PMMA Composite Thick Films as Gas Sensors

[1]S. Devikala, [2]P. Kamaraj, [3]M. Arthanareeswari and [4]V.K.Indira Priyadharshini

[1,2,3]Department of Chemistry, SRM University, Kattankulathur-603 203, India.
[4]Department of Chemistry, SRM University, Vadapalani Campus, Chennai, India.
Email: [1]sdevikala@gmail.com, [2]kamaraj97@yahoo.co.in, [3]arthanareeswari@gmail.com, [4]doctorindira@gmail.com

[Received: 28 Aug. 2014; Revised: 3 Sept.2014; Accepted: 3 Sept.2014]

Abstract— Gas sensors play vital role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. The composite prepared by mixing carbon black with PMMA has very good gas sensing applications. The gas sensors based on Carbon nanotube / polymer, ceramic and metal oxide, epoxide, polyimide, PMMA / $BaTiO_3$ and SnO_2 have also been developed. In the present work, a thick film of composite was prepared by using PMMA and Ammonium dihydrogen phosphate (ADP). Then, the composite's gas sensing behaviour for acetone vapour was tested by measuring the resistance change of the composite at room temperature. An increase in resistance has been observed with a response time of about ten seconds. The PMMA/Ammonium dihydrogen phosphate (PMADP) composites were characterized by using PXRD. The electrical conductivity of PMADP composites was also studied. The results show that the thick film of PMADP composite can function as a very good gas sensor for acetone vapours.

Keywords: Polymer composite, PMMA, Ammonium dihydrogen phosphate, PMADP, gas sensor

I. INTRODUCTION

Acetone is a commonly used chemical reagent in industry, for instance it is used to dissolve plastics, purify paraffin, dehydrate tissues and for pharmaceutical applications. People may develop a headache, fatigue and even narcosis when the concentration of acetone in air is higher than 10,000 ppm. Hence, detecting and measuring acetone concentrations in the workplace or human body are necessary for our safety and health. Several techniques have been developed to measure the concentration of acetone, such as gas/liquid chromatographic analysis, spectroscopy and sensors[1-3]. Among them, detection by sensors may be the most promising method due to the simplicity, precision and convenience. At present, various types of acetone sensors based on different sensing principles have been fabricated; such as, semiconductor sensors[1]and[4], chemiluminescence-based sensors[5], optical –fibre sensors[6] and piezoelectric sensors. In practical use, the sensors have to be measured with respect to the s criteria of gas sensors which are: sensitivity, selectivity, stability and speed. Many gas sensors do not sufficiently fulfill the requirements. However, these sensors still have some short-comings such as low selectivity, short life time, unsuitability and low sensitivity. The present work aims at overcoming these draw backs. Successful attempts have been made by a number of groups to overcome these problems by investigating semi conducting metal oxides operated at higher temperatures. This includes materials like $BaTiO_3$, $SrTiO_3$, Ga_2O_3, WO_3, Nb_2O_3, MoO_3, CeO_2 with operating temperatures being typically between 400°C and 900°C[7]. However, independent of the operating temperature regime, the problem of sensor selectivity affects all semi conductor metal oxide sensors: the sensing material does not respond to one specific gas only, but to a group of gases with similar chemical behavior. The present work reports on strategies and results on how to successfully overcome the selectivity problem. Gas sensors have found wide application in industrial production, environmental monitoring, protection, etc. It has been known for a long time that the process of gas adsorption on porous semiconductor surface can change the electrical properties of the surface. Gas sensors generally operate based on different principles. Various gas sensing elements have been developed for the past years. However these sensing elements typically operate at an elevated temperature for maximum performance. This may cause higher power consumption, which is not suitable for many applications. Over the last decade, PMMA composites have attracted considerable attention, and great efforts are being made to exploit their unusual electronic and mechanical properties. These properties make them potential candidates for building blocks of active materials in nanoelectronics, field emission devices, gas storage and gas sensors. Among these, the room temperature gas sensing property is very attractive for many applications [8,9] . Interaction with any gas can change the electrical properties of PMMA composites at

