Applied Surface Science 339 (2015) 69–74

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Room temperature ammonia sensor based on copper nanoparticle intercalated polyaniline nanocomposite thin films

U.V. Patil[a,b,d], Niranjan S. Ramgir[a,*], N. Karmakar[c,d], A. Bhogale[d], A.K. Debnath[a], D.K. Aswal[a], S.K. Gupta[a], D.C. Kothari[c,d]

[a] Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Wilson College, Chowpatty, Mumbai 400 007, India
[c] National Centre for Nanosciences & Nanotechnology, University of Mumbai, Santacruz (E), Mumbai 400 098, India
[d] Department of Physics, University of Mumbai, Santacruz (E), Mumbai 400 098, India

ARTICLE INFO

Article history:
Received 10 December 2014
Received in revised form 12 February 2015
Accepted 23 February 2015
Available online 3 March 2015

Keywords:
Polyaniline
Nanocomposites, thin film
Ammonia, sensor

ABSTRACT

Thin films of copper nanoparticles intercalated-polyaniline nanocomposites (NC) have been deposited at room temperatures by in situ oxidative polymerization of aniline in the presence of different concentrations of Cu nanoparticles. The response characteristics of the NC thin films toward different gases namely NH_3, CO, CO_2, NO and CH_4 were examined at room temperature. Both pure polyaniline (PANI) and NC films exhibited a selective response toward NH_3. Incorporation of Cu nanoparticles resulted in an improvement of the sensors response and response kinetics. The response and the recovery times of composite film toward 50 ppm of NH_3 were 7 and 160 s, respectively. Additionally, the NC sensor film could reversibly detect as low as 1 ppm of NH_3 concentrations. The enhanced response of NC films toward NH_3 is attributed to the deprotonation and reprotonation processes as also supported by Raman investigations.

1. Introduction

Thin films of metal oxides such as SnO_2, ZnO etc. have been extensively investigated for their use as gas sensors [1,2]. Temperature dependent selectivity and high operating temperatures (150–500 °C) are the main drawbacks of such sensors [3,4]. Conducting polymers (CPs) have received increasing interest as an alternative to metal oxide semiconductors for smart sensor applications. This is due to their room-temperature operation, short response and recovery times, low fabrication cost, ease of deposition onto a wide variety of substrates, and their rich structural modification chemistry [5]. As a result, CPs like polyaniline (PANI) [6,7], polypyrrole [8–10], polyacetylene [11], polythiophene [12] and their derivatives are widely investigated for their use as a gas sensing material.

Among these, PANI in particular has become one of the technologically important CP owing to its relatively easier synthesis, excellent environment stability and excellent electronic and electro-chromic properties [13,14]. It has been widely used in organic solar cell and gas sensing applications. However, PANI is not as sensitive as metal oxides and its poor solubility in organic solvents further limits its application. Efforts are now being made toward the improvement of its solubility by involving protonation with organic acids, grafting with copolymers or preparing it using emulsion polymerization in the presence of surfactants [15,16]. Polymer based gas sensors often suffer from the drawbacks of lack of specificity, sluggish reaction kinetics and poor mechanical strength. To overcome these drawbacks inorganic materials in the form of nanoparticles are commonly mixed with CPs. This helps to improve the effective surface area, conductivity and porosity of polymers, thereby leading to enhanced gas sensing capability. Though polymers are easy to synthesize, it is quite difficult to embed inorganic nanoparticles uniformly by simple blending or mixing in molten state. One of the methods is the encapsulation of inorganic nanoparticles inside the shell of CPs during the polymerization process itself [17–19].

Ammonia is one of the highly toxic gases and a key component of various industrial processes and power plants. It has a short term (10 min) and long term (8 h) exposure limit of 35 and 25 ppm, respectively [20]. Due to the introduction of more stringent regulations governing air-pollution, detection of ammonia in air is of critical interest for environmental monitoring and process control. Also, it has become important to focus research on the development of low-cost gas sensors in order to access applications where

---

* Corresponding author. Tel.: +91 22 2559 5839; fax: +91 22 2550 5296.
E-mail address: niranjanpr@yahoo.com (N.S. Ramgir).

http://dx.doi.org/10.1016/j.apsusc.2015.02.164

the use of conventional analytical systems is not possible [21]. Sutar et al. [22] have reported an ammonia sensor based on nanofibrous polyaniline film obtained using self-assembled monolayer (SAM) technique. Incorporation of Au [23], ZnO [24], MWCNT [25], graphene [26] and TiO_2 [27] into PANI matrix forming a NC films has been demonstrated to result in sensor with improved response kinetics. For example, Pawar et al. [28] reported PANI/TiO_2 NC thin film sensor that can detect NH_3 in the concentration range from 20 to 100 ppm. At 20 ppm the response time (t) was 72 s. Metals like gold, copper, silver and platinum are preferred in polymer NC because of their catalytic effect [29–32] that helps in improving the response kinetics. Of these, Cu in particular is considered to be the low-cost catalyst which helps in improving the conductivity, thermal stability and adsorption–desorption of test gases on the surface of sensor film [33–36]. In the present work, we have investigated the gas sensing properties of copper nanoparticles incorporated PANI NC thin films. These films could reversibly detect low concentrations (up to 1 ppm) of NH_3 at room temperature with improved response kinetics.

