

PPB-LEVEL AMMONIA SENSOR BASED ON TERNARY FLEXIBLE ZNO/PPY-AG THIN FILM

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Abstract

Detection of hurtful and noxious gases has become more and more crucial for the environmental monitoring, manufacturing/monitoring of industrial products and for human health safety. Into this bargain, an innovative ammonia (NH₃) gas sensor based on ternary composites of ZnO/PPy-Ag, deposited in ITO-PET thin film was successfully synthesized via photopolymerization process. The chemical structural state and morphology of ZnO/PPy-Ag (0.5 to 3M), PPy-Ag (1M) and ZnO nanofibers samples were fully revealed by Fourier Transform Infrared spectroscopy (FTIR-ATR), RAMAN Spectroscopy and Scanning Electron Microscopy (SEM), confirming its successful fabrication. The electrical conductivity was carried out using the common four probes method. Obviously, the ternary ZnO/PPy-Ag (1M) composites sensor exhibited a highest conductivity of 0.699 S.cm⁻¹ with an extremely low detecting level. Moreover, the composites ternary layers showed an ultra-fast response/recovery time at room temperature and robust operation reproducibility during five cycles. Meanwhile, the experimental results promising an alternative approach for the production of a new ternary materials and a novel insight for high-performance ammonia sensing applications.

Keywords: Thin film, ammonia, gas sensor, ternary composites

1. INTRODUCTION

Ammonia is a toxic and corrosive gas, widely used in industrial processes, agricultural activities, and environmental pollution. Due to its harmful effects on human health and the environment, ammonia detection at low concentrations is highly relevant for safety and monitoring applications [1-3]. Traditional methods of detection usually suffer from disadvantages involving high cost, long response times, and low sensitivity. During past years, development of a new sensing materials has taken place in the field based on metal oxides [4-8], conducting polymers [9-13], and nanomaterials, characterized by increased sensitivity and selectivity with a reduction in the response time towards ammonia gas detection.

In this study, a new and low-cost ITO-PET/ZnO with polypyrrole-silver nanocomposite flexible substrate material was prepared through an in situ photopolymerization of pyrrole in the presence of silver nitrate AgNO₃ and zinc oxide deposited in indium tin oxide-polyethylene terephthalate (ITO-PET) via an electrochemical pathway. The silver nitrate was used as a photo initiator. The as-fabricated ITO-PET/ZnO/PPY-Ag ternary material was black, exfoliated with a polypyrrole-rich surface decorated with silver nanoparticles in metallic state and deposited on ZnO. The morphology of ZnO and the effect of silver particles in the thin film is discussed and investigated by the usual method of characterization.

2. MATERIALS AND METHODS

2.1 Materials

Pyrrole (Sigma-Aldrich, purity ~ 98.0%) was purified by distillation and kept in dark condition at low temperature (~ 18 °C). Silver nitrate (Sigma-Aldrich, purity ~ 99.9%) was used as photo-initiator. Potassium nitrate KNO₃ (Fluka-Chemie, purity ~ 99.0%), Zinc nitrate Zn (NO₃)₂ (Fluka-Chemie, purity ~ 99.0%), Acetone (Sigma-Aldrich, purity ~ 99.0%), Ethanol (Sigma-Aldrich, purity ~ 99.8%), and Ammonia NH₃(sigma-Aldrich, purity ~ 99.0%) were used without any further purifications. Deionized water was used as a solvent for all the studies. ITO (thickness, 150 nm; sheet resistance, 30–50 Ω/square)-coated polyethylene terephthalate (PET) substrates (thickness: 100 μm) were purchased from Sigma-Aldrich with size dimension (20 mm × 10 mm). ITO-coated PET substrates were ultrasonically washed using acetone, ethanol, and distilled water for 7 min each, and then dried for 2 h at 60 °C in an oven.

2.2 Electrochemical deposition of ZnO nanowires on ITO-PET

The ZnO was electrochemically deposited on ITO-PET flexible sheets using the Model Parstat 4000 potentiostat under computer control and at 75 °C temperature condition, forming the working electrode with surface area of 2 cm². A platinum and silver electrode (KCl) were used as the counter and referred electrode, respectively. The electrolyte contained 0.1 M zinc nitrate and 1 M potassium nitrate in aqueous solution.

