

Study on NH_3 Gas Sensing Properties of PANI-WO_3 Nanocomposites

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ABSTRACT

We dispersed WO_3 nanoparticles with average particle size of 20-30 nm into aniline monomers and prepared PANI-WO_3 nanocomposites by chemical oxidative polymerization. PANI-WO_3 nanocomposites were spin-coated on substrates with interdigital carbon electrodes to form PANI-WO_3 nanocomposites films and to study the NH_3 gas sensing properties at room temperature. The gas sensing properties of pure PANI and PANI-WO_3 with different blending ratios were compared and evaluated. The minimum detectable concentration of NH_3 gas of the sensor fabricated from $\text{PANI-20\%WO}_3$ nanocomposites is 3 ppm, and the sensitivity of 100 ppm NH_3 gas is 31, which is five times higher than that of pure PANI. In addition, the response time and recovery time were faster than pure PANI, especially the recovery characteristics were significantly improved.

INTRODUCTION

Among these conducting polymers, Polyaniline(PANI) with unique electrical and optical properties is frequently used because of its easy processing capability, flexibility, high electrical conductivity and good environmental stability[1, 3].

PANI is prepared by oxidative polymerization of aniline monomers by chemical or electrochemical methods [1,3,5]. The electrical conductivities of PANI vary with doping and the concentration of NH_3 gas. Therefore, PANI has been widely used as a NH_3 gas sensing material. The gas sensor using PANI is operating at room temperature, has low power consumption, good environmental stability and long life [7]. On other hand, metal oxide semiconductor materials such as SnO_2 , TiO_2 , Fe_2O_3 , ZnO , CeO_2 , and WO_3 are widely used to detect toxic gases, which have the advantages of high sensitivity, fast response time and recovery time. However, sensors based on these materials have the disadvantage of high operating temperatures of 300-500°C and lack of selectivity. To overcome these drawbacks, hybrid nanocomposites of conductive polymers and metal oxides can be employed to enhance the gas sensing characteristics such as sensitivity, selectivity and stability[1]. Among the conductive polymers, PANI is used as a material for sensing toxic gases such as NH_3 , NO_x , H_2 , CO , CO_2 , H_2S , etc. [2,4,5,7,8].

The gas sensing properties of the hybrid nanocomposites of PANI and metal oxides are much improved over pure PANI, which might be caused by some chemical interaction between PANI and metal oxides and be also attributed to the p-n heterojunction formed at the surface between p-type PANI and n-type metal oxides[5]. Especially PANI-WO_3 nanocomposites showed maximum response to NH_3 gas as compared other target gases because of the strong interaction between the PANI-WO_3 film and adsorbed NH_3 gas molecules, also the rate of reaction in between the surface of PANI-WO_3 film and NH_3 gas molecules is greater compared to other target gases, as result PANI-WO_3 film showing higher selectivity to NH_3 gas [1, 14].

In the present study, we report the NH_3 gas sensing characteristics of the sensor fabricated with the PANI-WO_3 nanocomposites film on the interdigital carbon electrodes.

Experiments

Materials and measurement apparatus

WCl₆ (Aldrich Chem.Co.), ethanol (Aldrich Chem.Co.), polyethylene glycol (polyethylene glycol, 99%, Aldrich Chem.Co.), aniline monomer(Thomas Baker), ammonium persulfate (APS, Thomas Baker), HCl(Thomas Baker)

In order to evaluate the electrical resistance change of PANI-WO₃ nanocomposites films with the different NH₃ gas concentration, the thickness and electrical resistance of the films were measured after drying by spin-coating PANI-WO₃ nanocomposites on a plastic substrate (7×7 mm) with the interdigital carbon electrodes.

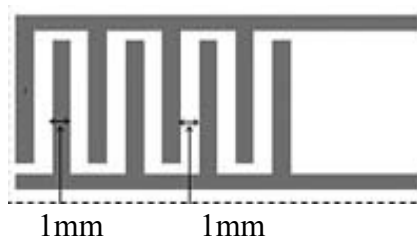


Fig. 1 The structure of the interdigital carbon electrodes

The thickness and electrical resistance of PANI-WO₃ nanocomposite films was measured by a thickness meter (SANKO SDM-mini) and a digital multimeter (Escort EDM 2347).

In the analyses of the samples TEM(FEI - TECNAI G2 20S – TWIN) and XRD(D8, ADVANCED), SEM(Zeiss model-SUPRA VP/500)were used.

The NH₃ sensing properties of PANI-WO₃ nanocomposites were evaluated by sensitivity S.

$$S = R_g/R_a$$

where R_a and R_g are the electrical resistances of the sensor in air and NH₃ gas, respectively.

The response time and recovery time are calculated as the times to reach 90% of the total resistance change in air or NH₃ gas.

