

CdS/PMMA-BASED INORGANIC/ORGANIC HETEROJUNCTION FOR H₂S GAS SENSING

M. A. IFTIKHAR*, A. M. AWATTIF

Department of Physics, Collage of science, Baghdad University, Baghdad, Iraq.

The performance of H₂S sensor based on poly methyl methacrylate (PMMA)–CdS nanocomposite fabricated by spray pyrolysis technique has been reported. XRD pattern diffraction peaks of nano CdS has been indexed to the hexagonally wurtzite structured. The nanocomposite exhibits semiconducting behavior with optical energy gap of 4.06 eV. SEM morphology appears almost tubes like with CdS/PMMA network. That means the addition of CdS to polymer increases the roughness in the film and provides high surface to volume ratio, which helps gas molecule to adsorb on these tubes. The resistance of PMMA–CdS nanocomposite showed a considerable change when exposed to H₂S gas. Fast response time to detect H₂S gas was achieved by using PMMA–CdS thin film sensor. The sensitivity, response and recovery time were calculated with different operating temperatures (50, 100, 150)°C.

(Received September 18, 2016; Accepted April 14, 2017)

Keywords: CdS, PMMA, Nanocomposites, Responsivity, Thin films, H₂S sensor

1. Introduction

The fabrication of polymer nano-composites (PNC) is an integral aspect of polymer nanotechnology. These PNC are composed of two main parts, filler and host matrix. The inorganic particles, having at least one dimension less than 100 nm, are acted as filler and these particles dispersed in polymer, which acts as host matrix. Recently, many efforts have been devoted to the synthesis of polymer nano-composite materials due to their synergistic and hybrid properties. The properties of polymer nano-composite (PNC) mainly depend upon filler material and host matrix. The PNC's show almost all properties of their parent materials together with some additional properties like increased mechanical strength, improved mold ability, chemical stability etc. These polymer nanocomposites (PNC's) are better than conventional composites because conventional composites require high content of filler. But PNC's achieve the same properties with a much smaller amount of filler and producing materials of lower density and higher mold ability. The functions of PNC's depend upon filler phase. So if we use semiconductor nano-particles as filler phase, the resultant composite material shows semiconducting properties like its parent. In the present study CdS nanoparticles were used as semiconducting filler material [1].

Gas sensor devices which are based on the change in conductivity by interaction with gas molecules and this property is mostly dependent on the operating temperature. Metal oxide gas sensors require high operating temperature [2,3]. Recently, polymers find place as gas sensors because of easy synthesis and low temperature operating devices [4-6]. Among several polymers studied, PMMA presents advantages for applications in electronic devices, storage devices and sensors, and additionally it presents thermal and environmental stability with low cost. Similarly PMMA has been processed into thin film form using different methods including spinning, vacuum sublimation, Langmuir–Blodgett (LB) techniques [7]. These films have been used in biosensors as [8,9,10]. However, with the best of our knowledge, there are no reports on the use of nanocomposites of PMMA–CdS for H₂S sensing. Being highly toxic gas H₂S is a serious problem. Consequently, there is a need for development of cost effective sensors to monitor H₂S at low operating temperature.

* Corresponding author: iftikhar.iq@gmail.com

In the present work, for the first time, describes a technique to form PMMA–CdS nanocomposites for monitoring toxic gas was reported . PMMA–CdS nanocomposites in thin film form have been fabricated using spray pyrolysis technique. Before fabricating the nanocomposites, the individual films were characterized by XRD and SEM techniques. The change in resistance was recorded before and after exposure to H₂S.

2. Experimental details

2.1 Synthesis of CdS nanoparticles

CdS nanoparticles were synthesized by co-precipitation method. First, CdCl₂ and thioacetamide (TAA) at 0.1 M for both materials were dissolved separately in distilled water, with vigorous stirring for 30min. Then they were mixed together and stirred with vigorous stirring for 1hour. Finally, NH₄OH was added dropwise with stirring for 30min. Afterward, the resulting yellow suspension was further stirred for 30 min. Then the reactor was cooled up to room temperature. The resulting precipitate was filtered and washed several times with water. Finally it was dried in an oven at 80 °C.