room temperature. Also they have fast response and good reversibility. Among the sensors investigated and developed, PMMA based sensors received much attention since they can detect a wide variety of gases with high sensitivity, good stability and also low production cost. However, like other gas sensors, PMMA sensors should be operated at higher temperatures, which brings about much inconvenience for practical applications and sometimes is even unsafe for detecting combustible gases. Acetone detection using chemoresistive sensors was reported before. For example, Ryabtsev et al.'s Fe_2O_3, SnO_2, CdO sensors[10] showed sensitivities less than 5.2 to 10 ppm acetone but no testing for selectivity was reported. The sensitivity of Li et al.'s WO_3 hollow-sphere gas sensors was only 3.53 to 50 ppm acetone. Zhu et al.'s TiO_2-doped ZnO thick film had cross sensitivity to many other VOCs[11].Teleki et al.'s TiO_2 nanoparticles showed cross sensitivity to isoprene. Khadayate et al.'s WO_3 thick film showed a 4.5 value of gas sensitivity to 50 ppm acetone (the only gas tested)[12]. An indium nitride (InN) gas sensor of 10 nm in thickness has achieved detection limit of 0.4 ppm acetone [13]. Acetone gas sensor based on WO_3 microspheres has been reported [14]. The present work reports the results of the gas sensing behavior of a sensor developed using thick film which shows a maximum response to the test gas at room temperature.

II. EXPERIMENTAL

The monomer MMA, Ammonium dihydrogen phosphate(ADP), benzoyl peroxide, chloroform and petroleum ether were obtained from SD Fine Chemicals Limited, Mumbai, India.

Preparation of PMMA

The purified monomer (MMA) (10ml) was taken in a polymerization tube and 50mg of benzoyl peroxide which acts as a catalyst was added to accelerate polymerization, in the polymerization reaction. The polymerization tube was then kept in a water bath at 60-70^{o}C with periodical shaking. A hard viscous polymer was obtained after 90 minutes of heat treatment. The polymerized mass was dissolved in chloroform and then transferred into a beaker. The viscous polymer solution was precipitated by the addition of petroleum ether. The precipitated polymer was then filtered and oven dried at 60^{o}C. The polymer formed was found to be syndiotactic[15].

Preparation of PMADP composites

A definite quantity of PMMA was dissolved in chloroform followed by the addition of a known quantity of ammonium dihydrogen phosphate and then it was made into a paste in an agate mortar and was subjected to heat at 100°C for 6 hours in a Muffle furnace and made into a powder. PMADP composites were prepared in the following proportions of PMMA and ADP: PMADP 1 – 9:1, PMADP 2 – 8:2, PMADP 3 - 7:3, PMADP 4 -6:4, PMADP 5 – 5:5 and PMADP 6 – 4:6.

Preparation of polymer composite thick films for gas sensing

A pasty solution of PMMA/ADP were coated on glass plates using a Apex Spin Coating unit (SCU 2005) and the samples were sintered in a Muffle furnace for about 6 hours at 100°C. Then these plates were used for gas sensing. Two parallel copper wires were fitted onto the corners of the glass strips. These wires act as electrodes to detect the presence of gas. The samples were placed in a closed chamber. The experiment was performed at room temperature. For this study, acetone and ammonia gases were used and the electrical resistance of PMADP composites over acetone vapours were determined using MECO 603 digital multimeter.

Characterization

PXRD

In order to understand the properties of composite material, it is essential to know about the details of its structure. Diffraction techniques were adapted to characterize the synthesized composites. X-ray diffraction (XRD) studies were done with Philips X pert PRO diffractometer using CuKα radiation (λ=0.15406 nm).

Electrical conductivity of PMADP composites

Electrical conductivity of the composites was studied at different proportions of ADP (20-50%) using Hewlett Packard model HP 4284A Precision LCR meter.

III. RESULTS AND DISCUSSION

Response of composites to acetone vapours

The sensor responses of the PMADP composite samples were measured and are shown in the figures 1(a) to 1(f). The responsiveness, S, of the composites to acetone vapours can be determined from the equation,

$$S = R_t / R_o$$

Where Ro is the initial resistance of the sensor value, and R_t is the maximum steady state response value of the sensor when it was exposed to the analyte vapour. In the present study, the vapours of acetone were detected by the sensor. The sample resistance increases in the acetone in ambience and reaches a saturation at a particular value and the sample resistance decreases in the air ambience. The sensing cycle is reversible upto to two cycles. The sensitivity increases with increasing concentration of ammonium dihydrogen phosphate in the composite samples. Sensing parameters were summarized in Table

1. The response time of the sensor was 10seconds while some recent studies report a higher response time[16] and the recovery time was 4hours. It can be seen from the figures 1(a) to 1(f), that the response of the sensor is fast and the sample PMADP 6 shows highest sensitivity when compared to other PMADP composite samples. This is due to higher proportion of ammonium dihydrogen phosphate in PMADP 6. In order to validate the selectivity of the gas sensor, PMADP composite plates were exposed to ammonia and ethanol vapours which do not show any response.