Preparation of WO₃ nanoparticles

0.1g of WCl₆ and 20 mg of polyethylene glycol were dissolved in 2ml of ethanol and stirred for 3 h. The precursors were dried thoroughly at 40-50°C and sintered at 500°C for 1 h to obtain nanocrystalline WO₃ powders.

Preparation of PANI-WO₃ nanocomposites

PANI was prepared by chemical oxidative polymerization from aniline monomers.

To prepare the PANI-WO₃ nanocomposites, the aniline monomer and WO₃ nano powder were mixed in a constant ratio and added to 1 mL HCl and stirred for 15 min. In another beaker, a certain amount of ammonium persulfate(APS) was dissolved in HCl. The two solutions were mixed together at 0-5°C and the reaction mixtures were stirred until the color of the mixture turns deep green. After stirring, the sample was left for 24 h, and the PANI-WO₃ precipitate was filtered and washed with distilled water and acetone. The final product was dried at 80°C. The PANI-WO₃ nanocomposites was mixed with a certain amount of 10% PVA to prepare a paste that could be coated on the substrate.

The polymerization of anilineis an exothermic reaction, which is maintained at a constant temperature at the

early stage, and the reaction mixture exhibits a light brown color as a oligomerization intermediate.

When the polymerization reaction starts, the temperature increases, the color of the mixture changes to dark blue and becomes slurry. Also, the surface of the reaction vessel was brown metallic by PANI coating. After a certain time, the color of the reaction solution changes to dark green, and the surface of the reaction vessel is colored green.

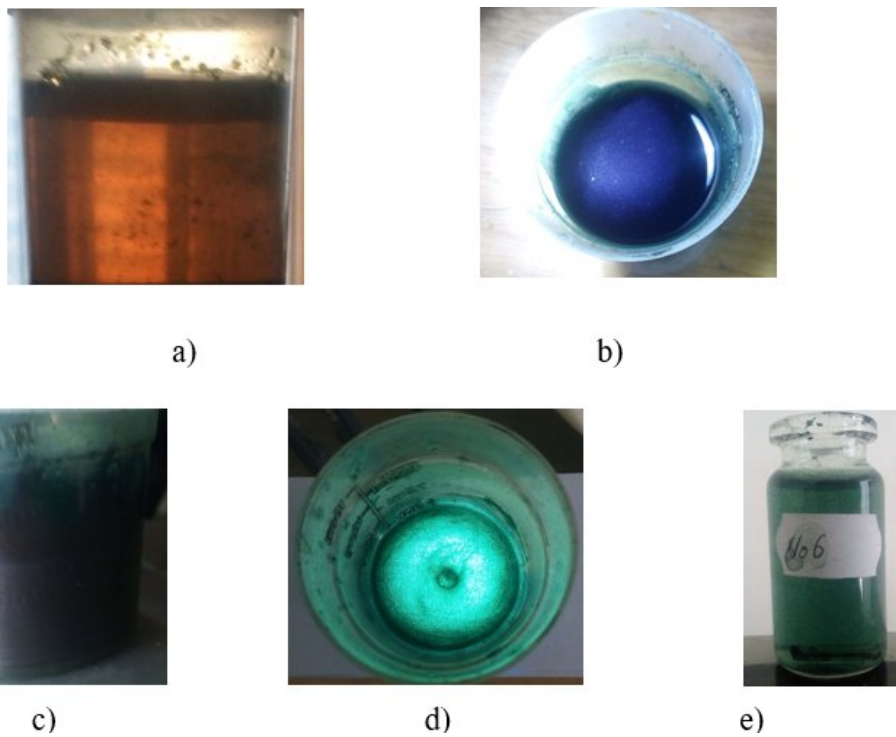


Fig.2 Preparation of PANI

RESULTS AND DISCUSSION

Grain size and crystal structure of WO_3 nanoparticles

The morphology and microstructure of WO_3 nanoparticles were measured by transmission electron microscope (TEM, FEI-TECNAI G2 20S-TWIN) (Fig. 3)

As shown in Fig.3, the structure of WO_3 nanoparticles is mostly spherical with uniform grain size and the average particle size of WO_3 nanoparticles is 20-30 nm.

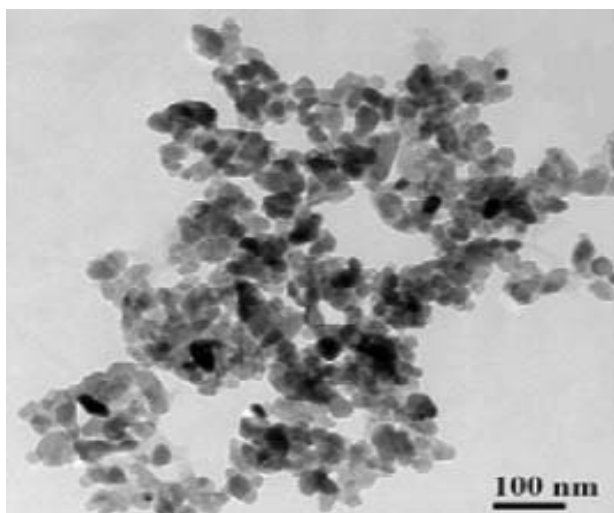


Fig. 3 TEM image of WO_3 nanoparticles

The crystal structure of WO_3 nanoparticles was determined by XRD measurement (XRD, D8, ADVANCED).