2. Experimental

2.1. Materials

Aniline (GR grade) and APS ($(NH_4)_2S_2O_8$) (AR grade), from MERCK were used for polymer synthesis. All the other chemicals were of AR grade and used in as-received condition except aniline which was distilled under reduced pressure.

2.2. Synthesis of Cu NPs and NC films

For the synthesis of Cu NPs, 5 ml aqueous solution of $CuSO_4$ (0.83 mM) was added dropwise (1 ml/min) in 20 ml of $NaBH_4$ (1 mM), under constant stirring (500 rpm). During the addition of $CuSO_4$ solution, color of the solution changes from colorless to reddish. Different concentrations of Cu NPs colloids were prepared using different amounts of $CuSO_4$ solution (2 ml, 3.5 ml, 5 ml, 7 ml and 9 ml) for the above process.

The NC film was prepared by in situ chemical oxidation polymerization of aniline monomer in the presence of Cu NPs colloid. The polymerization was initiated by drop wise addition of the oxidizing agent $(NH_4)_2S_2O_8$ (dissolved in minimum amount of water) in an acidified solution of monomer containing 25 vol.% of Cu NPs colloid under constant stirring at ~5 °C. The monomer to oxidizing agent ratio was kept constant as 1:1. HCl was used as a dopant during in situ polymerization process. The above process was carried out in a glass beaker containing previously cleaned glass slides as substrates at the bottom of the beaker. The substrate-slides were kept in the beaker for 8 h to allow the formation of film over the substrate surface. The as grown films were washed with doubled distilled water (DDW) and dried at 60 °C. PANI films were also prepared using similar method but without any addition of Cu NPs colloid. Polymer containing solution in the beaker was filtered and washed with DDW many times to remove the other remains after the polymerization. The filtrate was further dried in air, at 60 °C. It was further dried using vacuum drying technique. The polymer composite so obtained in the powder form was used for further characterization.

2.3. Material characterization

The surface morphology of the films was studied using scanning electron microscope (SEM, TESCAN VEGA MV2300T). The percentages of Cu and X-ray elemental mapping were performed using an energy dispersive X-ray analysis unit (EDAX; model: Oxford INCA X-ACT) attached to SEM. The film thickness and surface roughness were measured using Veeco, Decktak 150 surface profilometer. Transmission electron microscope (TEM) image of Cu NPs was taken using JEOL-JEM 210 TEM microscope operating at accelerating voltage of 200 kV. To study the nature of bonding, FTIR spectra of PANI and NC powder were taken using Varian Cary series spectrometer. The Raman spectra were recorded using Renishaw inVia Raman spectrometer equipped with confocal microscope. Raman shifts were recorded in the range of 1150–1750 cm^{-1} using 514 nm red laser excitation in combination with 100× objective magnification. UV–vis absorption measurements were performed with Varian Cary 5000, UV-VIS Spectrophotometer in the wavelength range of 300–900 nm.

2.4. Gas sensing measurements

For sensing measurements, gold contacts (two probes) were deposited on the thin films by vacuum evaporation technique with 1 mm spacing between the electrodes. All the measurements were performed at room temperature (~26 °C) with relative humidity between 40 and 50%. The resistance of the sensor films was found to be in the range of 600–1200 Ω. Gas sensing measurements were performed in a static mode using the experimental set-up as shown in Fig. 1. In brief, the sensor films were mounted in a stainless steel test-chamber (volume: 1000 cm^3). Required concentration (ppm) of test gas in the test chamber was achieved by introducing a measured quantity of test gas with the help of gas tight syringe. For this a calibration gas mixtures of 1000 ppm of impurity gases in N_2 environment, as obtained from Chemtron Science laboratories Pvt. Ltd., Navi Mumbai, were used. Response curves were recorded by measuring the change in current as a function of time upon exposure to gas at a constant voltage using Keithley Picoammeter/Voltage Source Model 6487. Sensor recovery was achieved by exposing the samples to the ambient air i.e., opening the lid of the static gas testing unit to ambient atmosphere.

Sensor response was calculated using the relation:

$$\text{Response}\,\% = \left(\frac{I_a - I_g}{I_a}\right) \times 100 \qquad (1)$$

where I_a and I_g are current in air and test gas, respectively. Response and recovery times were defined as the times needed for 90% of total change in current on exposure to gas and fresh air, respectively.

3. Results and discussion

3.1. Sensor characterization

Morphology plays an important role in governing the sensor-response kinetics. The surface roughnesses, porosity, surface area to volume ratio and film thickness are the crucial parameters for gas sensing. Fig. 2 shows the SEM image of PANI and NC film. The NC thin film as shown in Fig. 2(b) and (c) exhibited a granular morphology as compared to that of pure PANI films (Fig. 2(a)). More specifically, NC films exhibited non-uniform grains with the average size of ~200 nm. Elemental mapping was also performed to check the distribution of Cu NPs over the sensor surface. Fig. 2(d) and (e) shows the mapping of C and Cu over the NC sensor film. Cu is found to be uniformly distributed over the sensor surface. TEM studies indicated that the average size of the pristine Cu NPs is 7.5 nm as also shown in Fig. 3. Surface profilometer studies indicated that the thickness of the as grown films was ~500 nm with surface roughness of ~110 nm. The grain growth of NPs in composite films is basically governed by two mechanisms; diffusion limited cluster aggregation (DLCA) and reaction limited cluster aggregation (RLCA). In DLCA mechanism, the interaction potential between the particles is purely attractive and the aggregation process is solely