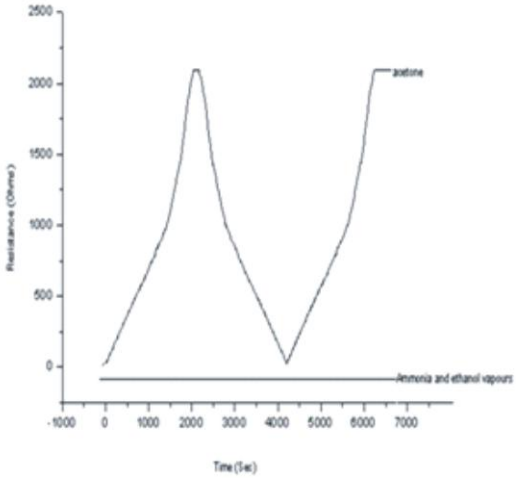

Fig. 1(a) Sensor response of PMADP 1 to acetone vapour

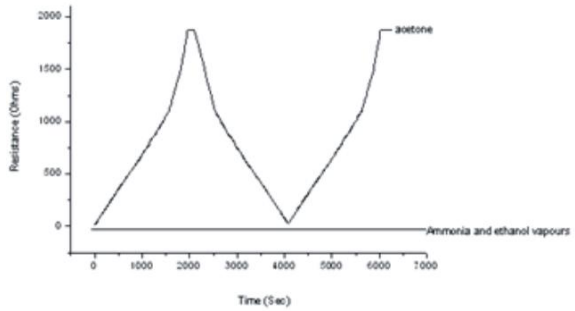

Fig. 1(b) Sensor response of PMADP 2 to acetone vapour

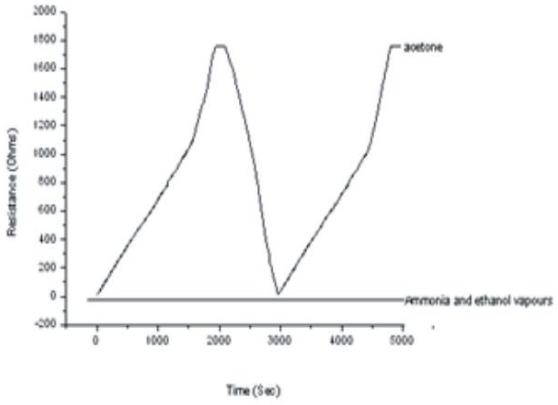

Fig. 1(c) Sensor response of PMADP 3 to acetone vapour

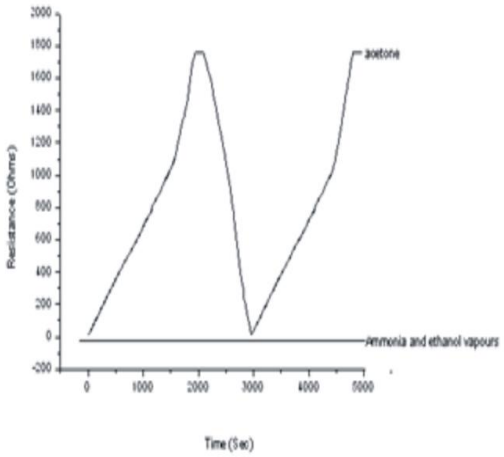

Fig. 1(d) Sensor response of PMADP 4 to acetone vapour

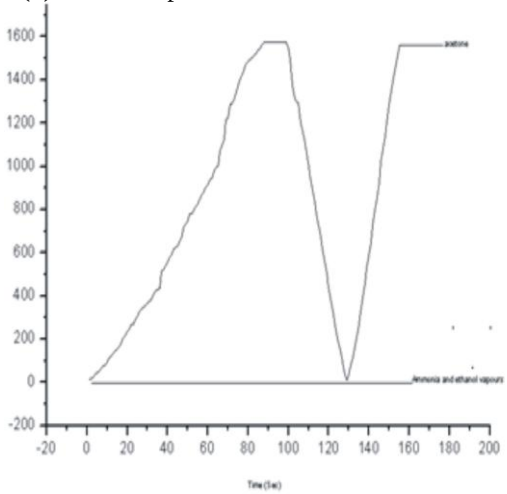

Fig. 1(e) Sensor response of PMADP 5 to acetone vapour

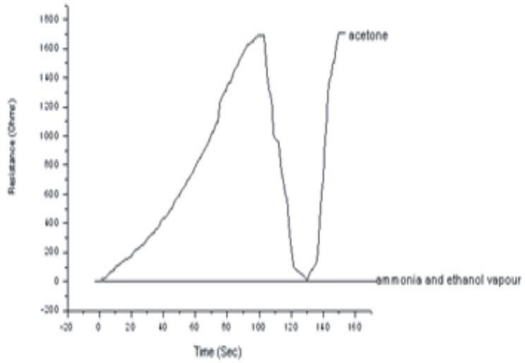

Fig. 1(f) Sensor response of PMADP 6 to acetone vapour

Table. 1. Sensor response of PMADP composite films for acetone vapours

PMMA/ ADP composites	R0 Ω (Initial resistance)	Rt Ω (Maximum steady state resistance)	Rt/R0 (Sensitivity)
PMADP 1	28	2096	74.85
PMADP 2	24	2010	83.75
PMADP 3	21	1880	89.52
PMADP 4	18	1760	97.77
PMADP 5	15	1576	105.066
PMADP 6	16	1690	105.625

Gas sensing mechanism

It is generally agreed in literature that when exposed to air, electrons are removed from the semiconductor conduction band leading to a build up of O^- on the surface.

$$O_{2\,(gas)} + 2e^- \rightarrow O^-_{(adsorbed)}$$

