Facile one step synthesis and gas sensing behavior of PANI/Mn_3O_4 nanocomposite

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Abstract

In this work, we present the first investigations of Mn_3O_4 nanoparticles doped in polyaniline (PANI) matrix for gas sensing application. PANI/Mn_3O_4 nanocomposite (NC) was synthesized by facile one step reduction method with varied dopant concentrations (1mM and 3mM) of synthesized Mn_3O_4 nanoparticles followed by its characterization for optical, structural, morphological, thermal and electrical properties. Optical characterization by UV-Vis and FT-IR confirmed the doping of Mn_3O_4 in polymer matrix. TGA analysis showed improvement in the thermal stability of the NC. SEM images portrayed agglomerated morphology of PANI whereas the NC depicted fibre-like structures symptomatic of more porosity. Gas sensing behavior was investigated towards acetone, ethanol and benzaldehyde vapours. The sensor with 3mM dopant concentration exhibited significant sensing response with a sensitivity of 1.5 at room temperature towards acetone vapour, which can be attributed to the controlled and improved properties at the interface via molecular and supramolecular interactions. The synthesized NC has a potential use as acetone sensor with fast response and recovery.

Keywords: PANI, Mn_3O_4, nanocomposite, gas sensing, acetone.

Introduction

Colossal demand for the gas sensors in the industrial, biomedical, food, automotive sectors etc. have prompted the researchers for the exploration of novel materials. In this regard, during the last decades much attention has been paid on the metal oxide and conducting polymer based gas sensors **[1-3]**. Both of the gas sensing techniques has its intrinsic limitations and diverse applicability. Generally, sensors based on metal/metal oxide semiconductors have been proven widely effective for inorganic vapors. Also, the high operation temperature of the metal oxide sensors demands high cost and complicated configurations which are the major drawbacks of this type of sensors. Whereas, the conducting polymer based sensors have been reported more sensitive for the detection of extensive range of volatile organic compounds (VOC) **[2]** at ambient temperature which makes them attractive candidate as gas sensing elements. Actually, the electrical and optical properties of the conducting polymers are different from the conventional system which is due to presence of highly delocalized and easily polarizable π- electrons. Although, the conductivity of pure polymer is too low to act as a sensing material but it can be improved by doping the polymer chemically, electrochemically, through redox reaction, photo chemically, etc. or by adding some fillers such as carbon black, metal particles, carbon fibers or aluminium flakes, etc. [**4**].

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), poly(*p*-phenylene) (PPP), etc. are the basic conducting polymers having conductivity range from 3.0 to 10^5 Scm^{-1} and optical absorption edge from 1.5-3.2 eV [**4**].

Among conducting polymers, PANI has been investigated widely due to its remarkable overall properties, for instance, low cost, simple synthesis & granular metals like behavior [**5**]. It has wide application in the area of microelectronic devices, light weight batteries [**6, 7**], sensors [**8, 9**], supercapacitors [**10**], microwave absorption [**11**], corrosion inhibition [**12**], catalysis [**13**] etc. Various metal oxides such as TiO_2 [**14**], SnO_2 [**15**], In_2O_3 [**16**], MoO_3 [**17**], WO_3 [**18**], NiO [**19**], chalcogenides [**20**], etc. nanoparticles have been doped with PANI to enhance its unique physical properties. Recently, electrical and magnetic behavior of PANI/ Mn_3O_4 has been reported [**21**]. However, Mn_3O_4 doped PANI has not been explored yet for gas-sensing except its application as humidity sensor [**22]**.

In this work, a simple and novel approach has been adopted for the synthesis PANI/Mn_3O_4 nanocomposites by an in-situ polymerization. In addition, influence of dopant concentration on the gas-sensing properties of PANI nanocomposite (NC) has been investigated for three VOCs viz. acetone, ethanol and benzaldehyde.

Experimental

Materials

All the reagents used were of analytical grade. Potassium permanganate ($KMnO_4$) and monohydrate hydrazine (NH_2NH_2) were purchased from Qualigens Fine Chemicals, Mumbai. N-cetyl-N, N, N-trimethyl ammoniumbromide(CTAB), Tetrabutylammonium bromide(TBAB), aniline, ammonium peroxysulfate (APS), acetone and benzaldehyde were purchased from Loba Chemie, Mumbai whereas ethanol was procured from Fisher Scientific, UK. Aqueous solutions were prepared from the double distilled water having resistance $10^{18}\Omega$.

