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Monocarboxy Tetraphenylporphyrin functionalized ZnO nanorods photoactivated gas sensor

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Abstract

In this work, gas sensing properties of monocarboxy tetraphenylporphyrin functionalized ZnO nanorods under different light illumination, were investigated. These studies showed that the sensitivity to triethylamine of porphyrin functionalized ZnO nanorod device are greatly enhanced under illumination with visible light. This photoactivated nanostructure composition has the potential for gas sensor device applications.

Keywords: ZnO nanorods; Monocarboxy Tetra phenyl Porphyrin; Photoactivated gas sensor

1. Introduction

ZnO is one of the well-established gas sensing semiconductor metal oxides, which has been extensively studied for detection of inflammable and toxic gases, such as NO_2, C_2H_5OH, CO and H_2 [1]. 1D ZnO nanostructures have been studied as a promising material to improve gas sensing properties, because of their high surface to volume ratio [1]. However, the exploitation of ZnO nanorod arrays for gas sensor has hardly been reported. Investigating low temperature fabrication is deemed necessary for low cost sensors. Herein, hydrothermal method was employed to grow C-axis vertically well aligned ZnO nanorods on transparent conductive indium-doped tin oxide (ITO) substrate (fig. 1a) [2]. It has been recently shown that gas sensitivity of pure ZnO nanorods is photoactivated under UV light illumination [3]. The investigation of organic materials functionalized semiconductor metal oxides based photoactivated

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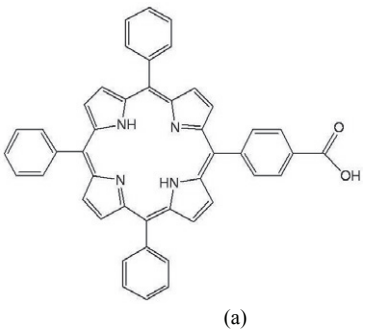
chemical and gas sensors is a very active area of research due to the need for efficient, environmentally friendly, and economically viable sensor devices. In order to improve the photocatalytic performance of ZnO, the simplest method is surface functionalization using organic materials to improve the photochemical performance of the semiconductor. Suitable chosen organic material can extends the photoactivation of ZnO nanorods to the visible region. Efforts have been made in the past to employ porphyrin derivatives to sensitize semiconductor materials [4]. Porphyrins possess good chromophores activities over the visible region and good electron donating properties due to their large π-electron systems. The molecular structure of 5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrin (H_2TPPCO_2H) is shown in the fig. 1a.

In this paper, we report on the fabrication of a low cost and room temperature gas sensor device based on a vertically aligned ZnO nanorods array synthesized by hydrothermal route. The synthesized ZnO nanorods were functionalized using monocarboxy TPP. In this work, the usefulness of monocarboxy TPP functionalized ZnO nanorod photo activated gas sensing behaviour in different light illuminations were investigated.

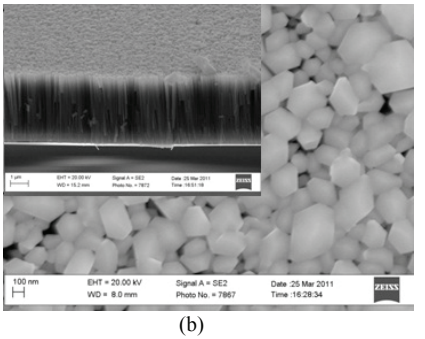
2. Experimental Procedure

2.1. Synthesis of ZnO nanorods

ZnO nanowires were synthesized using a hydrothermal method on indium tin oxide (ITO) substrate. The ZnO seed layer solution was prepared using 0.005M zinc acetate dehydrates dissolved in 50ml absolute ethanol. The formation of the seed layer on ITO substrate was conducted by using drop coating method. After ZnO seed layer coating on the ITO substrates, the substrates were annealed in air at 400^{o}C for 30 min in a furnace. Then, ZnO nanorods were grown on the seed layer using hydrothermal method in 0.025M aqueous solution of zinc acetate dehydrate ($Zn(Ac)_2.2H_2O$, Sigma-Aldrich, 99%) and hexamethyltetramine (HMTA, Sigma-Aldrich, 99%) at 90^{o}C for 4 hr. The diameter and length of ZnO nanowires were characterized by scanning electron microscopy (SEM), as shown in Fig.1b. From SEM images, the diameter and length of ZnO nanowires were in the range of 100-200 nm and 2-3μm, respectively.



(a)



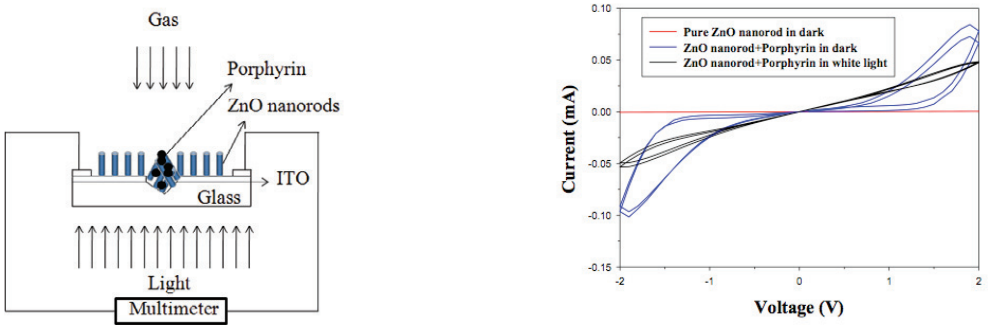
(b)

Fig. 1. (a) Molecular structure of 5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrin (H_2TPPCO_2H); (b) Top and cross sectional view of pure ZnO nanorods SEM images.