Diffraction peaks were observed at $2\theta = 23.05, 23.54, 24.30, 28.83, 34.07, 55.97, 61.66$ and 63.2 , which correspond to (002), (020), (200), (202), (420), (422), (413) planes respectively, of monoclinic WO_3 with a lattice constant of $a = 7.319 \text{ \AA}$, $b = 7.55 \text{ \AA}$, $c = 7.71 \text{ \AA}$.

NH_3 gas sensing properties of PANI- WO_3 nanocomposites

The uniform film was formed by spin-coating PANI- WO_3 -PVA on the substrate with interdigital carbon electrodes (Fig. 4). As shown in the SEM (Zeiss model-SUPRA VP/500) image of PANI- WO_3 -PVA film, the surface of the film consists of fibers with porous structure and the diameter of the fibers is uniform. WO_3 nanoparticles are surrounded by a network of PANI-PVA fibers.

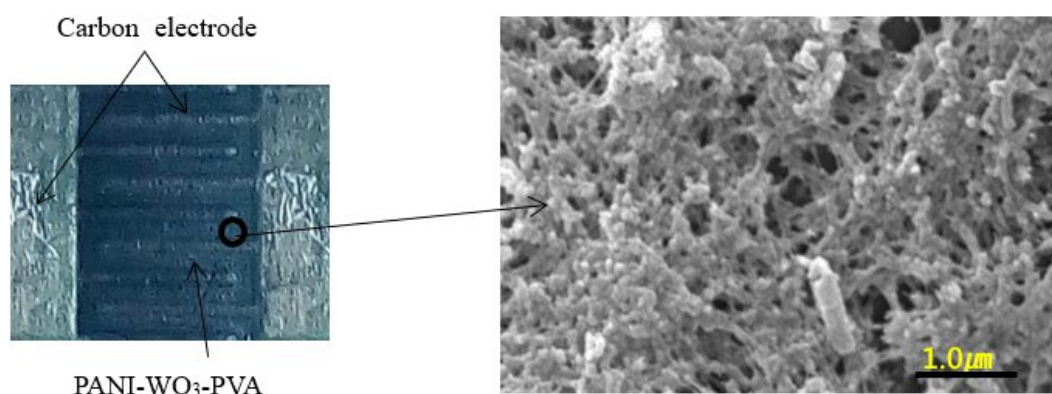


Fig. 4 The structure and SEM image of sample

- NH_3 gas sensing characteristics

The NH_3 gas sensing characteristics according to the mixture ratio of PANI- WO_3 nanocomposites at room temperature are shown in Fig. 5.

The sensitivity of PANI- WO_3 nanocomposites in 100 ppm NH_3 increased with increasing WO_3 percentage, decreased above 20 wt%, and showed maximum value of 31 at 20 wt%. The NH_3 sensing mechanism in PANI- WO_3 nanocomposites material can be explained mainly by the depletion layer between PANI and WO_3 .

Generally, after exposure to NH_3 gas, emeraldine salt form of PANI was reduced to emeraldine base resulting into decrease in density in PANI which causes increase in resistance.

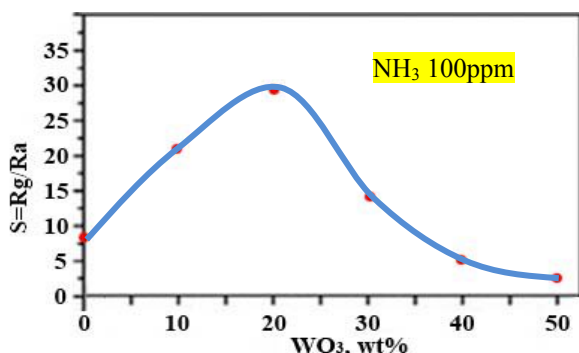


Fig. 5 NH_3 gas sensing characteristics according to the mixture ratio of PANI- WO_3 nanocomposites at room temperature

In PANI- WO_3 nanocomposites, n-type WO_3 nanoparticles form depletion layers with p-type PANI. When the sensor was exposed to NH_3 gas, the width of depletion layer increases resulting into increase in resistance.

Thus, in NH_3 gas the electrical resistance of PANI- WO_3 nanocomposites changes more than that of pure PANI. When the WO_3 percentage exceeds a certain value, the resistance decreases and the sensitivity decreases.

