www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2015.5795 Published online by the VBRI Press in 2015

Polyaniline niobium pentoxide composite as humidity sensor at room temperature

S. Kotresh[1], Y. T. Ravikiran[1*], S.C. Vijaya Kumari[2], H.G. Raj Prakash[3], S. Thomas[4]

[1]*Department of PG Studies and Research in Physics, Government Science College, Chitradurga 577501, India*
[2]*Department of Physics, SJM College of Arts, Science and Commerce, Chitradurga 577 501, India*
[3]*Department of Physics, JNN College of Engineering, Shimogga 577 204, India*
[4]*International and Inter University centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam 686 560, India*

[*]Corresponding author. Tel: (+91) 8194234270; E-mail: ytrcta@gmail.com

Received: 06 January 2015, Revised: 13 March 2015 and Accepted: 21 March 2015

ABSTRACT

In this present work, Polyaniline (PANI) and Polyaniline-Niobium Pentoxide (PANI-Nb_2O_5) composite were synthesized separately at room temperature by chemical polymerization of aniline without/with Nb_2O_5. Comparative study of XRD pattern of PANI and the composite confirms superficial deposition of PANI on Nb_2O_5 and the average size of the composite particle was found to be 10 nm. Aggregated granular morphology of the composite as compared to pristine PANI was confirmed by SEM images. Sensitivity of PANI-Nb_2O_5 composite to humidity at room temperature was tested using digital LCR meter at a selected frequency of 100 Hz and the results showed consistent variation in impedance from 60 KΩ to 360 KΩ within the relative humidity (RH) range 25% - 95%. Further, the response and recovery time of the composite were measured to be 80s and 90s respectively and the composite showed stable sensing ability over a period of one month. Copyright © 2015 VBRI Press.

Keywords: Polyaniline composites; humidity sensor; sensitivity; stability.

Introduction

Increasing demand for reliable fabrication of devices by precise, optimized and cost effective methods is currently the major concern of many researchers. So, researchers are involved in the synthesis of composites by incorporating metal/metal oxides into the conducting polymers via chemical or electrochemical route **[1-7]**. These composites have proved to be highly flexible materials in terms of enhancing their electrical and mechanical properties and thus offer exciting opportunities in various fields such as sensors, super capacitors, catalysis, light emitting diodes and fuel cells **[8-12]**.

Rapid modernization with the use of high technology has led to an increasing demand for humidity control in wide areas like food processing and preservation, agriculture, medicine and electronic industries **[13]**. As already established, major disadvantages of metal oxide/ceramic based humidity sensors besides operating at high temperature are, low sensitivity, high power consumption, complex fabrication and high cost **[14]**. To overcome these draw backs, conducting polymer composites have been extensively synthesized and studied because of their favourable properties such as easy processability, degree of miniaturization and their operation at room temperature. Among all the conducting polymers, PANI is the most desired material because of its unique characteristics like controllable chemical and electrical properties, simple preparation and low cost **[15]**. But pure PANI in itself has low sensitivity to humidity because of its low hygroscopicity **[13]**. To improve its sensitivity retaining all its favourable properties, composites based on PANI have been extensively studied as humidity sensors. M.V. Fuke et al. have fabricated a humidity sensor using Ag-polyaniline nanocomposite deposited on optical fibre clad and tested for its sensitivity in the range 5% RH - 95% RH **[16]**. They have also studied humidity sensing properties of spin coated co-polyaniline composite in the relative humidity range 20% RH - 95% RH **[17]**. They have reported that sensitivity of the composite increases with humidity and thickness of the film. The composite has also shown quick response and recovery time with a low hysteresis effect. Q. Lin fabricated and studied humidity sensing properties of electrospun PANI composite nanofibres deposited on surface acoustic wave resonator with a central frequency of 433 MHz **[18]**. These fibres have shown good sensitivity, recovery and response time. Humidity sensing of orange dye PANI composite film deposited on glass substrate between silver electrodes has been studied by M.T.S. Chani et al **[19]**. They have reported a uniform change in impedance with relative humidity. Y. Li and others have studied surface acoustic wave impedance humidity sensor based on PANI-PVA composite **[20]**. Their study has shown an increase in