2.2. Gas sensor device fabrication

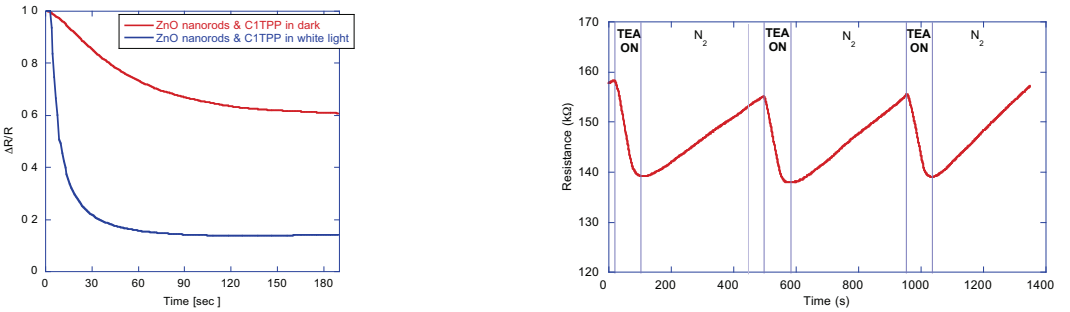
For gas sensor device fabrication, ZnO nanorods were synthesized on the sensor device (fig. 2a) by hydrothermal method. The synthesized ZnO nanorods were functionalized by casting deposition of

monocarboxy TPP dissolved in a methanol solvent; after drop coating, the nanorods were allowed to dry at room temperature around 1hr. After being treated with the monocarboxy-TPP solution, the surface of white ZnO nanorod displayed light brown colour due to the porphyrin heteroaggregate. A schematic of the monocarboxy TPP ZnO nanorod photoactivated gas sensor device is shown in the fig.2a.



(a) (b)

Fig. 2. (a) A scheme of the mono carboxy TPP ZnO nanorod photoactivated gas sensor device; (b) I /V characteristics of pure and mono carboxy TPP functionalized ZnO nanorod under different light.



(a) (b)

Fig. 3. (a) Relative resistance shift (ΔR/R) of porphyrin coated nanorods exposed to triethylamine in dark and under white light; (b) Sensor resistance modulation elicited by three repeated exposures to triethylamine (TEA) vapors. TEA concentration was 150 ppm in pure nitrogen gas flow.

3. Result and Discussion

Fig. 2b shows I-V characteristics of pure and monocarboxy TPP functionalized ZnO nanorod under different light. From the figure, pure ZnO nanorods were indicated ohmic behaviour in dark condition. I-V characteristics of the monocarboxy TPP functionalized ZnO nanorod showed that the presence of porphyrins at the ZnO surface resulted in a large increase of conductivity. This indicates that a remarkable electron transfer process from the porphyrins to ZnO occurs and then a charge accumulation region between ZnO nanorods and monocarboxy TPP is formed, which is further enhanced illuminating the device with white light. As expected, porphyrin-ZnO structure is a photoconductor in the visible range and, more interestingly, the exposure to visible light enhances the gas sensitivity.

Fig. 3a shows the change of the resistance when the sensor is exposed to a pulse of triethylamine in dark and under white light illumination. Photoactivation enhances the sensor response of about 70%. The

influence of light in enhancing the catalytic effect was also recently observed [5]. Fig. 3b shows the sensor resistance modulated by three repeated exposures to 150 ppm of Triethylamine in pure nitrogen flow.

Fig.4 shows the relative sensor shift as a function of the concentration, the response curve shows a nonlinear behaviour typical of specific adsorption processes when the number of adsorption sites is limited. It is noteworthy to observe that the surface layer of porphyrin shifts the photoactivation of ZnO gas sensors from UV to visible light.

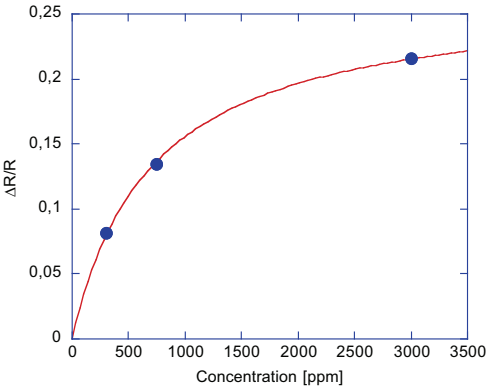


Fig.4. Relative resistance shift versus triethylamine concentration. Continuous curve shows the fitted Langmuir equation.

4. Conclusion

A photoactivated gas sensor for trimethylamine detection based on hydrothermally synthesized and monocarboxy TPP functionalized vertically aligned ZnO nanorod device have been developed. The change of the resistance showed when the sensor is exposed to a pulse of tiethylamine in dark and under white light illumination. Photoactivation enhances the sensor response of about 70%. The influence of light enhancing the catalytic effect was observed. The relative resistance shift as a function of the concentration showed the nonlinear behaviour of specific adsorption processes, when the number of adsorption sites is limited. It is also interesting to observe that light modulation (wavelength and intensity) is expected to tune the sensor sensitivity and selectivity, hence photoactivation introduce a further degree of freedom for gas sensor array development.

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