



Effects of Addition of ZnO and SnO₂ Nanofillers on the Performance of Polyaniline-Based Ammonia Sensors

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Abstract

This paper addresses the preparation of polyaniline (PANI) and polyaniline-based nanocomposites (PANI/ZnO and PANI/SnO₂) as ammonia sensor elements. The chemical structure and crystalline nature of the synthesized PANI and PANI composites was studied by Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD), respectively. The ammonia sensing performance of the PANI was investigated and the sensing mechanism of the sensor has been discussed. The effect of addition of metal oxide nanoparticles on the response of the PANI-based sensor in presence of ammonia was studied as well.

Keywords: Polyaniline-Nanofillers-Ammonia Sensor-Zinc oxide-Tin oxide.

Introduction

The detection of ammonia in air is of great significance for environmental monitoring and process control due to the high toxicity of this gas. One of the most frequently used systems in ammonia detection is based on conductive polymers (CPs). Polyaniline (PANI) is one of the most intensively CPs studied during the last decade because of its environmental stability, ease of synthesis and reversible redox properties [1]. The electrical conductivity of this polymer can be improved in presence of some metal oxide fillers as well as exposed gases [2]. The key feature of an effective sensor that affects its sensitivity and performance is the surface area available for adsorption and detection of a gas or vapor. Thus nanomaterials, including nanocomposites, seem to be promising in this regard and have received great attention in recent years [1-4]. In this paper, the effects of addition of nanofillers, including zinc oxide (ZnO) and tin oxide (SnO₂), on the ammonia sensibility of polyaniline-based sensor have been studied.

Experimental

Materials

The aniline, hydrochloric acid (HCl), ammonia, and ammonium persulphate (APS) were all purchased from Merck (Germany). ZnO ($d_{avg} = 10-30$ nm) and SnO₂ ($d_{avg} = 50-70$ nm) were supplied from US Nano Inc. and Nabond Technology (Hong Kong), respectively.

Preparation method

For preparation of PANI nanocomposites, 0.1 mol aniline and specified amount of APS were dissolved in

100 ml HCl (1 M), separately. Specified amount of SnO₂ or ZnO was added to the aniline solution. After stirring and sonication, the two solutions were mixed rapidly in a flask (at 0-4 °C). After 2 h, the PANI nanocomposite was collected by gravity filtration and washed several times. The obtained PANI-based dispersions in water were drop-casted onto the glass substrate and left to dry for one day. A same procedure was applied in the preparation of pristine PANI without adding any filler.

Characterization

The FT-IR spectroscopy was performed via a JASCO FT-IR-6300 spectrometer (Japan) with a resolution of 4 cm⁻¹ in the range of 400-4000 cm⁻¹. XRD analysis was carried out on a Bruker D8 Advance X-ray diffractometer (Germany) using CuK α radiation (40 kV, 40 mA, and $\lambda = 1.54$ Å). Samples were scanned at 2°/min in the range of $2\theta = 5-80^\circ$. For ammonia sensing measurements, polymers coated on the glass substrates were inserted in the electrical DC circuit covered by a transparent plastic box, as testing chamber. The specified amount of ammonia in liquid state was injected into the sensing chamber, equipped with a circulating fan.

Results and Discussion

Chemical structure

The FT-IR spectra of PANI, PANI/SnO₂, and PANI/ZnO are shown in Fig. 1. The broad peak appeared at 3000-3400 cm⁻¹ in Fig. 1-a could be related to the stretching of N-H and C-H bonds. The peaks observed at 1558 cm⁻¹ and 1475 cm⁻¹ are related to the quinoid ring stretching and benzenoid stretching bonds,



respectively. The benzenoid-NH⁺-quinoid vibrations occurred at 1116 cm⁻¹ indicates the conductive emeraldine salt form of PANI [5]. As it is clear, all characteristic peaks of PANI can be observed in the FT-IR spectra of nanocomposites. However, some peaks of modified PANI have shifted slightly due to interactions of PANI with SnO₂ and ZnO.