2.3 Synthesis of ITO-PET/ZnO/PPY-Ag ternary films

Facile in situ photo-polymerization process was successfully used for preparing ITO- PET/ZnO/PPY-Ag ternary composite films on flexible substrate. Briefly, the photo-polymerization of pyrrole on ZnO deposited in ITO-PET flexible sheet was done in a glass bottle containing fixed quantity of distilled pyrrole 0.26 g (1 M) along with 0.5 M AgNO₃ (0.34 g) in 4 ml of distilled water. AgNO₃ is added to the synthesis as a photo-initiator for the monomer. Finally, after a uniform mixing, the ZnO-coated ITO-PET sheet was immersed in the pyrrole-AgNO₃ aqueous solution's glass bottle and placed under a UV lamp (VILBERT LOURMAT, VL-4LC) set at wavelength ~ 365 nm, UV source to sample distance ~ 13 cm, intensity ~ 5 mW/ cm² for 6 h. After UV exposure, the flexible sheet was carefully rinsed with distilled water and dried in oven at 60 °C for 24 h. Under the same experimental conditions, the flexible sensors with fixed concentration of pyrrole (1 M) and varied concentration of AgNO₃ as 0.5 M, 1 M, 2 M, and 3 M were also synthesized to study the effect of AgNO₃ concentration on sensing.

2.4 Methods

The chemical composition of the obtained ITO-PET/ZnO/PPY-Ag ternary flexible sheets were investigated using Fourier transform infrared spectroscopy (ATR-FTIR) which was acquired on by Nicolet IR spectrophotometer for wavenumbers ranging from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ over 50 Scans. The RAMAN spectra were characterized in the Raman shift range from 50 to 3550 cm⁻¹ with laser wavelength: 532 nm by THERMO SCIENTIFIC DXR 2 spectrometer at room temperature. The morphological observations of ITO-PET/ZnO/PPY-Ag films sensors were recorded by scanning electron microscopy type (FEI-Quanta 600). The electrical conductivity of the ZnO/PPy-Ag flexible films was measured using a Jundel RM 3000 4-probe technique with 1mm equidistance probes, by measuring the resistance.

3. RESULTS AND DISCUSSIONS

3.1 Fourier Transform infrared analysis (FTIR)

The molecular structure and functional groups of the flexible synthesized film are confirmed by Fourier Transform infrared spectroscopy (FTIR) in the wave number range of 4000-500 cm⁻¹. The FTIR spectra of

PPy-Ag (1M) and ZnO/PPy-Ag (1M) are shown in **Figure 1**. The mean FTIR peaks located at 769 cm^{-1} and 666 cm^{-1} are related to the C-H out of plan vibration and C-C out of plane ring deformation. The peak at 900 cm^{-1} is assigned to the ring deformation. The observed peaks at 1154 cm^{-1} and 1021 cm^{-1} are for the C-H vibrations in plans of PPy. The observed intense peak at 1384 cm^{-1} is assigned to the interactions at the interface of PPy and Ag nanoparticles. The peaks at 1535 cm^{-1} and 1463 cm^{-1} are attributed to the C=C and C-N stretching vibration, respectively. It should be noted that the appearance of a new tow weak peaks at 2852 cm^{-1} and 2921 cm^{-1} for ZnO/PPy-Ag (1M) sample were attributed to the asymmetric vibrations of C-H group and confirmed the interaction of ZnO with PPy. The strong broad N-H stretching vibration absorption band of the prepared samples at 3444 cm^{-1} is observed. All observed characteristic peaks are in agreement with literature results which indicate the successful polymerization of pyrrole monomer [14-16].

