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Stereo-regulated Schiff base siloxane polymer coated QCM sensor for amine vapor detection

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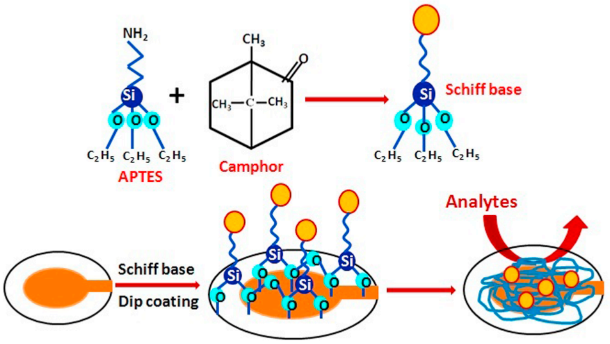
HIGHLIGHTS

- Stereo-regulated siloxane film is prepared from the Schiff base of APTES and keto group compounds.
- Siloxane polymers with camphor shows the highest sensitivity for the detection of amines.
- The polymer film shows high sensitivity, fast response for aliphatic amine detection.
- Aliphatic amine vapor detection has linearity up to 250 ppm with sensitivity 1.20–2.59 Hz/ppm.

GRAPHICAL ABSTRACT

Schematic of formation of bulky Schiff base film on QCM surface.



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ABSTRACT

Stereo-regulated siloxane film was prepared from the Schiff base of 3- (aminopropyl)triethoxysilane(APTES) and organic compounds having keto group by condensation reaction. The organic compounds such as benzaldehyde, acetophenone, heptaldehyde and camphor were chosen for making various sizes of pores in polymer films. The film was coated on quartz crystal microbalance (QCM) surface for the detection of aliphatic amine vapors such as methylamine, ethylamine, diethylamine, triethylamine, tert-butylamine and ammonia. The structures, morphology and surface roughness of films were studied by FTIR, FESEM and AFM respectively. It was noticed that, the film prepared from camphor has the highest sensitivity for the detection of amines which was due to the bulky globular structure of the camphor molecule by producing reasonable pores of desired size. The polymer film obtained from camphor and APTES was highest sensitivity and fast response towards the detection of organic amine vapors. The linearity of detection was measured up to 250 ppm and the sensitivity of the sensor was found to be 1.20–2.59 Hz/ppm.

1. Introduction

The development of rapid, reliable sensors for environmental monitoring, medical field, molecular biotechnology and industry are of great demand [1,2]. Generally, aliphatic amines are liberated from agricultural waste, chemical industry, cattle feed manufacturing operations etc. [3–5]. It is known that dimethylamine and trimethylamine are biomarkers for uremia. Similarly, aniline and *o*-toludine are known

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biomarker for lung cancer. The quality estimations of fish and meat are performed by measuring the concentrations of trimethylamine, dimethylamine and ammonia vapors are reported earlier [6,7]. Ammonia vapor is widely used for manufacturing of explosives and industrial coolant which is hazardous to human being. It may damage the human olfactory system even in 5 ppm level of concentration. Hence, the detections of organic amines are important for the quality control of food, medical diagnosis and other environmental monitoring. A number of sensors have been developed for the detection of organic amines using electro chromic polymers [8], tin oxide sensors [9–11], potentiometric or conductometric techniques [12–14].