Material synthesis

Firstly, Mn_3O_4 nanoparticles were synthesized by our earlier reported protocol [**23**]**.** In brief, 0.5 mmol of CTAB, 0.1 mmol TBAB and 0.5 mmol of $KMnO_4$ were mixed together with 100 ml of water in a round bottom flask. The reaction mixture was allowed to get homogenized for 10 minutes under slow stirring in order to avoid froth formation. Further, 0.5 mmol of NH_2NH_2 was added rapidly to this solution under vigorous magnetic stirring. The color of the reaction mixture changed from dark purple to dark brown and finally to brown with a tinge of orange. It was further heated to 70 ºC for 1 hr and then cooled to room temperature resulting in complete precipitation. The precipitate was separated by centrifugation followed by several washing cycles with ethanol and then dried in vacuum for three hrs at 40 ºC.

In order to synthesize PANI/Mn_3O_4 composite, two different concentrations (1.0 mM and 3.0 mM) of synthesized Mn_3O_4 nanoparticles were prepared in 20.0 ml of HCl (0.2 M) solution. Then, 91.3 µl of aniline was added to the each Mn_3O_4 solution and kept for stirring for an hour. Another solution of the oxidant APS (0.285 g) in HCl (0.2 M) was prepared. Then, this oxidant solution was added drop wise to the aniline and Mn_3O_4 solution and kept for stirring for an hour. The resultant products were filtered, washed with acetone, DI and dried at 24˚C.

Sample preparation for SEM analysis

Thin films of the PANI and PANI/Mn_3O_4 were developed using spin coating technique. 5 mg of sample was dissolved in NMP (100 µl) and kept for stirring for 3-4 hrs. Then, thin films were prepared using spin coating (Millman, single stage coating unit) at the 1200 rpm for 15 sec.

Characterizations

The different instruments used for the characterization of samples included a UV-Vis spectrophotometer (UV-Vis-NIR, Varian Cary 5000), Fourier-transform infrared spectroscope (FTIR, Perkin Elmer), thermo gravimetric analyzer (TGA, Thermo Scientific) and field-emission scanning electron microscopy (FESEM, Hitachi S4800).

Gas sensing set up & response measurements

Test samples to be used as a sensor were prepared in the pellet form. Compressed pellets of specimens were prepared under the hydraulic pressure of 10 psi load. A chromel/alumel sensing wire was inserted in each pellet. All the pellets were 15.0 mm in diameter and 0.92 mm in thickness. The gas sensing measurements were carried out in a customized testing set-up [**24**], using Agilent B2901A source-measure unit. Different concentrations of analyte vapours in the range of 1.0 ppm-100.0 ppm were injected in the test chamber and the corresponding sensor response was measured. The sensitivity(S) was calculated using the following equation:

$$S = \frac{R_g}{R_0} - 1$$

where, Rg = Saturated maximum resistance in the presence of analyte, R_0 = Baseline resistance of the sensor.

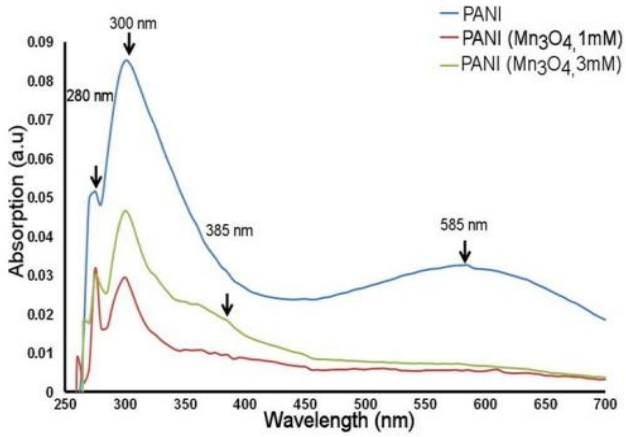

Fig. 1. UV-Vis spectral overlay of PANI & PANI/Mn_3O_4 (1 mM, 3 mM).