Crystalline structure

Fig. 2 represents the XRD pattern of PANI and its nanocomposites. The observed peak at $2\theta = 25.9^\circ$ in Fig. 2-a, is the characteristic peak of the PANI salt, suggesting the semi-crystalline structure for the PANI sample [3]. The intense peaks observed for the PANI/SnO₂ sample, indicates that by addition of SnO₂, the crystalline nature of PANI enhanced significantly. However, the ZnO particles seemed to have no obvious effect on the crystalline structure of the PANI. This probably suggests better interactions between PANI and SnO₂ when compared to ZnO.

Ammonia sensing performance

The response of the sensors is reported as $\Delta R/R_0$, where R_0 and R are the values of the electrical resistance before and after contact between the polymer and the analyte (ammonia), respectively. Fig. 3 represents the response profile of PANI and its composites vs. time. The resistance of all samples increased when exposed to ammonia. In fact, PANI undergo dedoping process in which the protons on -NH- groups are transferred to NH₃ molecules to form ammonium ions leading to the formation of neutral polymer chains and results in the decrease of charge carrier density [4]. This process is almost reversible, so that, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and proton. As can be seen in Fig. 3, the obtained responses for the nanocomposites-based sensors are much higher than that of PANI-based one which could be attributed to the enhanced surface area due to the presence of nanoparticles [3,4]. On the other hand, formation of p-n junctions between PANI and SnO₂ or ZnO results in an increase in the width of the depletion region which consequently decreases the conductivity of the nanocomposite [2]. In addition, the highest response intensity achieved for PANI/SnO₂, might be due to the better polymer/filler interactions in the case of PANI/SnO₂ when compared to PANI/ZnO sample. On the other hand, one may relate the better sensibility of PANI/SnO₂ to the higher carrier concentration of SnO₂ in comparison with ZnO [6].

Conclusion

The ammonia sensing performance of the PANI was investigated and it has been observed that the resistance of PANI increased when exposed to ammonia due to the dedoping process. The effect of addition of metal

oxide nanoparticles, including zinc oxide and tin oxide, on the ammonia sensing performance of PANI-based sensor was studied. The obtained responses for the nanocomposites-based sensors were much higher than that of PANI which could be related to the enhanced surface area in presence of nanoparticles and doping effect of the nanofillers via formation of p-n junctions.

References

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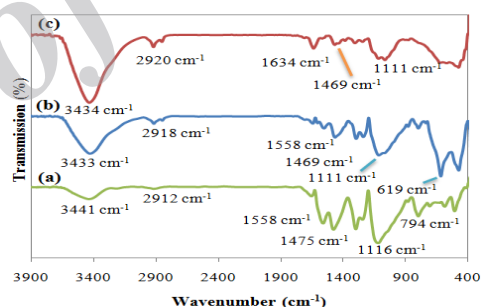


Fig. 1. FT-IR spectra of a) PANI, b) PANI/ZnO, c) PANI/SnO₂

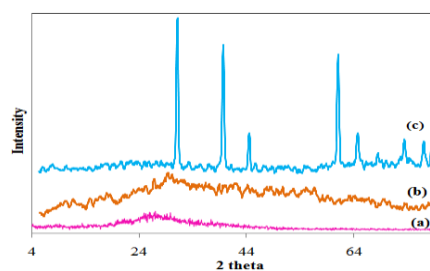


Fig. 2. XRD patterns of a) PANI, b) PANI/ZnO, c) PANI/SnO₂

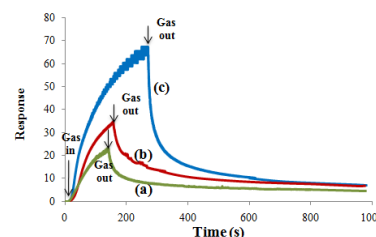


Fig. 3. Ammonia response profile of a) PANI, b) PANI/ZnO, c) PANI/SnO₂