sensitivity at room temperature indicated by decrease in impedance of the composite in the relative humidity range 10% RH - 90% RH with a short response and recovery time. Humidity sensing response of PANI-Cr_2O_3 composite has been studied by K.C. Sajjan et al. and have reported better sensing response of the composite in the relative humidity range 20% RH - 95% RH **[21]**. Though these sensors show improved sensitivity, their processability needs to be made simpler. Hence, to address this major concern , we have preferred niobium pentoxide as a component with PANI because it is a white n-type transition metal oxide semiconductor with a wide band gap (3.2-4eV) and has large dielectric constant (~40) **[22]**. Due to its compatible physical properties, it has been considered for use in fibre optics, gas sensors, catalysts, biocompatible materials, electrolytic capacitors and dye sensitized solar cells **[23, 24]**. So, this is the first ever attempt to fabricate humidity sensing device based on PANI -Nb_2O_5 composite because it was found to be easily processable, operable at room temperature and so would be cost effective.

In this direction, PANI and PANI-Nb_2O_5 composite were synthesized separately by chemical polymerization method and then they were structurally characterized using XRD and SEM techniques. Based on these studies, humidity sensitivity at room temperature of the composite has been tested and analyzed. Also, to examine the efficiency of the composite as a humidity sensor, its stability, recovery and response time have been studied with a special focus on its ability to work at room temperature.

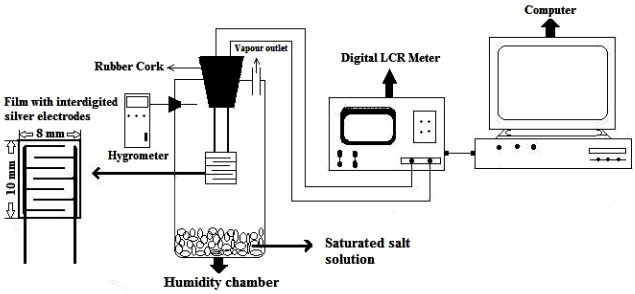

Fig. 1. Experimental setup for humidity sensing studies.

Experimental

Materials

Aniline ($C_6H_5NH_2$) (99.5%), ammonium persulfate [$(NH_4)_2S_2O_8$] (98%), hydrochloric acid (HCl) (34.5%) and niobium pentoxide (Nb_2O_5) (99.5%), all of analytical grade reagents were purchased from s.d. Fine Chemicals, Mumbai, India. Aniline monomer was doubly distilled before use.

Preparation of PANI-Nb_2O_5 composite

PANI-Nb_2O_5 composite was synthesized as follows: 0.67 g Nb_2O_5 powder (10 Wt. % with respect to aniline concentration) was dispersed in 180 ml de-ionized water at ambient temperature. 6.7g aniline monomer and 60 ml of 1 M HCl solution were introduced into the above mixture and then the mixture was sonicated for 15 minutes to facilitate the adsorption of aniline on niobium pentoxide surface. 7.5g ammonium persulfate in 60 ml de-ionized water was added drop wise into the above mixture after being stirred for 30 minutes and was allowed to polymerize at room temperature for at least 8 to 10 hours. Reaction product was collected by centrifugation and washed successively with 1 M HCl, deionized water and acetone until the filtrate became colourless and then dried in vacuum at 60^{o}C for 24 h till a dark green powder was obtained. Similarly, pristine PANI was synthesized under similar conditions without Nb_2O_5.

Characterisation of the samples

XRD patterns of PANI and PANI-Nb_2O_5 composite were investigated using a Siemens D-5000powder X-Ray diffractometer with CuKα source radiation of wavelength 1.54×10^{-10} m. SEM images of PANI and composite samples were recorded using Hitachi S-520 scanning electron microscope.