2.2 Synthesis of CdS/PMMA composite material

In order to disperse CdS particles in polymer matrix (PMMA), we dissolved 500 mg PMMA in DCM and left the sealed vial overnight. Afterward, the mixture was sonicated for 30 min. When all PMMA dissolved completely, 50 mg CdS filler particles were added to the solution and sonicated the suspension for further 45min. In the last step, this solution was sprayed on glass and silicon substrates that heated to 80°C.

2.3 Characterization

X-ray diffraction (XRD) data were taken by X-ray diffractometer (SHIMADZU-XRD 6000) using Cu-K α radiation ($\lambda=1.54056 \text{ \AA}$) at room temperature. The optical absorbance was measured using UV/ Visible SP – 8001 spectrophotometer over the range 190–1000 nm.

3. Results and Discussion

3.1 XRD analysis

The diffraction peaks in XRD pattern of nano CdS has been indexed to the hexagonally wurtzite structured CdS which are consistent with the standard values for CdS given in JCPDS file (80-006). X-ray diffraction of prepared CdS is illustrated in fig. 1. X-ray diffraction result of polymer nanocomposite materials shows that there is amorphous structure because of the high quantity of polymer in the thin film and the small amount of CdS that well dispersed in the polymer host.

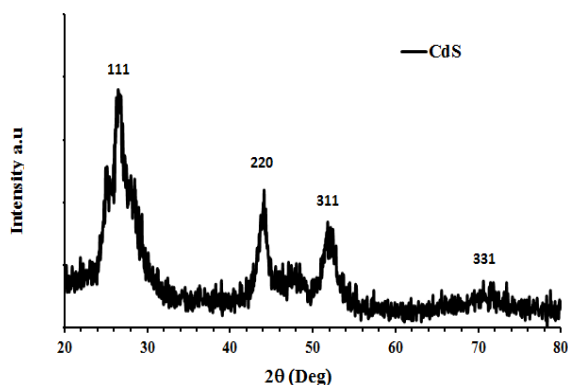


Fig. 1: XRD spectrum of CdS powder

3.2 Surface Morphology analysis

Fig.2 shows the surface morphologies of PMMA and CdS/PMMA nanocomposite. The change in the surface morphology has been observed with the addition of CdS in PMMA polymer (Fig.2(a and b)). The morphology appears almost tubes like with CdS/PMMA network. That means the addition of CdS to polymer increases the roughness of the film and provides high surface to volume ratio that helps gas molecule to adsorb on these tubes.

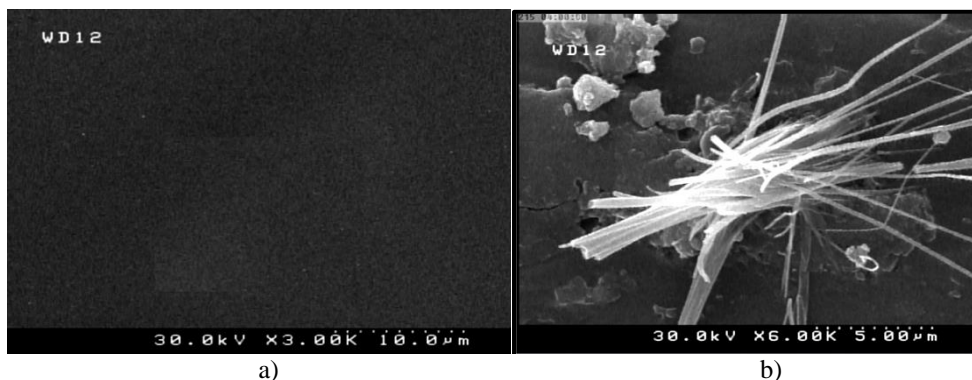


Fig. 2: SEM micrographs: (a) PMMA thin film; (b) CdS/ PMMA thin film

3.3 Optical properties

3.3.1 Absorption and band gap determination for CdS/PMMA film

Synthesized CdS/PMMA has been recorded to measure its band-gap using UV-Vis absorption spectrum as shown in Fig.3. CdS/PMMA has good absorption for light within the range of wavelength 190-330 nm and this peak position reflects the band gap of the nanocomposite. The peak of the spectrum corresponds to the fundamental absorption edges in CdS/PMMA, this fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap of the prepared CdS/PMMA. The maximum absorption edge for the sample is observed at 280 nm assigned to the optical transition of the first excitonic state of CdS/PMMA composite and its narrow shape is an evidence of the very small size of the dispersed particles.