Results and discussion

UV-Vis analysis

The UV/vis spectra of PANI and PANI/Mn_3O_4 were recorded in N-methylpyrrolidone (NMP) as solvent and presented in **Fig. 1**. The absorbance maximas seen at 275 nm and 300 nm are due to the π-π* transition of benzenoid ring and the maxima at 585 nm corresponds to the polaron -π* transition [**25]**. Whereas, in case of NCs a new band appears at 370 nm, which corresponds to the highest occupied molecular orbital of the benzenoid to the lowest unoccupied molecular orbital of the localized quinoid ring and the two-surrounding imine nitrogens in the emeraldine base form of PANI (π-π* transition) [**26**]. Also peak at 585 nm diminished and an additional shoulder appeared at wavelength lower than 275 nm, which can be attributed to the successful interaction of metal oxide with the polymer chain.

SEM analysis

Fig. 2 shows the SEM morphology of PANI and PANI/Mn_3O_4 thin film. It indicates that PANI/ Mn_3O_4 possess a very porous structure with an interconnected network of nanofibers. However, PANI has a rough surface including two-dimensional slab surface. Porous structure of NC may affect the diffusion of gas molecules which is beneficial for the gas sensor application due to their highly specific surface and excellent channels for charge transmission [**27, 28**]**.** It is believed that, during the polymerization of PANI, Mn_3O_4 nanoparticles in the reaction system play a role as reaction core, resulting in the adsorption of monomer on the surface of nanoparticles and on overwrought growth around these particles [**29**].

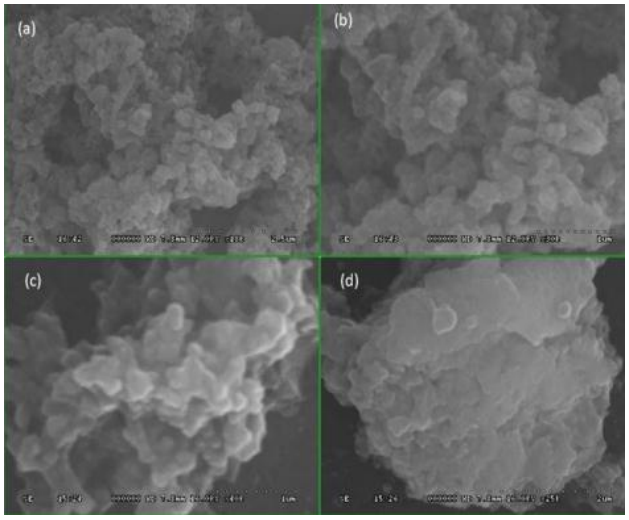

Fig. 2: SEM images of (a) PANI/Mn_3O_4(× 18 k); (b) PANI/Mn_3O_4 (× 12.0 k); (c) PANI (× 40 k); (d) PANI (× 25 k).

FT-IR analysis

The FTIR spectrum of PANI and PANI/Mn_3O_4 (1 mM, 3 mM) is depicted in **Fig. 3** and the observed bands are described in **Table 1**.

Table 1. FT-IR peak assignment.

PANI	PANI/Mn_3O_4 (cm^{-1})	Type of Stretching
-	410.7	$Mn_{octahedral}$-O stretching[31]
-	514.9, 619.0	Coupling between $Mn_{octahedral}$-O & $Mn_{tetrahedral}$-O stretching modes[32-33]
819.5	819.5	C-H out of plane bending vibrations[30]
1261.2	1261.2	C-N stretching of the benzenoid ring[34]
1475.2	1471.4	C=C stretching vibration of benzenoid ring[34]
1558.2	1550.9	C=C stretching vibration of quinoid ring[34]

FTIR spectra of PANI show the main characteristic peaks at 1558.2, 1475.2, 1261.2 and 819.5 cm^{-1}. The bands at 1558.2 and 1475.2 cm^{-1} are attributed to stretching vibrations of N=Q=N ring and N-B-N ring respectively (where B refers to benzoid-type rings and Q refers to quinoid-type rings). The bands at 1261.2 cm-1 correspond to the symmetric component of the C-C stretching modes. The peak at 819.5 cm-^{1} can be attributed to the out-of-plane bending vibration of C-H on the 1, 4-disubstituted aromatic rings **[19]**.