Humidity sensing measurements

For humidity sensing measurements, PANI-Nb_2O_5 composite's film was prepared by dissolving the composite in m-cresol and then coated on a glass plate in the form of a film of about 2 μm (measured using Dektak Profilometer, Bruker) thickness using spin coating unit (Make: Delta Scientific Pvt. Ltd, India, Model: Delta Spin I). Then, the film on which interdigitated silver electrodes were printed was placed in a specially designed glass chamber with facilities for evacuating and maintaining required relative humidity as shown in (**Fig. 1**). The chamber was fitted at the top with a cork through which the electrodes connected to the film pass through. The other ends of the electrodes were connected to a digital LCR meter (Make: Hioki, Japan, Model: 3532-50) to record impedance changes before and after exposing the sample to humidity, at a selected frequency of 100 Hz. The relative humidity in the chamber was varied using saturated salt solutions and monitored using humidity meter (Mextech-DT-615).

Results and discussion

X-ray diffraction

The XRD pattern of PANI, PANI-Nb_2O_5 composite and that of Nb_2O_5 with assigned *hkl* values are shown in (**Fig. 2**). The XRD pattern of pristine PANI [**Fig. 2**(a)] reveals some degree of crystallinity with the appearance of broad peaks corresponding to (100) and (110) planes [JCPDS File No. 53-1718] in the region 2θ = 15˚ - 25˚ similar to those reported in our earlier literature **[3, 25]**.The XRD pattern of Nb_2O_5 (**Fig. 2**(c)) clearly shows peaks corresponding to the planes (001) (100) (101) (002) (110) and (102) in the range 2θ = 20˚ - 60˚ and the peaks when compared with JCPDS File No. 27-1312 were confirmed to be of Nb_2O_5 thus attributing to its monoclinic structure. The same pattern for Nb_2O_5 has been confirmed in the previous literature **[26]**.

Comparison of XRD patterns of PANI and PANI-Nb_2O_5 composite (**Fig. 2**(b)) shows predominance of Nb_2O_5 in the composite. This implies that the presence of Nb_2O_5 suppresses short range order of PANI.

However, the diffraction pattern of PANI-Nb_2O_5 composite is similar to that of pure Nb_2O_5, indicating that

there is no intercalation of PANI into Nb_2O_5 and that PANI has just deposited on Nb_2O_5 particles and has no effect on the crystalline behavior of Nb_2O_5 **[25]**. Applying the Sherrer formula **[27]** using Eq. (1) to the most prominent sharp peak at 23°, we obtained the size of the crystallite *t* to be 10nm.

$$t = \frac{k\lambda}{b\cos\theta} \qquad \text{---------- (1)}$$

where b is the breadth in radians, θ is the Bragg angle and λ is the wavelength of radiation. The coefficient *k* normally takes a value close to 0.9.

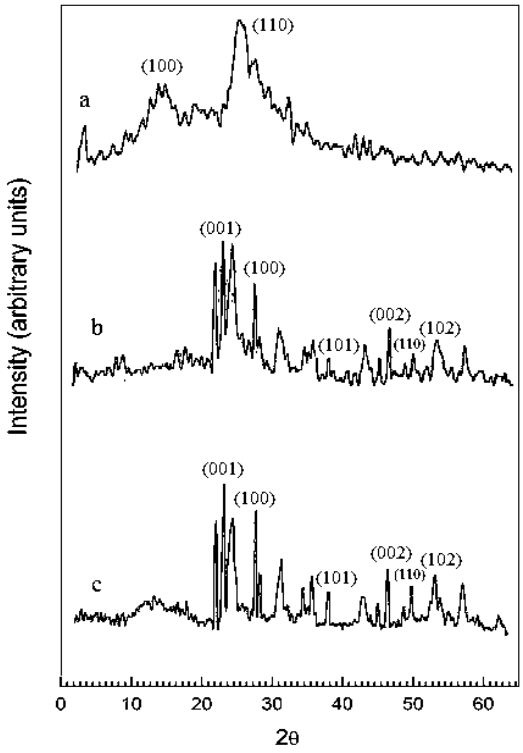

Fig. 2. X-ray diffraction pattern of (a) Pristine PANI (b) PANI-Nb_2O_5 composite and (c) Nb_2O_5.