Quartz crystal microbalance sensor (QCM) is a mass sensitive device which is simple, highly sensitive, easy to use, and low cost which can work at room temperature. The selective interaction of the analyte can be possible by using thin sensing film on the surface of the QCM. The sensitivity of the sensor is determined by the chemical structure, physical properties of the coated film and also on the nature of the interaction between sensing film and analyte molecules. It is found that the polyaniline coated QCM sensor is used for the selective detection of triethylamine [15]. We have reported in our earlier study that the polymerized castor oil is used as a sensing film for the detection of aliphatic amine vapor [16]. In literature, it is also found that polyaniline/emeraldine based (PANI/EB) film is used on QCM sensor for amines vapor detection [17]. Adsorption of TiO_2 and polyacrilic acid (PAA) sensing film is coated on QCM sensor for *n*-butylamine and ammonia vapor detection [18]. It is reported that aliphatic amine vapors are detected by chitosan sensing film on QCM surface [19]. Molecular imprinted polymer on QCM surface is synthesized from acrylamide (AM) as a functional monomer and trimethylolpropane trimethacrylate (TRIM) as a cross-linking agent. This polymer film is selective for the discrimination of L- and D-tryptophan enantiomers in citric acid buffer solutions with a detection limit of 8.8 μM [20]. Further, it is reported that nanostructured TiO_2 sensitive film is used for the detection of NO_2 vapors in ppm level. The applications of the developed sensor can be extended in medical and chemical diagnostics [21]. The molecularly imprinted polymer is prepared on QCM surface using hydroquinone and phenol as templates that generate shape selective cavities in a poly(acrylic) or poly(methacrylic) polymer matrix. The developed sensor is used for the detection of organic vapors in ppm [22]. Calix [4] arene modified QCM sensors is developed for the detection of VOCs such as acetone, acetonitrile, carbon tetrachloride (CTC), chloroform, methylene chloride (MC), N,N-dimethylformamide (DMF) etc. However, the sensing ability of the sensor coated with amino and imidazole groups has more sensitivity towards methyl chloride vapors with a detection limit of 54.1 ppm [23]. Trace amount of ammonia vapors are selectively detected using polyacrylic acid (PAA) based QCM sensor. The coating of polymer film on gold coated electrode is carried out through an electrospray/electrospinning process [24]. The non-conductive polymer such as polyvinyl alcohol (PVA) and poly (acrylic acid) (PAA) are sensitive to *o,o*-dimethyl-*o*-2,2-dichlorovinyl phosphate (DDVP) in the frequency range from 10 to 20 Hz. The conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) and a copolymer of PEDOT with poly(styrene sulphonic acid) (PEDOT/PSS) modified QCM sensors are sensitive to DDVP vapors range from 20 to 115 Hz and 18–60 Hz respectively [25]. Pentacene is also an organic polymer used as a sensing film on quartz crystal microbalance (QCM) at room temperature for the detection of VOC such as benzene, toluene or xylenes [26].

In present study, a sensing film was prepared from polymerization of Schiff base produced from 3- (aminopropyl)triethoxysilane (APTES) with aldehydes or ketones. The bulky head group of aldehydes or ketone was producing siloxanes polymers by the simple chemical method. Polysiloxane film was coated on the surface of the quartz crystal microbalance by solution dip coating method. The motivation for the present work was obtained as; APTES was used as a coupling agent to increase the adhesion in fiberglass-epoxy composites for the modification of silica surfaces [27–32]. APTES has three ethoxy groups ($-O-CH_2-CH_3$) and one amine group which acts as a coupling agents for the grafting of other molecules. This molecule has been widely used for the stationary phase preparation in chromatography and immobilization of various biomolecules and ions [33–35]. It has the possibility to covalently attach with a biomolecule due to its bifunctional nature. The fuctionalization of silicon oxide substrate is carried out using APTES for the attachment of biological molecules [36]. Herein it acts as a cross linking agent for the polymerization reactions of aryl chlorides with the diamino-alkylene oxide. Aminopropyl-functionalized silica (APS) is synthesized by grafting of 3-aminopropyl-triethoxysilane (APTES) onto the surface of silica gel [37]. Nanoporous graphene oxide (G-COOH)/polystyrene (PS) nanofiber with an average particle size of 569 nm are fabricated by electrospinning method. The nanofibers have a diameter of 37 nm of ultrathin nanowires. The mesoporous structured G-COOH/PS composite nanofibers is sensitive for ammonia vapor [38]. Based on the above literature, we have prepared a new promising polymer sensing film on the QCM surface for the detection of aliphatic amine vapors with higher sensitivity. We have used APTES to form Schiff base organosilane for the generation of poly-siloxane introducing the cage like structure with a bulky organic head group. The polysiloxane film has reasonable molecular pores to accommodate organic amines through H-bonding with -N=CH- of Schiff base. The polymer film is used as a sensing film on the QCM for the detection of amine vapors. A comparison table of the sensitivity of different sensing film on QCM surface for aliphatic amine detection is presented in Table 1.