The characteristic peaks of Mn_3O_4 (410.7, 514.9, and 619. 0 cm^{-1}) are observed in the spectra of PANI/Mn_3O_4. The transmittance bands due to stretching vibrations of quinoid (1550.9 cm^{-1}) and benzoid (1471.4 cm^{-1}) rings in PANI/Mn_3O_4 confirmed the polymerization of aniline in the presence of Mn_3O_4. The interaction between PANI and Mn_3O_4 nanoparticles was confirmed as these bands were found to be shifted to lower wavelengths as well the intensity of the bands was diminishing.

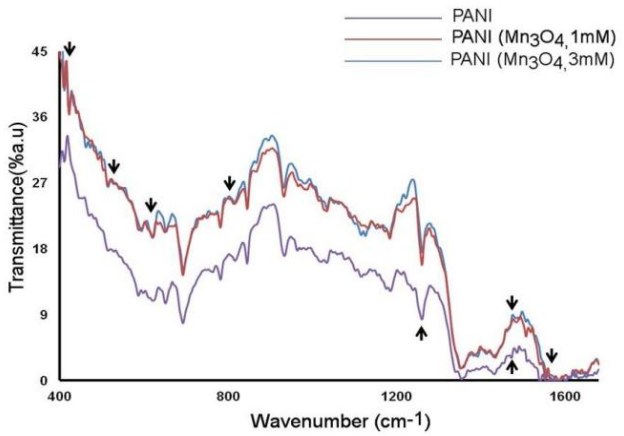

Fig. 3. FT-IR spectral overlay of PANI & PANI/Mn_3O_4 (1 mM, 3 mM).

TGA analysis

Thermal analysis of PANI and PANI/Mn_3O_4 in the temperature range of 30°C to 1000°C in N_2 atmosphere reveals two gradual weight loss transition phases corresponding to moisture loss and decomposition of organic matter (**Fig. 4**). The degradation of PANI/Mn_3O_4 begins at a much lower temperature. This behavior could be originated from the fact that Mn_3O_4 particles behave as catalysts, thus reducing the degradation temperature of PANI [**35**].

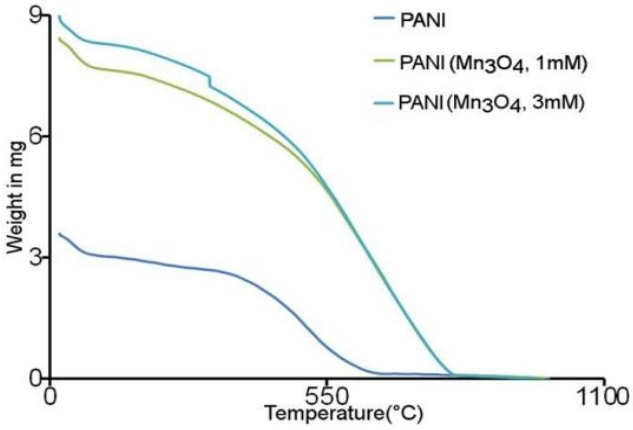

Fig. 4: TGA thermogram of PANI & PANI/Mn_3O_4 (1 mM, 3 mM).

Also, as the concentration of the dopant is increasing (**Fig. 4**), the degradation temperature is also increasing (810-860°C). The improvement in the thermal stability for

the PANI/Mn_3O_4 is attributed to the interaction between PANI and Mn_3O_4. This interaction restricts the thermal motion of PANI chains and shields the degradation of PANI in the NCs [**30**].

Gas sensing results

The dynamic gas sensing response characteristics of the PANI/Mn_3O_4 (1 mM) & PANI/Mn_3O_4 (3 mM) doped sensor at room temperature are shown in **Fig. 5(a) & 5(b)** respectively. It can be observed that the resistance of both the sensors decreases dramatically after exposed to acetone vapours. PANI/Mn_3O_4 (1 mM) is much less sensitive to acetone than PANI/Mn_3O_4 (3 mM) sensor. Poor & noisy response has been observed towards 60 ppm of acetone vapours in case of Mn_3O_4 (1 mM). The resistance of the sensor decreased on exposure to volatile vapours, which can be attributed to the fact that adsorption of vapour molecules resulted in the increased mobility of dopant ions. On removal of acetone vapours, the sensor quickly recovered back to its baseline resistance.

