for high concentrations (1–4%) [10]. In another report, electrochemically synthesized polypyrrole films have been investigated for ammonia sensing in range of 8–1000 ppm, but the sensor stabilizing time after introduction of gas is high (~1 h) indicating sluggish response to gas [11]. Polypyrrole films are deposited on modified plastic substrate and developed as flexible NH₃ sensor, but with a lengthy and tedious sensor fabrication process [12], template based electrochemically synthesized polypyrrole nanowires have been reported as room temperature NH₃ sensor, but there are no results about selectivity studies of sensor [13], another report describes polypyrrole–SWNT composites for NH₃ sensing at room temperature, however response varies with content of SWNT and pure polypyrrole films exhibit lesser response at 150 ppm NH₃ [14]. It is known that the toxic limit of ammonia is 25 ppm in air and therefore the sensor should be designed in such a way that it can sense the gas concentrations well below this limit. In present paper, we discuss NH₃ sensing properties of chemically (in situ) deposited polypyrrole thin films at room temperature with fast response time and good selectivity for NH₃ than other interfering gases. The sensor shows a linear response in the range 4–80 ppm and saturates thereafter.

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2. Experimental

Pyrrole monomer was distilled using fractional distillation method prior to use. Analytical grade ammonium per-sulphate APS, (Loba Chemie) 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. Thin films of polypyrrole were in situ deposited simply by keeping a pre cleaned glass substrate (size 1 cm × 1 cm) at the bottom of the beaker. The polymerization was carried out for a period of 3 h. After termination of polymerization, films were washed with distilled water and dried at room temperature. The morphological examination of polypyrrole films was carried out using scanning electron microscope (SEM) (Vega, MV 2300/T40, Tescan) using acceleration voltage of 25 kV. For this purpose thin layer of gold (50 Å) was deposited on the film. Chemical structure of thin film was examined by FTIR technique (FT-8400 spectrophotometer, Shimadzu) using uncoated glass as reference. X-ray photoelectron spectra were recorded using MgK α (1253.6 eV) source (XPS system attached with RIBER MBE). The binding energy scale was calibrated to Au 4f_{7/2} line of 84 eV. In order to measure the gas response, the resistance of the films was measured in air ambient and in gas atmosphere. For resistance measurement, two gold electrodes separated by 1 mm, were deposited on polypyrrole film and silver wires were attached using silver paint and dried at room temperature. The resistance was measured using 3½ digit LCR meter. For monitoring the response of the films to various gases, the films were mounted in 250 ml air tight container and the known gas (NH₃, NO) of particular concentration was injected through a syringe. All the gas sensitivity measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 presents typical microstructure of a polypyrrole thin film. The film has a uniform granular morphology and the average grain size is ~0.6 μm . The uniform granular morphology is preferred for gas sensing applications as it promotes adsorption of gas molecules through the film surface [9,15].

Fig. 2 shows typical FTIR spectrum for polypyrrole film with peaks at 811 and 920 cm^{-1} attributed to C–H wagging [9,16], in range of 725–1110 cm^{-1} for C–H in and out of plane deformations, C–H out of plane deformations and C–N stretching vibrations indicated by peaks in range of 1446–1672 cm^{-1} . The characteristic peak

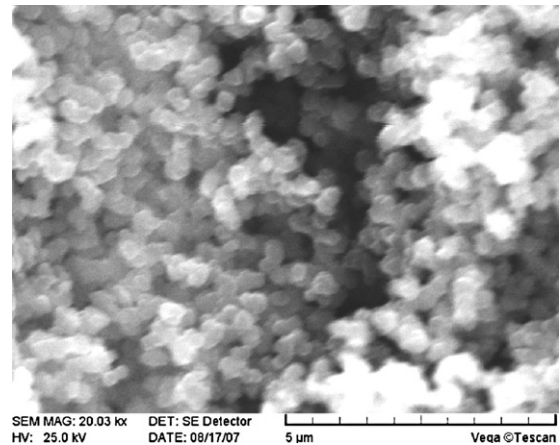


Fig. 1. SEM image of polypyrrole film.

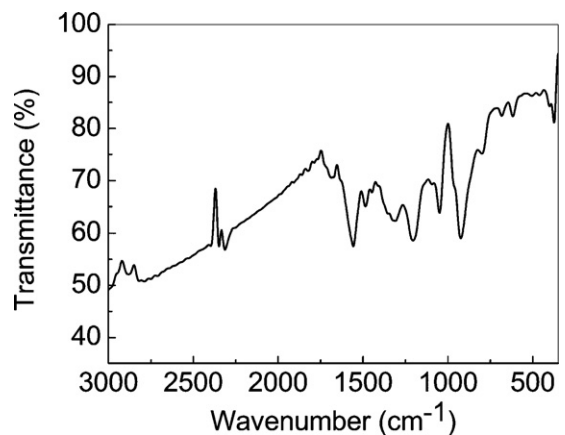


Fig. 2. FTIR spectrum of polypyrrole film.

for polypyrrole is observed at 1545 cm^{-1} ; which is also attributed to C=C stretching and pyrrole ring fundamental vibrations, peak at 1310 cm^{-1} is indicative of =C–H in plane vibration and corresponding to incorporation of sulphonate group. This is due to doping by oxidant during chemical polymerization process. The broad peaks in range of 3400–3500 cm^{-1} , especially at 3436 cm^{-1} is ascribed to

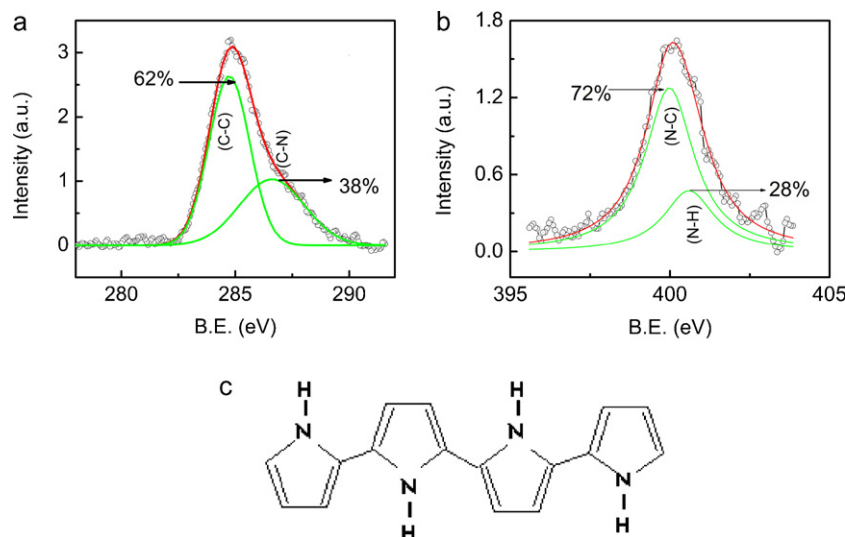


Fig. 3. (a) Core level C1s. (b) N1s XPS spectra of synthesized polypyrrole. (c). Schematic illustrating polymerization of pyrrole.

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