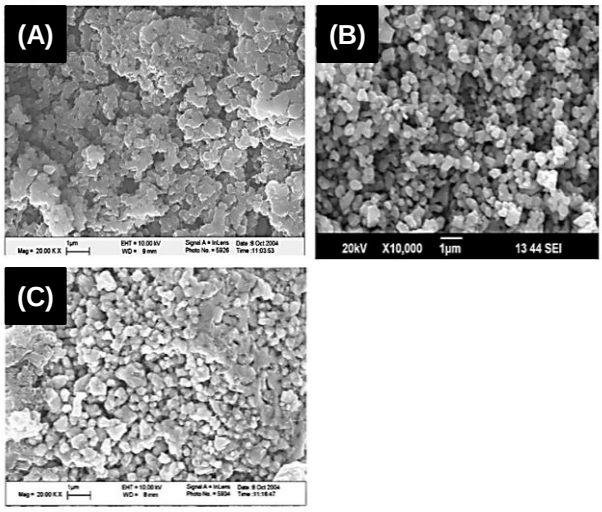

Fig. 3. Scanning electron micrograph of (a) Pristine PANI (b) Nb_2O_5 and (c) PANI- Nb_2O_5 composite.

Scanning electron microscopy

The morphology of PANI, Nb_2O_5 and PANI-Nb_2O_5composite are shown in (**Fig. 3**). The morphology of pristine PANI shown in (**Fig. 3(a)**) is a typical agglomerated structure and the material shows spherical particles/grains of few microns in size. Combination of a few particles into larger grains of irregular shape is also seen.

Scanning electron micrograph of Nb_2O_5 shown in (**Fig. 3(b)**) reveals a spherical morphology with uniform surface. This surface may act as template during the growth of PANI enabling fast and uniform deposition of PANI on Nb_2O_5. (**Fig. 3(c)**) shows the morphology of the composite in which Nb_2O_5 particles appear to have influenced the growth mechanism of PANI-Nb_2O_5 composite leading to aggregated granular porous morphology with submicron size particles.

The average grain size D_{av} of the composite material calculated using Mendelson's formula **[28]** using Eq. (2) is 0.5μm.

$$D_{Avr} = \frac{1.56 \times C_L}{M\acute{N}_i} \qquad \text{---------- (2)}$$

where C_L is total length of the test line used, N_i is number of intercepts and $M¢$ is the magnification of the photograph.

Humidity sensing response studies

Sensing response percentage S of the composite for various RH % was measured at 100 Hz using fractional base line manipulation method **[29]** using Eq. (3).

$$S_H = \frac{Z_0 - Z_{RH}}{Z_0} \times 100 \qquad \text{---------- (3)}$$

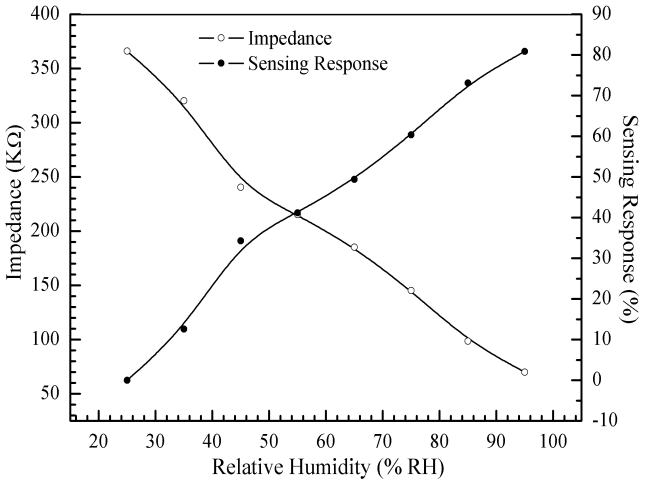

Fig. 4. Variation of Sensing response and impedance with relative humidity at 100 Hz.