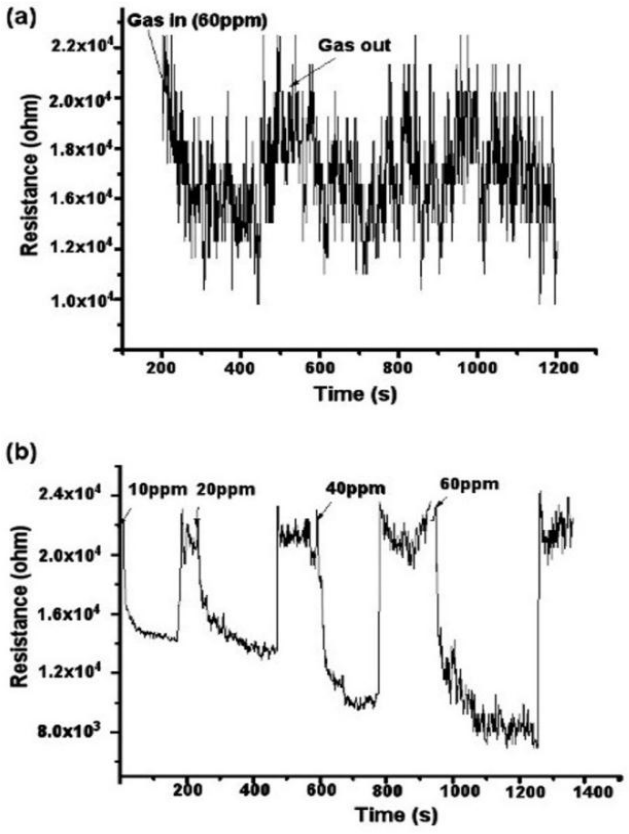

Fig. 5: Dynamic gas response for acetone of (a) PANI/Mn_3O_4 (1 mM) and (b) PANI/Mn_3O_4 (3 mM).

The change in the electrical behavior of the polymer on exposure to any gas can be correlated to the direction of the partial charge transfer and this phenomenon is dependent on the electronegativity of the vapour and work function of the polymer [**36**]. VOCs may be interacting with the polymer composite via physisorption mechanisms such as induced dipole/induced dipole interactions (also named London dispersion), dipole/induced dipole interactions, dipole/dipole interactions and hydrogen bonds (Lewis acidity/basicity-concept) [**37**].

PANI/ Mn_3O_4 (3 mM) has been exposed to acetone, ethanol and benzaldehyde in the concentration range from 10-60 ppm and the dynamic reponse for the acetone vapours has been depicted in **Fig. 5(b)**. With increase in vapour concentration, sensitivity increases owing to the increased number of adsorbed vapour molecules. Sensitivity for each gas has been plotted in **Fig. 6**. The sensor with 3 mM dopant concentration exhibited significant sensing response with a sensitivity of 1.5 at room temperature towards acetone vapours. The sensor is highly selective towards acetone vapours as seen in **Fig. 6**. Thus, the result suggests that this sensor could provide an excellent sensing platform for acetone sensing.

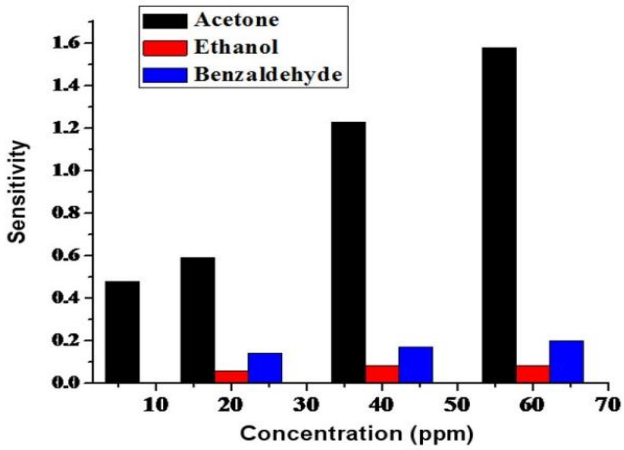

Fig. 6: Sensitivity of PANI/Mn3O4 towards acetone, benzaldehyde dan ethanol.

Conclusion

Facile route has been devised for the synthesis of PANI/Mn_3O_4. Effect of dopant on the structural morphology has been demonstrated. PANI/Mn_3O_4 NC has been found to be more porous as compared to undoped PANI which also implicates the more aptness of the NC for gas sensing. This NC formed has been found to be more suitable in terms of electrical conductivity, thermal stability and VOC sensing. The synthesized NC has a promising use as acetone sensor with fast response and recovery.