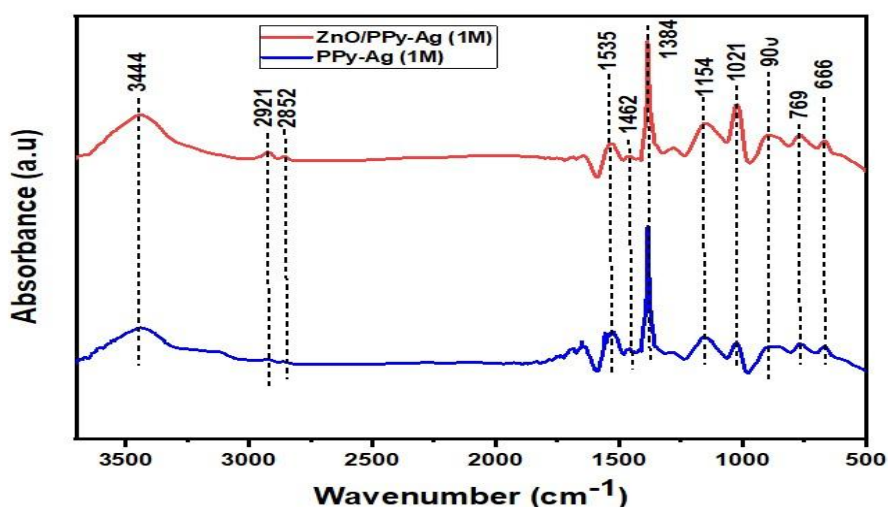


Figure 1 FTIR spectroscopy of ZnO/ PPy-Ag (1M) and PPy-Ag (1M) sensors

3.2 RAMAN spectroscopy analysis

The chemical structure of the as-fabricated samples was further investigated using Raman spectroscopy analysis on the prepared films. As shown in **Figure 2**, two characteristics Raman bands are presented in the spectrum located at 1328 cm^{-1} and 1567 cm^{-1} assigned to the ring stretching mode and the symmetric stretching of the C=C bonds of polypyrrole, respectively. The additional results confirm that the monomer was successfully polymerized through an efficient photo-polymerization method [17].

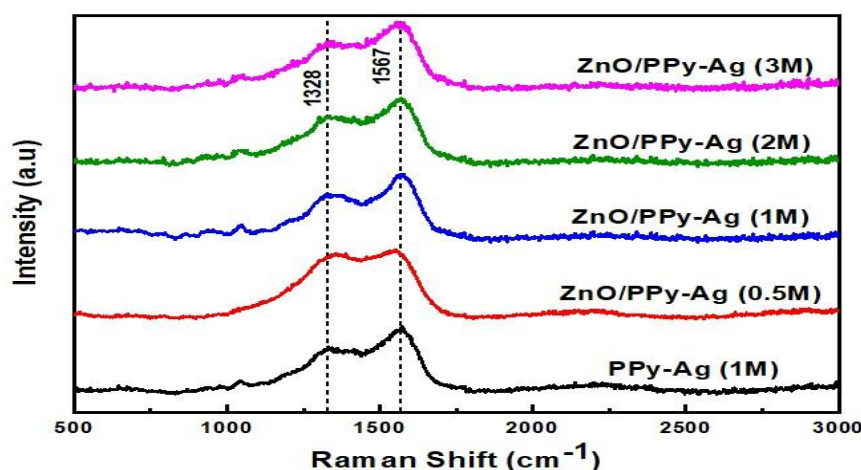


Figure 2 RAMAN spectroscopy of ZnO/ PPy-Ag (0.5 to 3M) and PPy-Ag (1M) sensors

3.3 Scanning electron microscopy analysis (SEM)

Figure 3 presents scanning electron microscopy (SEM) images of the flexible ZnO/PPy-Ag (1M) film at different magnifications. As revealed in the SEM micrograph, the ternary ZnO/PPy-Ag (1M) thin film is composed of nanofibers of ZnO, formed by electrodeposition, coated with dense homogenous semi-spherical and spherical granular of PPy structures. According to **Figure 3**, small white nanoscale Ag particles are observed to be embedded on the surface of the spherical PPy. The nanoparticles are uniformly distributed within the ZnO chain, exhibiting either spherical or semi-spherical shapes. The preparation process produced silver nanoscaled particles, spherical PPy and nanofibers ZnO with an average diameter of <103 nm, $1,308$ μm and $1,186$ μm , respectively. The globular structure of the flexible film is suitable for gas sensing applications.