Sensing responses characteristic curve of the composite thus obtained by the above method is shown in **Fig. 4**. It can be seen that the composite is sensitive and its response is linear in the range 25 % RH - 95 % RH. Also,

Increase in Sensing response of the composite in the range 25 % RH - 95 % RH with increasing humidity can be attributed to the following probabilities; (i) Under dry conditions, the polymer chains would tend to curl up into compact coil form restricting the mobility of Nb_2O_5 ions which are loosely attached to the polymer chain by weak van der walls forces of attraction. On the contrary, at high humidity, the composite absorbs water molecules resulting in the uncurling of the compact coil form into straight chains that are aligned with respect to each other which would facilitate faster hopping of charge carriers **[21, 30]**. (ii) Geometry of the polymer with pores as revealed by SEM studies is favourable for enhanced mobility of Nb_2O_5 ions across the polymer chains leading to decreased impedance response of the composite **[13]**.

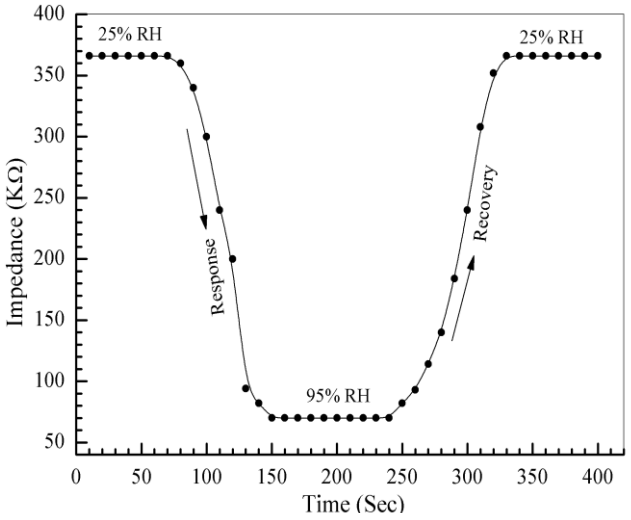

Fig. 5. Response and recovery characteristic curves of PANI-Nb_2O_5 composite at100 Hz.

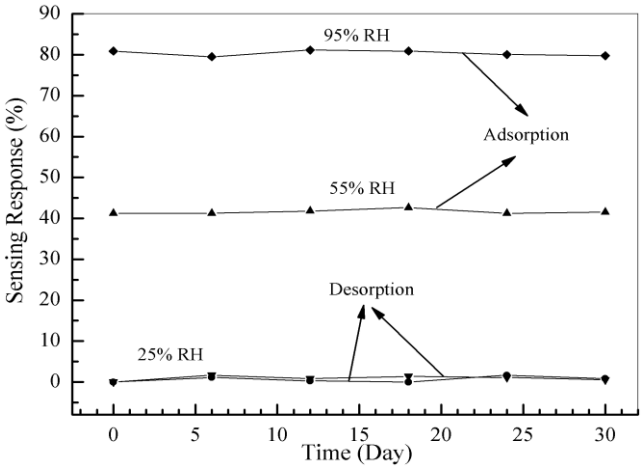

Fig. 6. Stability of PANI-Nb_2O_5 composite at 100 Hz.

Response and recovery time are the important parameters to test the efficiency of the composite to act as sensor **[31]**. Humidity sensing response and recovery characteristic curve of PANI-Nb_2O_5 composite at 100 Hz is shown in **Fig. 5**. For the purpose, two chambers, one with 25 % RH and another with 95 % RH were maintained separately. The response time of 80 s was recorded when the sample was moved from dry air to 95 % RH and a recovery time of 90 s was recorded when the sample was moved from 95 % RH to dry air, switching time being 1s in both the cases. These results show that the composite can become a good humidity sensing device. To examine the practical viability of the composite for devising it as a sensor, variation of sensing response at 55 % RH and at 95 % RH at a frequency of 100 Hz after every one week for one month was studied **[32]**. It is seen from the **Fig. 6** that the material had stable sensing ability both while adsorption and desorption during that period with a negligible degradation of 1 % in sensing response. This finding suggests that the composite apart from being a good sensor is also stable and so it can be practically feasible to device it as a sensor.