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Author's contributions

Conceived the plan: AB, AS, SB; Performed the experiments: AS, VK, SK, SB, PD; Data analysis: AS, SK, SB, PD; Wrote the paper: AS, PD, SK, SB, AB. Authors have no competing financial interests.

References

1. Sun, Y. F.; Liu, S.-B.; Meng, F.-L.; Liu, J.-Y.; Jin, Z.; Kong, L.-T.; Liu, J.-H.; *Sens.*, **2012**, *12*, 2610. **DOI**: 10.3390/s120302610
2. Liu, X.; Cheng, S.; Liu, H.; Hu, S.; Zhang, D.; Ning, H.; *Sens.*, **2012**, *12*, 9635. **DOI**:10.3390/s120709635
3. Tricoli, A.; Righettoni, M.; Teleki, A.; *Angew. Chem., Int. Ed. Engl.*, **2010**, *49*, 7632. **DOI:**10.1002/anie.200903801
4. Dai, L. (Eds.); Conducting Polymers, In Intelligent Macromolecules for Smart Devices; Springer-Verlag: UK, **2004**. **DOI**:10.1007/b97517
5. Stamenov, P.; Madathil, R.; Coey, J. M. D.; *Sens. Actuators, B*, **2012**, *161*, 989. **DOI**:10.1016/j.snb.2011.11.082
6. Gurunathan, K.; Amalnerkar, D. P.; Trivedi, D. C.; *Mater. Lett.*, **2003**, *57*, 1642. **DOI**:10.1016/S0167-577X(02)01045-5
7. Amado, F. D. R.; Krishnamurthy, S.; *Adv. Mater. Lett.*, **2016**, *7*, 719. **DOI**: 10.5185/amlett.2016.6127
8. Radhapyari, K.; Khan, R.; *Adv. Mater. Lett.*, **2015** *6*, 13. **DOI:** 10.5185/amlett.2015.5607
9. Deng, J.; He, C.; Peng, Y.; Wang, J.; Long, X.; Li, P.; Chan, A. S. C.; *Synth. Met.*, **2003**, *139*, 295. **DOI**:10.1016/S0379-6779(03)00166-8
10. Peng, C.; Zhang, S.; Jewell, D.; Chen, G. Z.; *Prog. Nat. Sci.*, **2008**, *18*, 777. **DOI**:10.1016/j.pnsc.2008.03.002
11. Makeiff, D. A.; Huber, T.; *Synth. Met.*, **2006**, *156*, 497. **DOI**:10.1016/j.synthmet.2005.05.019
12. Sathiyanarayanan, S.; Karpakam, V.; Kamaraj, K.; Muthukrishnan, S.; Venkatachari, G.; *Surf. Coat. Technol.*, **2010**, *204*, 1426. **DOI**:10.1016/j.surfcoat.2009.09.037
13. Zhou, Q.; Shi, G.; *J. Am. Chem. Soc.*, **2016**, *138*, 2868. **DOI**:10.1021/jacs.5b12474
14. Ma, X.; Wang, M.; Li, G.; Chen, H.; Bai, R.; *Mater. Chem. Phys.*, **2006**, *98*, 241. **DOI**:10.1016/j.matchemphys.2005.09.027
15. Ram, M. K.; Yavuz, Ö.; Lahsangah, V.; Aldissi, M.; *Sens. Actuators, B*, **2005**, *106*, 750. **DOI**:10.1016/j.snb.2004.09.027
16. Sadek, A. Z.; Wlodarski, W.; Shin, K.; Kaner, R. B.; Kalantar-zadeh, K.; *Nanotechnol.*, **2006**, *17*, 4488. **DOI**: 10.1088/09574484/17/17/034
17. Wang, J.; Matsubara, I.; Murayama, N.; Woosuck, S.; Izu, N.; *Thin Solid Films*, **2006**, *514*, 329. **DOI**:10.1016/j.tsf.2006.02.030
18. Parvatikar, N.; Jain, S.; Khasim, S.; Revansiddappa, M.; Bhoraskar, S. V.; Prasad, M. V. N. A.; *Sens. Actuators, B*, **2006**, *114*, 599. **DOI**:10.1016/j.snb.2005.06.057