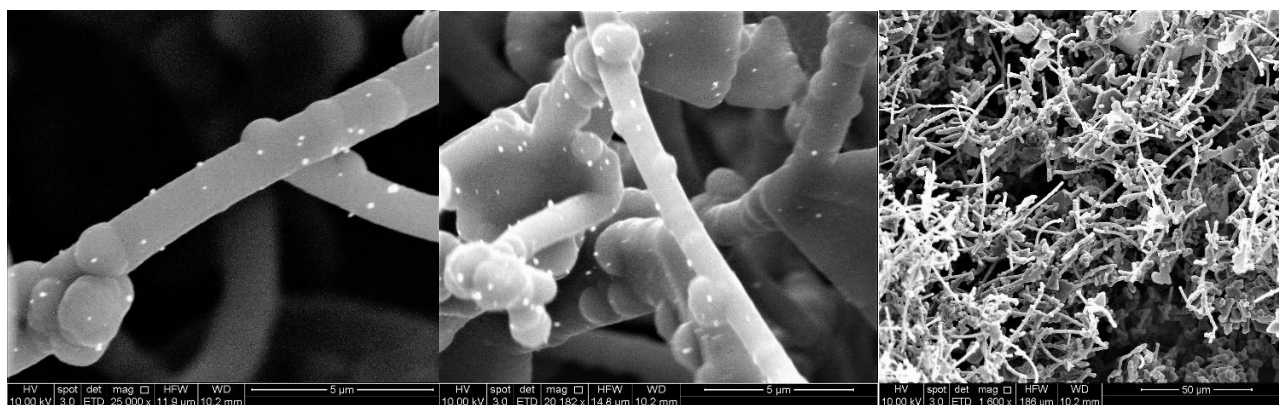


Figure 3 SEM micrographs with different magnifications

3.4 Electrical characteristics

As presented in table 1, the electrical conductivity values of ZnO/PPy-Ag on their different concentration AgNO_3 (~ 0.5, 1, 2, 3M), PPy-Ag (1M) and ZnO nanofibers were measured using the four-point technic. The electrical conductivity of the ternary ZnO/PPy-Ag (0.5M) and ZnO/PPy-Ag (1M) flexible films increased sharply, from 0.3 $\text{S}\cdot\text{cm}^{-1}$ (for PPy-Ag (1M)), to 0.392 $\text{S}\cdot\text{cm}^{-1}$ and 0.699 $\text{S}\cdot\text{cm}^{-1}$, respectively. This suggests that the contribution of the n-type ZnO nanofibers metal oxide enhances the conductivity of the sensitive sheets. On the other side, due to the presence of silver clusters in the surface matrix sensor, the ZnO/PPy-Ag (2M) and ZnO/PPy-Ag (3M) composite films revealed a diminution in the conductivity values with 0.204 $\text{S}\cdot\text{cm}^{-1}$ and 0.117 $\text{S}\cdot\text{cm}^{-1}$, respectively. The highest electrical conductivity was recorded for the ternary ZnO/PPy-Ag (1M) flexible sheet, with a value of 0.699 $\text{S}\cdot\text{cm}^{-1}$.

Table 1 Electrical conductivity values for the as-prepared ZnO/PPy-Ag, PPy-Ag (1M) and ZnO nanofibers sensors measured by four-point method

Sample	Resistance (Ω)	Conductivity ($\text{S}\cdot\text{cm}^{-1}$)
PPy-Ag (1M)	111,110	0,300
ZnO-PPy-Ag (0.5M)	85,034	0,392
ZnO-PPy-Ag (1M)	47,714	0,699
ZnO-PPy-Ag (2M)	163,776	0,204
ZnO-PPy-Ag (3M)	285,646	0,117
ZnO nanofibers	1166,108	0,029

3.5 Gas sensing performance

Representative normalized response curves of pure ZnO NWs, PPy-Ag (1M) and ZnO/PPy-Ag (1M) films toward 25 ppm of NH₃ are presented in **Figure 4**. the following inferences can be drawn: (i) pure ZnO NWs films show a reduction in resistance upon exposure to NH₃, which is characteristic of the typical n-type conduction behavior of ZnO. Pure PPy-Ag (1M) films exhibit an increase in resistance upon NH₃ exposure, indicating the p-type conduction behavior. (iii) ZnO/PPy-Ag (1M) films exhibit a pronounced increase in the resistance on exposure to NH₃, which can be attributed to the uniform coating of p-type PPy-Ag. This layer dominates the charge transport mechanism, leading to an overall p-type conduction behavior. The ZnO/PPy-Ag (1M) films demonstrate an ultrafast sensing performance, with response and recovery times of 1.0 s and 2.65 s, respectively.