Conclusion

In this work, selection of Nb_2O_5 as composite material with PANI, synthesis of the composite by chemical polymerization method and its structural characterization by XRD and SEM techniques has yielded a good humidity sensing material. Impedance measurements of the composite in the relative humidity range 25% RH - 95% RH have shown consistency in sensing response. Response and recovery time of the composite at 95% RH were found to be 80s and 90s respectively thus confirming the practical viability of the composite to device it as sensor. Also, the composite has shown stable sensing ability over a period of one month. All these results confirm that the composite has the potential to become an efficient humidity sensing device operable at room temperature besides being easily processable and cost effective. This study also has expanded the scope of selection of PANI-Nb_2O_5 composite for various gas sensing and thus extends the area of applications of the composite.

Acknowledgements

The author is thankful to University Grants Commission, New Delhi, for their financial support provide under major research project (41-917/2012 (SR) dated: 23/07/2012), to carry out this work. Author wishes to acknowledge SAIF, Cochin, for providing facility for characterization of the samples.

Reference

1. Yasir, A, Y.; Vijay, K.; Sonkawade, R.G.; Shirsat, M.D.; Dhaliwal, A.S.; *Vacuum*, **2013**, *93*, 79. **DOI:** 10.1016/j.vacuum.2013.01.007
2. Yasir, A.; Kashma, S.; Vijay Kumar.; Sonkawade, R.G.; Dhaliwal, A.S.; *Appl. Surf. Sci.* **2013**, *280*, 950. **DOI:** 10.1016/j.apsusc.2013.05.116
3. Yasir, A.; Vijay, K.; Sonkawade, R.G.; Dhaliwal, A.S.; *Vacuum*, **2013**, *90*, 59. **DOI:** 10.1016/j.vacuum.2012.10.001
4. Kadam, S.B.; Datta, K.; Ghosh, P.; Kadam, A.B.; Khirade, P.W.; Kumar, V.; Sonkawade, R.G.; Gambhire, A.B.; M.K. Lande.; M.D. Shirsat.; *Appl Phys A*, **2010**, *100*, 083. **DOI**: 10.1007/s00339-010-5705-1
5. Ghoreishi, K.B.; Yarmo, M.A.; Nordin, N.M.; Samsudin, M.W.; Journal of Chemistry, **2013**, Volume 2013, article ID 264832, 10. **DOI:** 10.1155/2013/264832
6. Lee, S.B.; Lee, S.M.; No Il Park.; Lee, S.; Chung, D.W.; *Synthetic Metals*, **2015**, *201*, 61. **DOI**: 10.1016/j.synthmet.2015.01.021
7. Kanwal, F.; Siddiqi, S.A.; Batool, A.; Imran, M.; Mushtaq, W.; Jamil, T.; *Synthetic Metals*, **2011**, *161*, 335. **DOI:** 10.1016/j.synthmet.2010.12.001
8. Tang, W.; Peng, L.; Yuan, C.; Wang, J.; Mo, S.; Zhao, C.; Yu, Y.; Min, Y.; Epstein, A.J.; *Synthetic Metals*, **2015**, *202*, 140.

