SYNTHESIS OF POLYANILINE-ZINC OXIDE COMPOSITES AND ITS USAGE AS AMMONIA GAS SENSOR

By

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ABSTRACT

This paper presents the synthesis of Polyaniline-Zinc Oxide Composites and their usage as Ammonia Gas Sensor. The authors have adopted a novel chemical route for the synthesis of polyaniline composites via chemical method. These samples were prepared by oxidation of aniline via rapid mixing method. Aniline solution is prepared in sulphuric acid with addition of fixed wt % of zinc oxide. PANI-ZnO composites were synthesized by rapid mixing of ammonium persulphate to aniline solution in an ice bath. The synthesized samples were characterized using X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) techniques. The morphology of the synthesized samples exhibited fibrous and spherical structures. The thick films were prepared salt deposited on alumina substrate for gas sensing application. These sensors exhibited excellent response and recovery time, when exposed to different concentrations of ammonia gas at room temperature.

Keywords: Polyaniline, Zinc Oxide, Gas Sensors, Conducting Polymers, Composites.

INTRODUCTION

Conducting polymers has attracted a lot of attention due to its unique electrical properties [1]. The conducting polymers have relative ease of synthesis, environmental stability and very rich doping/de-doping chemistry [2]. Polyaniline (PANI) has proved to be a promising material among the conducting polymers with numerous applications like gas sensors, modified electrodes, solar cells, electrochromic materials, microelectronics and in rechargeable batteries [3-6]. PANI can easily be synthesized by oxidation of aniline monomer at room temperature [7]. However its synthesis at low temperatures yields PANI with molecular weight five to ten times higher than that synthesized at room temperature [8]. Lately, the research interest of scientific fraternity is growing to study the properties and applications of organic-inorganic composites due to their low cost, ease of synthesis and their novel properties. In this regard polyaniline-metal oxide composites [9-11] have been investigated by several researchers.

In the present study, polyaniline-zinc oxide composites have been synthesized by the oxidation of aniline using rapid mixing technique with the addition of zinc oxide powder. The synthesized samples were characterized by using X-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) techniques. Further these samples were used for ammonia gas sensing at room temperature.

1. Experimental Details

1.1 Synthesis of polyaniline-ZnO composites

Aniline, zinc oxide (ZnO), Ammonium Persulphate (APS), Hydrochloric acid (HCl), Sulphuric acid (H2SO4), N-methyl-2-pyrrolidone (NMP) and m-cresol were procured from Spectrochem, India. All chemicals used were of analytical grade and were used without further purification. To synthesize these samples, aniline was oxidized with Ammonium Persulphate (APS) in aqueous acid solution with the addition of ZnO powder. The solutions of aniline and APS with monomer to oxidant molar ratio 1:1.25 were dissolved separately in 1 M H2SO4 solution. ZnO powder (20 wt% of aniline) was added to aniline solution with ultrasonication of few minutes. Both the solutions were placed in an ice bath (0-4o C) and then oxidant was added rapidly to aniline solution and kept in same ice bath for 4 hours. The obtained solution was kept at room temperature for polymerization for 24 hours. The polymerized salt was filtered and washed repeatedly with double distilled water to remove oligomers and excess acid. The resultant product was dried in air and then in vacuum at 60°C.

1.2 Material characterization

The structural and morphological analysis was done using X-ray diffraction and FESEM techniques. For crystal structure analysis, the prepared samples were characterized by powder X-ray diffraction (XRD) using Cu Kα radiation with Shimadzu 7000 Diffractometer and field emission scanning electron microscope (FESEM) with Ziess, model Supra 55.

1.3 Sensor fabrication and testing method

To fabricate gas sensors, a small amount of prepared powder was dissolved in m-cresol and thick films were deposited on alumina substrate by simple coating with paint brush and was dried at 60°C for 30 minutes in air. The fabricated sensor was placed in the test chamber at room temperature and a known quantity of ammonia gas was injected into the test chamber. Variation of real time voltage signal across the resistance was recorded with an experimental setup consisting of Keithley Data Acquisition Module KUSB–3100 and a computer. The sensor response magnitude was determined as the ratio of resistances of sensor in air-gas mixture and air ambience.

2. Result and Discussion

2.1 X-ray diffraction spectra

Figure 1 represents the x-ray diffraction pattern of pure polyaniline, polyaniline-zinc oxide composites and pure zinc oxide. The small characteristic peaks of ZnO were observed in the spectrum of composite, which are marked by red dots. Also, large peaks of polyaniline were found in the XRD spectrum and marked by black dots. This indicates that polyaniline material is more crystalline in the composite due to some kind of formation of polyaniline fibres with the addition of ZnO.