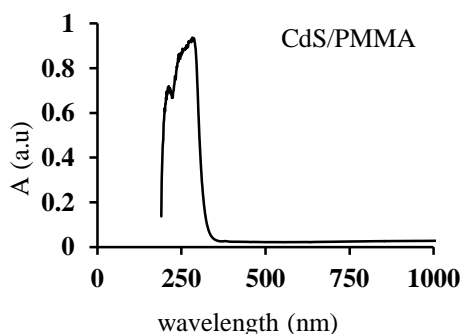


Fig. 3: UV-Vis absorption spectra of CdS/PMMA thin film.

3.3.2 The Optical Energy Gap

The energy gap was calculated by using Tauc's relation[11] $\{\alpha h\nu = A(h\nu - E_g)^m\}$ where A is a constant, which is different for different material, α is the absorption coefficient, $h\nu$ is the energy of incident photon, E_g is the band gap energy, and the exponent m indicates the type of transition. was applied to determine the band gap of the synthesized CdS/PMMA. The value of m is $\frac{1}{2}$, because CdS/PMMA is a direct band gap material. The linear part of the graph was

extrapolated to $\{(\alpha h\nu)^{1/m} \sim 0\}$ to determine the bandgap. From Fig.4, it has been determined that the optical band gap of CdS/PMMA is 4.06 eV.

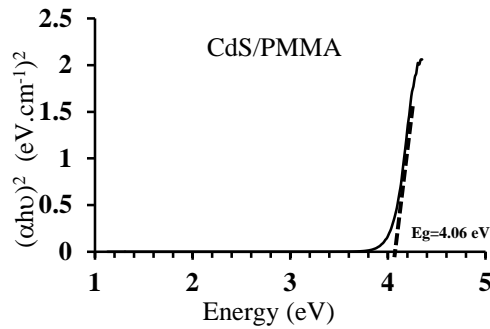


Fig. 4: Tauc plot of CdS/PMMA thin film

3.4 Gas sensing properties

The performance of CdS/PMMA thin film gas sensor was studied based on the resistance change of the sensor in ambient environment and in the presence of target gas (H_2S). The sensitivities of the CdS/PMMA gas sensor toward H_2S gas at various operating temperatures were determined using the following Eq.

$$S (\%) = \frac{R_a - R_g}{R_g} \times 100$$

where R_g and R_a are the resistances of the sensor in H_2S and air atmosphere, respectively.

The sensor response can be defined as [12]:

$$\text{Gas response} = R_a/R_g$$

The results of CdS/PMMA thin film gas sensor are presented in Figs. 5a, 5b, 5c that showed a response toward H_2S gas at 50, 100, 150 °C, respectively. Moreover, the gas sensors did not exhibit any response toward H_2S gas for PMMA thin film (Fig.6).

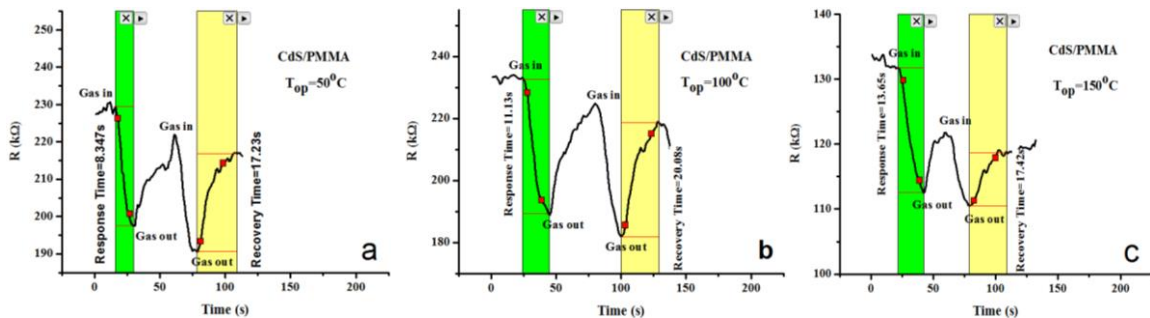


Fig. 5: Response and recovery time of a gas sensor based on CdS/PMMA nanocomposites