19. Nandapure, B. I.; Kondawar, S. B.; Salunkhe, M. Y.; Nandapure, A. I.; *Adv. Mat. Lett.*, **2013**, *4*, 134 **DOI:** 10.5185/amlett.2012.5348
20. Nguyen, D.; Yoon, H.; *Polymers*, **2016**, *8*, 118. **DOI**:10.3390/polym8040118
21. Shambharkar, B. H.; Umare, S. S.; Rathod, R. C.; *Trans. Indian Inst. Met.*, **2014**, *67*, 827. **DOI:**10.1007/s12666-014-0405-8
22. Singla, M. L.; Awasthi, S.; Srivastava, A.; *Sens. Actuators, B*, **2007**, *127*, 580. **DOI**:10.1016/j.snb.2007.05.018
23. Kohli, P. S.; Devi, P.; Reddy, P.; Raina, K. K.; Singla, M. L.; *J. Mater. Sci.: Mater. Electron*, **2012**, *23*, 1891. **DOI**:10.1007/s10854-012-0680-2
24. Kumar, S.; Bagchi, S.; Prasad, S.; Sharma, A.; Kumar, R.; Kaur, R.; Singh, J.; Bhondekar, A. P.; *Beilstein J. Nanotechnol.*, **2016**, *7*, 501. **DOI:** 10.3762/bjnano.7.44
25. Huang, H.; Zeng, X.; Li, W.; Wang, H.; Wang, Q.; Yang, Y. J.; *Mater. Chem. A*, **2014**, *2*, 16516. **DOI:** 10.1039/C4TA03332A
26. Alam, M.; Ansari, A. A.; Shaik, M. R.; Alandis, N. M.; *Arabian J. Chem*, **2013**, *6*, 341. **DOI**:10.1016/j.arabjc.2012.04.021
27. Ma, X.; Zhang, X.; Li, Y.; Li, G.; Wang, M.; Chen, H.; Mi, Y.; *Macromol. Mater. Eng.*, **2006**, *291*, 75. **DOI**: 10.1002/mame.200500296
28. Zhang, D.; Wang, Y.; *J Mater. Sci. Eng. B*, **2006**, *134*, 9. **DOI**:10.1016/j.mseb.2006.07.037
29. Somani, P. R.; Marimuthu, R.; Mulik, U. P.; Sainkar, S. R.; Amalnerkar, D. P.; *Synth. Met.*, **1999**, *106*, 45. **DOI**:10.1016/S0379-6779(99)00081-8
30. Jaidev; Jafri, R. I.; Mishra, A. K.; Ramaprabhu, S.; *J. Mater. Chem.*, **2011**, *21*, 17601. **DOI:**10.1039/C1JM13191E
31. Gupta, N.; Kumar, D.; Tomar, S. K.; *Int. J. Mater. Chem.*, **2012**, *2*, 79. **DOI**: 10.5923/j.ijmc.20120202.07
32. Ishii, M.; Nakahira, M.; Yamanaka, T.; *Solid State Commun.*, **1972**, *11*, 209. **DOI:**10.1016/0038-1098(72)91162-3
33. Wang, W. Z.; Xu, C. K.; Wang, G. H.; Liu, Y. K.; Zheng, C. L.; *Adv. Mater.*, **2002**, *14*, 837. **DOI**: 10.1002/1521-4095(20020605)14:11<837::AID-ADMA837>3.0.CO;2-4
34. Gupta, N.; Verma, A.; Kashyap, S. C.; Dube, D. C.; *J. Magn. Magn. Mater.*, **2007**, *308*, 137. **DOI**:10.1016/j.jmmm.2006.05.015
35. Durmus, Z.; Baykal, A.; Kavas, H.; Sözeri, H.; *Phys. B*, **2011**, *406*, 1114. **DOI**:10.1016/j.physb.2010.12.059
36. Hagleitner, C.; Lange, D.; Hierlemann, A.; Brand, O.; Baltes, H.; *IEEE J. Solid-St. Circ.*, **2002**, *37*, 1867. **DOI:** 10.1109/JSSC.2002.804359
37. Bai, H.; Shi, G.; *Sens.*, **2007**, *7*, 267. **DOI:** 10.3390/s7030267