DOI: 10.1016/j.synthmet.2015.01.031
9. Bahloul, A.; Nessark, B.; Briot, E.; Groult, H.; Mauger, A.; Zaghib, K.; Julien, C.M.; *J. Power Sources*, **2013**, *240*, 267. **DOI:** 10.1016/j.jpowsour.2013.04.013
10. Rajesh.; Ahuja, T.; Kumar, D.; *Sens. Actuat. B: Chemical*, **2009**, *136*, 275. **DOI:** 10.1016/j.snb.2008.09.014
11. Memioğlu, F.; Bayrakçeken, A.; Tuba Öznülüer, T.; Metin Ak.; *Int. J. Hydrog. Energy*, **2012**, *37*, 16673. **DOI:** 10.1016/j.ijhydene.2012.02.086
12. Shin, S.; Kim, S.; Kim, Y.H.; Kim, S.; *Cur. Appl. Phys.* **2013**, *13*, S144. **DOI:** 10.1016/j.cap.2013.01.016
13. Ramaprasad, A.T.; Rao, V.; *Sens. Actuat. B: Chemical*, **2010**, *148*, 117. **DOI:** 10.1016/j.snb.2010.05.044
14. Zeng, F.W.; Liu, X.; Diamond, D.; Lau, K.t.; *Sens. Actuat. B: Chemical*, **2010**, *143*, 530. **DOI:** 10.1016/j.snb.2009.09.050
15. MacDiarmid, A.G.; *Synt. Met.*, **2002**, *125*, 11.
16. Fuke, M.V.; Kanitkar, P.; Kulkarni, M.; Kale, B.B.; Aiyer, R.C.; *Talanta*, **2010**, *81*, 320. **DOI:** 10.1016/j.talanta.2009.12.003
17. Fuke, M.V.; Vijayan, A.; Kulkarni, M.; Hawaldar, R.; Aiyer, R.C.; *Talanta*, **2008**, *76*, 1035. **DOI:** 10.1016/j.talanta.2008.04.064
18. Lin, Q.; Li, Y.; Yang, M.; *Anal. Chim. Acta*, **2012**, *748*, 73. **DOI:** 10.1016/j.aca.2012.08.041
19. Chani, M.T.S.; Karimov, K.S.; Khalid, F.A.; Abbas, S.Z.; Bhatty, M.B.; *Chin. Phys. B*, **2012**, *22*, 010701. **DOI:** 10.1088/1674-1056/22/1/010701
20. Li, Y.; Deng, C.; Yang, M.; *Sens. Actuat. B: Chemical*, **2012**, *165*, 7. **DOI:** 10.1016/j.snb.2011.12.037
21. Sajjan, K.C.; Roy, A.S.; Parveen, A.; Khasim, S.; *J Mater Sci: Mater Electron*, **2014**, *25*, 1237. **DOI:** 10.1007/s10854-014-1715-7
22. Yoo, J.E.; Park, J.; Cha, G.; Choi, J.; *Thin solid films*, **2013**, *531*, 583. **DOI:** 10.1016/j.tsf.2013.01.062
23. Abari, A.F.; Cadien, K.C.; *Thin Solid Films*, **2011**, *519*, 3068. **DOI:**10.1016/j.tsf.2010.12.036
24. Kohli, A.; Wang, C.C.; Akbar, S.A.; *Sens. Actuat. B: Chemical*, **1999**, *56*, 121. **DOI:** 10.1016/S0925-4005(99)00191-4
25. Ravikiran, Y.T.; Kotrsh, S.; Vijayakumari, S.C.; Thomas, S.; *Cur. Appl. Phys.* **2014**, *14*, 960. **DOI:**10.1016/j.cap.2014.04.015
26. Kim, H.Y.; Vishvanathmurthy, P.; Bhattarai, N.; Lee, D.R.; *Rev. Adv. Mater. Sci*. **2003**, *5*, 224.
27. Patterson, A.; *Phys. rev*. **1939**, *56*, 978. **DOI:** 10.1103/PhysRev.56.978
28. Mendelson, M.I.; *J. Am. Ceram. Soc.* **1969**, *52*, 443. **DOI:** 10.1111/j.1151-2916.1969.tb11975.x
29. Sen, T.; Shimpi, N.G.; Mishra, S.; Sharma, R.; *Sens. Actuat. B: Chemical*, **2014**, *190*, 120. **DOI:**10.1016/j.snb.2013.07.091
30. Lin, W.D.; H.M. Chang, H.M.; Wu, R.J.; *Sens. Actuat. B: Chemical*, **2013**, *181*, 326. **DOI:**10.1016/j.snb.2013.02.017
31. Q, Q.; Zhang, T.; Wang, S.; Zheng, X.; *Sens. Actuat. B: Chemical*, **2009**, *137*, 649. **DOI:**10.1016/j.snb.2009.01.042
32. Zhang, Y.; Zheng, X.; Zhang, T.; Gong, L.; Dai, S.; Chen, Y.; *Sens. Actuat. B: Chemical*, **2010**, *147*, 180. **DOI**: 10.1016/j.snb.2010.03.045