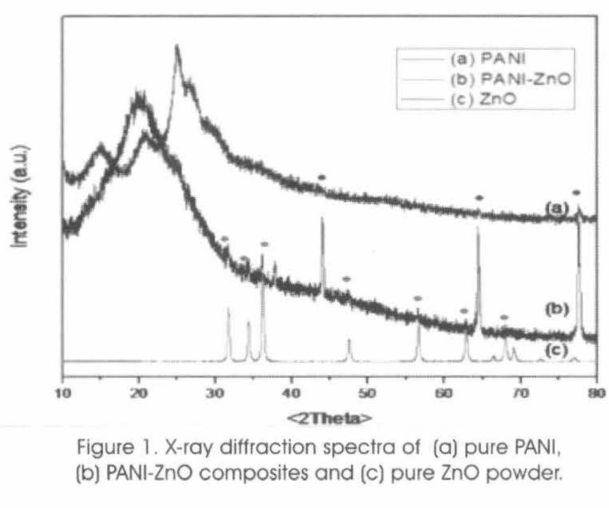

Figure 1. X-ray diffraction spectra of (a) pure PANI, (b) PANI-ZnO composites and (c) pure ZnO powder.

2.2 Field emission scanning electron microscopy

Figure 2 represents SEM image of PANI-ZnO composites prepared in acidic medium. It is observed from the morphological analysis that fibrous structures of PANI were formed with the addition of ZnO powder. Spherical particles of ZnO were also observed in the images having diameter near half micrometer.

Figure 3 represents the SEM image of PANI-ZnO composites at higher resolution. The length and width of these fibers is about 1 micrometer and 100 nanometers respectively. These fibers are made up of polyaniline material as

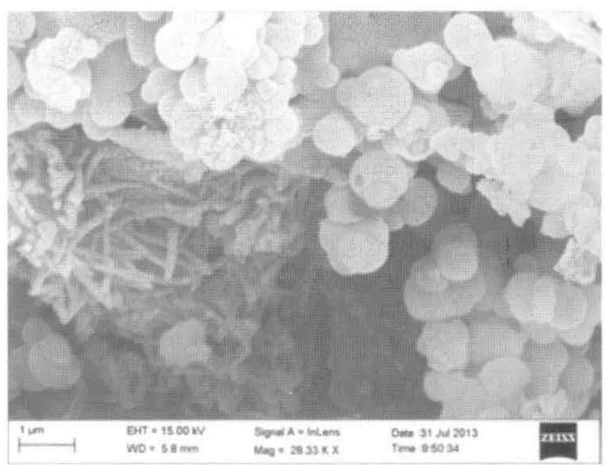

Figure 2. SEM image of PANI-ZnO composites.

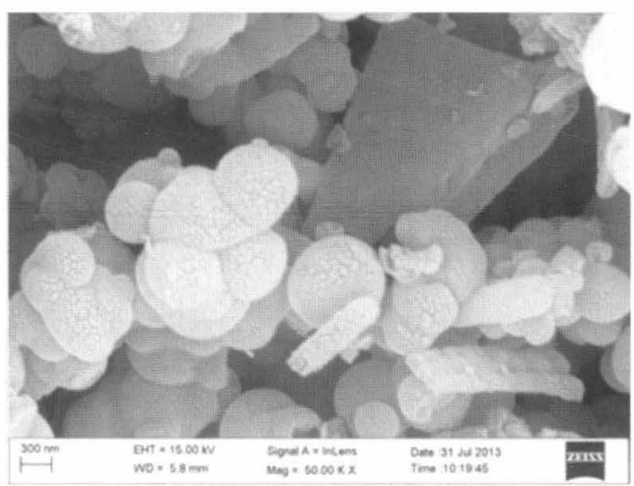

Figure 3. SEM image of PANI-ZnO composites at higher resolution.

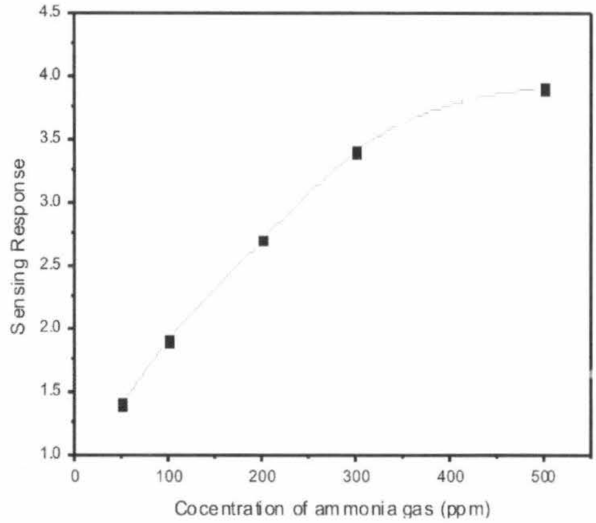

Figure 4. Sensing response of sensor for different concentration of ammonia

observed by large peaks of polyaniline in the XRD spectra of composites. The presence of ZnO during the polymerization of aniline supports the formation of PANI fibers.

2.3 Ammonia gas sensing

Figure 4 represents the sensing response of the PANI-ZnO composites to different concentrations of ammonia gas (50-500 ppm) at 27°C. It was found that the sensing response increases linearly with increase in gas concentration. The response time of this sensor is about 2-3 minutes while the recovery time is about 25-30 minutes.

Conclusion

The PANI-ZnO composites were prepared chemically by rapid mixing method. The X-ray diffraction spectrum confirmed the formation of highly crystalline PANI-ZnO composites. These results were confirmed with SEM images, which had shown the formation of polyaniline fibers in the samples. The prepared salt was used for ammonia gas sensing at room temperature and was found to have good sensing response.

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