When the sensor is exposed to acetone vapour, it reacts with the adsorbed oxygen ions (O^-) and gets oxidized to CO_2 releasing electrons(sensing) that can return to the conduction band of the semiconductor and therefore lowering the resistance of the sensor[18].

$$CH_3COCH_{3(gas)} + 8O^-_{(adsorbed)} \rightarrow 3CO_{2(gas)} + 3H_2O + 8e^-_{(conduction\ band)}$$

This typical behavior of sensor is depicted in figures 1(a) to 1(f) and was found for all sensors tested. Gas sensing properties are dominantly controlled by the surface adsorption. A dynamic equilibrium state will occur between the initial adsorption and the subsequent desorption. The amount of adsorbed acetone vapours increase with time and the adsorption attains a balance at a saturation state. After saturation, as the time increases further, the amount of gas adsorbed will reduce, and the desorption occurs resulting in a decreased value of resistance.

XRD

The XRD peaks of the PMMA, Ammonium dihydrogen phosphate and the composites were shown in the figures 2.(a) to 2.(e). The XRD analysis of PMADP1 to PMADP 6 showed a similar pattern. While analyzing the composite peaks, the intensities of the precursor peaks were not reflected. At the same time, the positions of few peaks in the composites have been shifted compared to ammonium dihydrogen phosphate peaks.