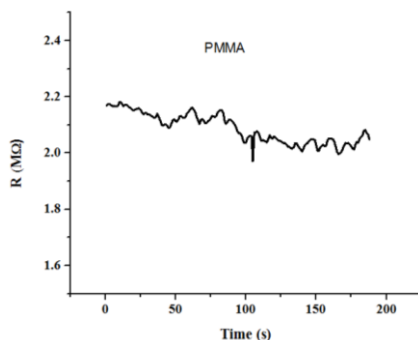


Fig. 6: No response for PMMA thin film

In order to explain the response transient and gas sensing mechanism of PMMA–CdS nanocomposite. It is postulated that PMMA and CdS may form a p–n junction and the observed increased response of the nanocomposite material may be due to the creation of positively charged depletion layer on the surface of CdS which could be formed owing to inter particle electron migration from CdS to PMMA at the junction. This would cause the reduction of the activation energy and enthalpy of physisorption for H_2S gas. Similar kind of sensing mechanism was discussed by Tai et al. [13] and Patil et al. [14] for PANi– TiO_2 nanocomposite for NH_3 gas sensing. The response time, τ_{Res} , can be specified as the time consumed to obtain 90% of the final sensor resistance value after the gas was injected, whereas the recovery time, τ_{Rec} , can be defined as the time required to attain 10% of the final resistance (steady state resistance) after the gas removal [15]. The response values of PMMA–CdS sensor film is plotted as a function of operating temperature in Fig. 7. It is observed that the response value is maximum at 100°C . Also, there is fast response and recovery time was achieved which was illustrated in Table 1