This might be explained by two factors.

First, the excess addition of WO_3 made PANI insufficient to completely cover the surface of WO_3 and certain amount of NH_3 was absorbed on the surface of WO_3 which would not improve the sensitive properties to NH_3 .

Second, the large amount of electrons generated by excess WO_3 made the depletion layer thicker at the heterointerface between PANI and WO_3 , which leads to a higher resistance and a lower resistance change, leading to a lower sensitivity.

Therefore, the excess addition of WO_3 was unfavorable to improve the sensitivity to NH_3 gas. The sensing properties of PANI-20 wt% WO_3 nanocomposites to NH_3 gas concentration at room temperature are shown in Fig. 6.

As shown in Fig. 7, the resistance of PANI-20 wt% WO_3 nanocomposites varies greatly with increasing NH_3 gas concentration and enhances by 31 times at 100 ppm.

The response and recovery times of PANI-20 wt% WO_3 nanocomposites at room temperature are shown in Fig. 7. As shown in Fig. 7, the response time is around 40 s, the recovery time is around 60-70 s, and the recovery time is about three times faster than that of pure PANI.

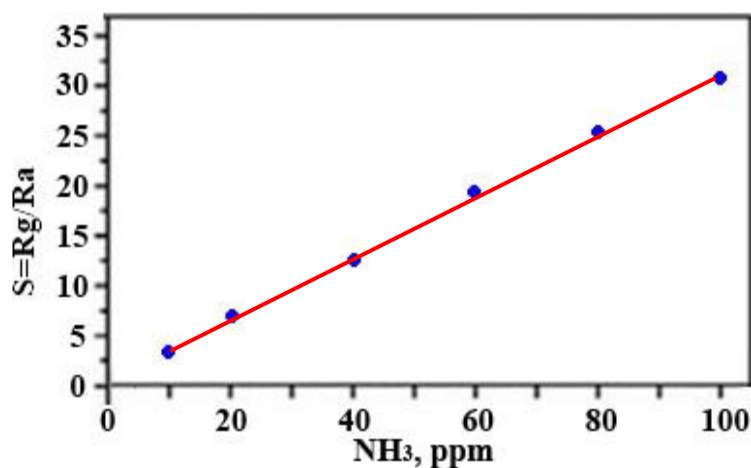


Fig. 6 sensing properties of PANI-20 wt% WO_3 nanocomposites to NH_3 gas concentration at room temperature

The resistance of pure PANI increased in the presence of NH_3 gas, recovered very slowly in air, and took a long time to reach the original resistance value.

PANI- WO_3 nanocomposites have faster recovery times than pure PANI and reach their original resistivity values.

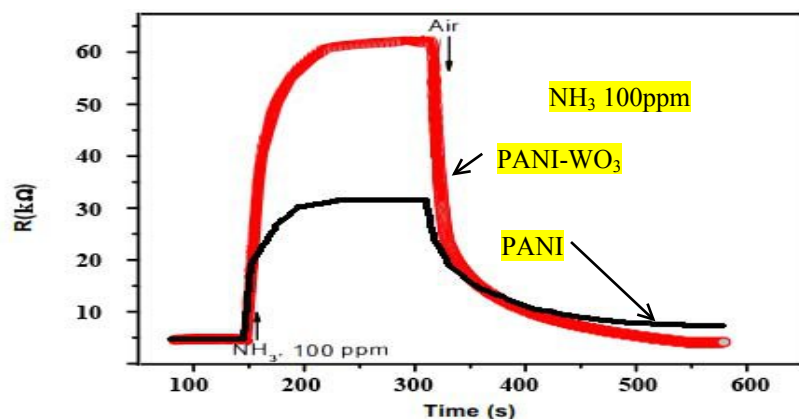


Fig. 7 Response characteristics of PANI-WO₃

CONCLUSIONS

The NH₃ gas sensing properties of sensors fabricated from a mixture of WO₃ nanoparticles prepared by sol-gel method and PANI prepared by chemical oxidative polymerization were investigated.

TEM, SEM and XRD analysis of PANI-WO₃ nanocomposites showed that the prepared WO₃ particles had the average size of 20-30 nm and the crystalline phase, and also showed that the PANI-WO₃ nanocomposites film had a porous structure.

The minimum detectable concentration of NH₃ gas of the sensor fabricated from PANI-20% WO₃ nanocomposites is 3 ppm, and the sensitivity of 100 ppm NH₃ gas is 31, which is five times higher than that of pure PANI.

In addition, the response time and recovery time were faster than pure PANI, especially the recovery characteristics were significantly improved.

The fabricated PANI-WO₃ nanocomposites can be used as good sensing material for NH₃ gas at room temperature, and can be widely used for the fabrication of NH₃ sensors with advantages of low cost, environmental safety and low power consumption.

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