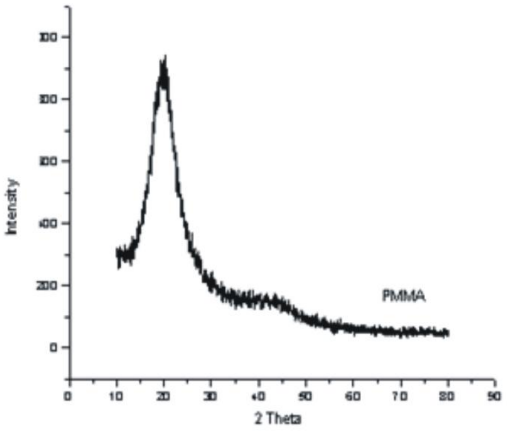

Fig. 2(a) XRD of PMMA

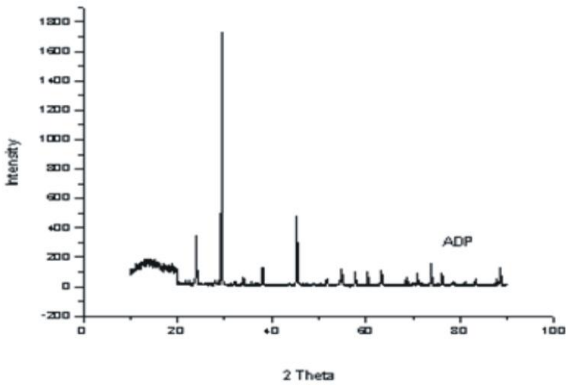

Fig. 2(b) XRD of Ammonium dihydrogen phosphate

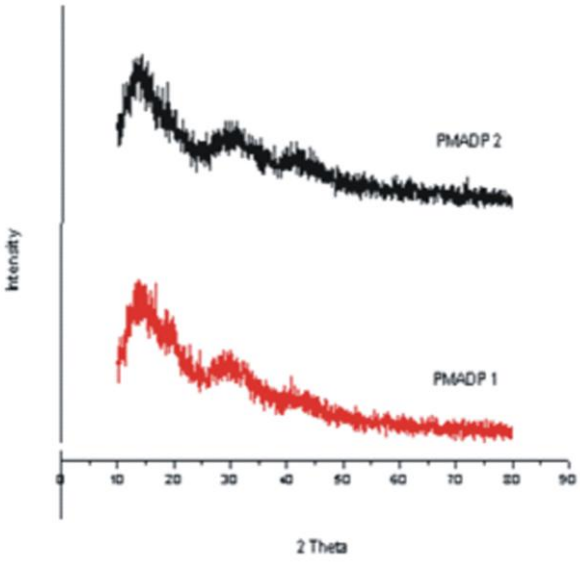

Fig. 2(c) XRD of PMADP 1 and PMADP 2

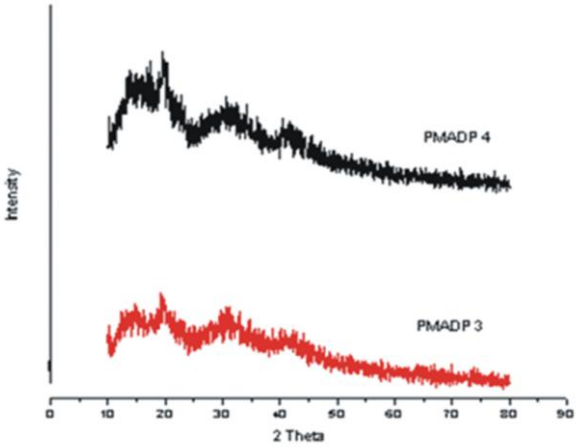

Fig. 2(d) XRD of PMADP 3 and PMADP 4

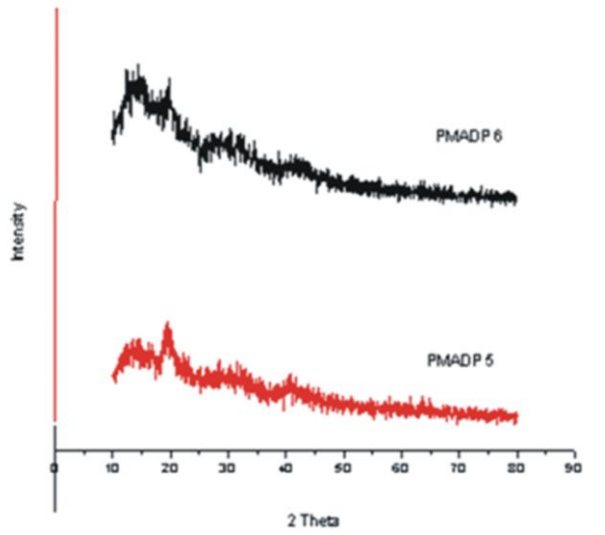

Fig. 2(e) XRD of PMADP 5 and PMADP 6

Electrical conductivity of PMADP composites

The conductivity data (Table 2.) reveals that there is an increase in conductivity of the composites with percentage of ammonium dihydrogen phosphate.