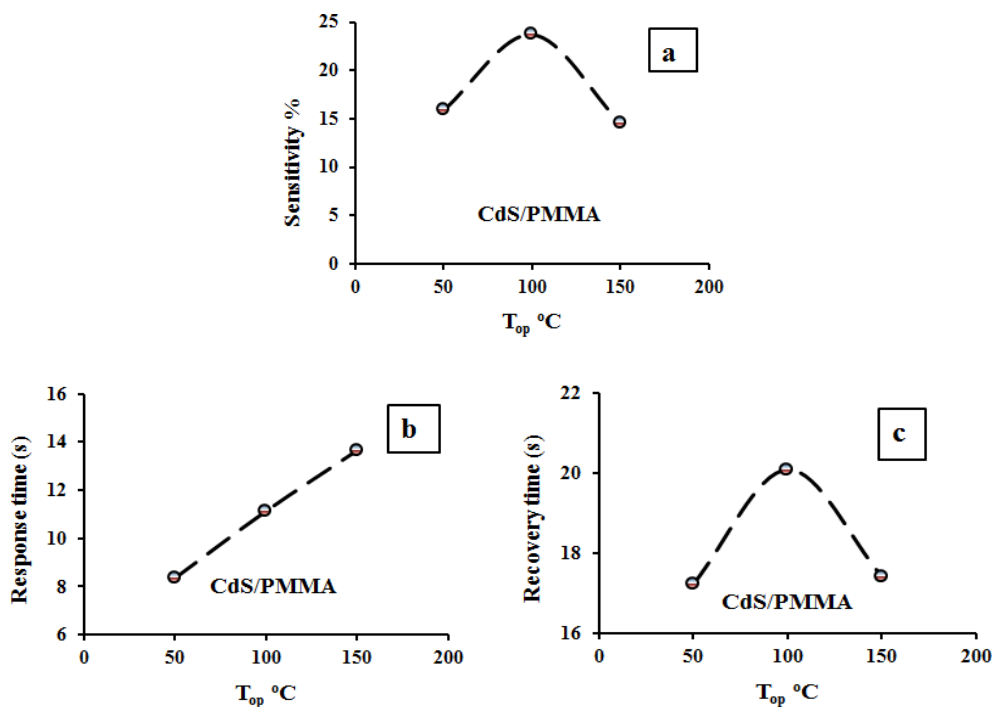


Fig. 7: (a) Sensitivity as a function of operating temperature for the CdS/PMMA nanostructure, (b) response time, (c) recovery time

Table 1: the gas sensitivity, response and recovery time of CdS/PMMA thin film gas sensor at different operating temperatures T_{op} .

T_{op} (°C)	S (%)	T_{res} (s)	T_{rec} (s)	Responsivity
50	15.9	8.347	17.23	1.16
100	23.7	11.13	20.08	1.23
150	14.5	13.65	17.42	1.16

4. Conclusions

Nanostructured PMMA–CdS thin film sensor was fabricated by spray pyrolysis technique on glass and silicon substrates at 80°C. It is observed that PMMA–CdS film has high surface area which contributes to a rapid adsorption of gas onto the film.

The response behavior observed of the PMMA–CdS nanocomposite thin film revealed good sensitivity values, faster response and recovery time to H₂S than that of pure PMMA. The gas- sensing properties of the PMMA–CdS thin film was an excellent candidate for H₂S recognition at low temperature.

Acknowledgment

Authors are grateful to the Department of Physics, Collage of Science, Baghdad University, Baghdad, Iraq.

References

- [1] Diwakar Padalia, U.C. Johri, M.G.H. Zaidi, *Physica B* **407**,838 (2012).
- [2] Vikas Patil, Shailesh Pawar, Manik Chougule, Bharat Raut, Mulik Ramesh, Shashwati Sen, *Sens. & Trans. J.* **128**,100 (2011).
- [3] S.G. Pawar, S.L. Patil, M.A. Chougule, B.T. Raut, S.A. Pawar, R.N. Mulik, V.B. Patil, *J. Sens. Technol.* **1**,9 (2011).
- [4] Q. Fang, D.G. Chetwynd, J.A. Covington, C.S. Toh, J.W. Gardner, *Sens. Actuators, B* **84**,66 (2002).
- [5] D. Xie, Y. Jiang, W. Pan, D. Li, Z. Wu, Y. Li, *Sens. Actuators, B* **81**,158 (2002).
- [6] F. Zee, J.W. Judy, *Sens. Actuators, B* **72**,120 (2001).
- [7] N.E. Agbor, M.C. Petty, A.P. Monkman, *Sens. Actuators, B* **28**,173 (1995).
- [8] L. Geng, Y. Zhao, Huang, S. Wang, S. Zhang, S. Wu, *Sens. Actuators, B* (2006).
- [9] A.A. Karyakin, O.A. Bobrova, L.V. Lukachova, E.E. Karyakina, *Sens. Actuators, B* **33**,34 (1996).
- [10] B. Adhikari, S. Majumdar, *Polymers in sensor applications, Prog.Polym.Sci.* **29**,699 (2004).
- [11] J.Tauc, R. Grigorovici, A. Vancu, *Phys. Stat. Sol.*, **15**, 627 (1966).
- [12] C. Gu, L. Shanshan, J. Huang, C. Shi, J. Liu, *Sens. Actuators B*, **177**,453 (2013).
- [13] H. Tai, Y. Juang, G. Xie, J. Yu, X. Chen, *Sens. Actuators, B* **125**,644 (2007).
- [14] S.G. Pawar, S.L. Patil, M.A. Chougule, Shashwati Sen, V.B. Patil, Room temperature ammonia gas sensor based on polyaniline/TiO₂ nanocomposites, *IEEE Sens. J.* doi:10.1109/JSEN.2011.2160392.
- [15] D. Aswal, S. Gupta, *Science and technology of chemi resistor gas sensor*, Nova Science Publishers, (2007).