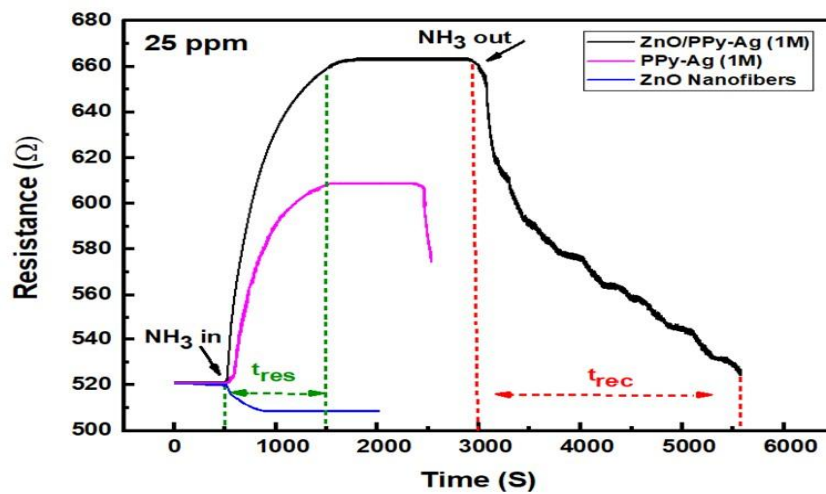


Figure 4 Resistance-time data of ZnO/PPy-Ag (1M) sample for 25 ppm of NH₃

Figure 5 shows the repeatability measurement of ZnO/PPy-Ag (1M) films for 10 ppm of NH₃ gases. Moreover, the ternary thin film displays a typical continuous response (263%) and recovery characteristic for 5 cycles at room temperature with a similar cycle curve. Hence, these ternary composite films were found to be stable in atmospheric conditions. The current sensor system has a LOD on the ppb order which is calculated to be 6.5 ppb.

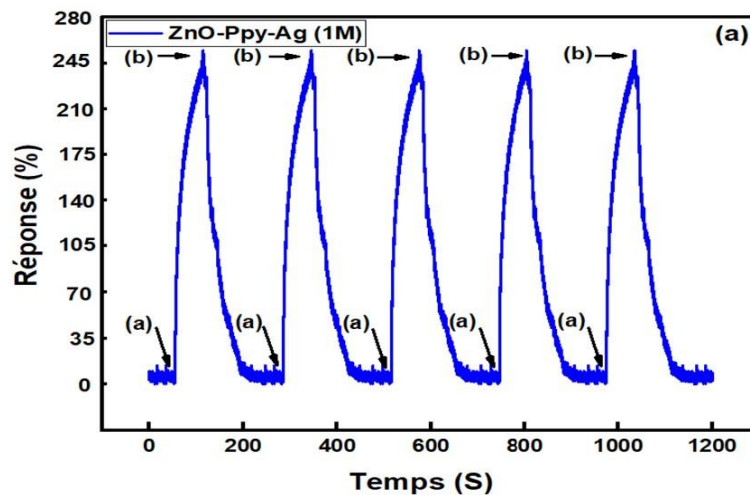


Figure 5 Response reproducibility of ZnO/PPy-Ag (1M) upon injection and desorption of 10 ppm NH₃

4. CONCLUSION

In summary, we successfully prepared ZnO nanofibers/ PPy-Ag spherical composites thin films using photopolymerization technique. The optimized ternary ZnO/PPy-Ag (1M) film sensor exhibits a high conductivity (0.699 S.cm^{-1}), a good selectivity and high sensitivity within a very low detection limit at room temperature. The obtained results displayed that the novel ternary sensor appears to be a promising sensing material for the ammonia detection even at ppb-level concentration.

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