Table. 2.Electrical conductivity of PMADP composite thick films

% of ADP in composite	Resistance ohm	Thickness cm	Area cm^2	Conductivity Scm^{-1}
20	3258	0.04	0.5026	2.44279×10^{-5}
30	4140	0.07	0.5026	3.36415×10^{-5}
40	3235	0.07	0.5026	4.30528×10^{-5}
50	2157	0.06	0.5026	5.5345×10^{-5}

IV. CONCLUSIONS

A gas sensor based on PMADP has been developed and the experimental results are evaluated. The resistance of the polymer composite got extremely increased in acetone vapours and reached equilibrium over time. The addition of ammonium dihydrogen phosphate to PMMA has increased the conductivity of the PMADP composites. The results have shown that PMADP composites have potential application for detecting acetone selectively at room temperature.

V. REFERENCES

[1] Makisimovich N, Vorotynstev V, Nikitina N, Kaskevich O, Karabun P and Martynenko F, "Adsorption semiconductor sensor for diabetic ketoacidosis diagnosis", Sensors and Actuators B: Chem., 36(1996) 419-421.

[2] Deng C H, Zhang J, Yu X F, Zhang W and Zhang X M, "Determination of acetone in human breath by gas chromatography–mass spectrometry and solid-phase microextraction with on-fiber derivatization", J.Chromtogr.B, 810(2004) 269-275.

[3] Deng C H, Zhang J, Yu X F, Zhang W and Zhang X M, "Rapid determination of acetone in human plasma by gas chromatography–mass spectrometry and solid-phase microextraction with on-fiber derivatization", J.Chromatogr.B, 805(2004) 235-240.

[4] Anno Y, Maekawa T, Tamaki J, Asano Y and Hayashi K, Sens. Actuator B: Chem., "Zinc-oxide-based semiconductor sensors for detecting acetone and capronaldehyde in the vapour of consomme soup", 24(1995) 623-632.

[5] Utsunomiya K, Nakagawa M, Tomiyama T, Yamamoto I, Matsuura Y, Chikamori S, Wada T, Yamshita N and Ymashita Y, "Discrimination and determination of gases utilizing adsorption luminescence," Sens. Actuator B: Chem., 11(1993) 441-445.

[6] Bene R, Kiss G, Perczel I V, Meyer F A and Reti F, "Application of quadrupole mass spectrometer for the analysis of near-surface gas composition during DC sensor-tests", Vacum, 50(1998) 331-337.

[7] Fleischer M and Meixner H, "Fast gas sensors based on metal oxides which are stable at high temperatures", Sensors and Actuators B, 43(1997) 1-10.

[8] Ong K G, Zeng K and Grimes C, "A wireless, passive carbon nano tube based sensor", IEEE Sensors J, 2 (2002) 8288.

[9] Philip B, Abraham J K, Chandarsaker A and Varadan V K, "Carbon nanotube/PMMA composite thin films for gas sensing applications", Smart Mater. Struct. 12 (2003) 935.

[10] Ryabtsev S V, Shaposhnick A V, Lukin A N and Domashevskaya E P, "Application of semiconductor gas sensors for medical diagnostics}, Sens. Actuators, B 59(1999) 26-29.

[11] Zhu B L, Xie C S, Wang A H, Zeng D W, Song W L and Zhao X Z, "Improvement in gas sensitivity of ZnO thick film to volatile organic compounds (VOCs) by adding TiO2", Mater. Lett., 58(2004) 624-629.

[12] Khadayate R S, Sali V and Patil P P, "Acetone vapor sensing properties of screen printed WO_3 thick films", Talanta, 72 (2007) 1077-1081.

[13] Kun-Wei Kao, Ming-Che Hsu, Yuh-Hwa Chang, Shangjr Gwo and J. Andrew Yeh "A Sub-ppm Acetone Gas Sensor for Diabetes Detection Using 10 nm Thick Ultrathin InN FETs", Sensors 2012, 12(6) 7157-7168.

[14] Yidong Zhang' , Weiwei He, Hongxiao Zhao, Pinjiang Li, **"**Template-free to fabricate highly sensitive and selective acetone gas sensor based on WO_3 microspheres", Vacuum**,** 95(2013), 30-34.

[15] Devikala S, Kamaraj P and Arthanareeswari M, "Electrochemical Performance of PMMA/Al2O3 Composite Coatings", International Journal of Advanced Chemical Science and Applications, 1(2) (2014), 9-15.

[16] Wang L, Kalyanasundaram K, Stanacevic M and Gouma P, "Nanosensor device for breath acetone detection", Sensor letters, 8 (2010), 709-712.

◈◈◈