2. Materials and method

2.1. Synthesis of Schiff base

3-(aminopropyl)triethoxysilane (APTES) was purchased from Sigma-Aldrich. Methylamine, ethylamine, diethylamine, triethylamine tert-butylamine, ammonia, ethanol, benzaldehyde, acetophenone, heptaldehyde and camphor were purchased from E.Merck, India. Quartz crystal microbalances of 10 MHz coated with silver electrode on both sides were purchased from Kesheng Electronics Ltd. (Yantai, China). The sensing film was prepared from the Schiff base reaction of 3- (aminopropyl)triethoxysilane (APTES) and organic ketone or aldehyde in ethanol as a solvent. The QCM surface was cleaned with piranha solution and then rinsed with deionized water before coating of polymer solution. The sensor was prepared by simple dipping QCM into the polymer solution and then dried at room temperature for 30 min followed by heating at 90 °C for 2 h in a hot air oven. The coating load

Table 1
Comparison table of the sensitivity of QCM sensor for aliphatic amine detection.

Polymer used	Methyl amine (Hz/ppm)	Ethyl amine (Hz/ppm)	Diethyl amine (Hz/ppm)	Triethyl amine (Hz/ppm)	Tert-butyl amine	Ammonia	Ref.
$(TiO_2/PAA_{400})_5$	–	–	–	–	–	0.33	[18]
Graphene oxide/polystyrene nano fibrous film	–	–	–	–	–	0.3	[31]
Polymerized castor oil	0.91	0.65	0.65	0.54	0.40	0.39	[16]
Schiff base polymer (Our work)	2.59	2.17	1.97	1.72	1.63	1.20	

on the QCM surface is maintained up to a maximum of 5–6 KHz. A QCM measurement set up based on static headspace sampling method is used for this experiment. It consists of sensor chamber of 100 ml volume, suction pump, multichannel frequency counter and an oscillating circuit [39]. Saturated concentration of amine in dry nitrogen gas was prepared by bubbling method using amine solution. In this measurement the polymer coated crystal was placed in the sensor chamber and the exact concentration of analytes was injected by a glass syringe through rubber septa. The drop in frequency due to additional mass loading with time was monitored into a computer through a National Instrument Card after the equilibrium response was reached. The sensor chamber was purged with dry nitrogen at an interval of 15 min. The concentration of the analytes is calculated as follows.

1 ppm of analyte(X) = (Molecular Weight (MW) of analyte/MW of air at room temperature) mg/m^3. Then 1 ppm of analytes was prepared in the desiccators of volume 10,000 ml by dividing the density of the analytes with X. The exact analyte in ppm to be injected to the sensor chamber of volume 100 mL (it needs to calculate the volume which can be drawn by the syringe of volume 60 mL) was calculated by using the principle of gas $V_1S_1 = V_2S_2$, Where V_1 is volume of the sensor chamber, S_1 is the concentration of gas which varies accordingly to characterize the sensor whereas V_2 is the syringe volume to be calculated to get the concentration of gas (S_2) in ppm.

2.2. Film preparation

Five sets of solutions were prepared such as pure APTES and APTES with four compounds such as camphor, benzaldehyde, acetophenon, heptaldehyde separately and were named as AS (only APTES), AC (APTES/Camphor), AB (APTES/Benzaldehyde), AA (APTES/Acetophenon) and AH (APTES/Heptaldehyde). APTES with camphor polymer solution was prepared by addition of 20 μl of APTES with 5 ml of ethanol and to this solution 0.5 mg of camphor was added and the solutions are sonicated for 10 min for homo-dispersion. Same procedure and condition is maintained for the preparation of AS, AB, AA and AH solution. The Schiff base is formed by the reaction of camphor, benzaldehyde, acetophenon and heptaldehyde and amine group of APTES. The possible reaction mechanism of the preparation of the Schiff base from APTES is presented below.

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\ (SiOC_2H_5)_3 + RR_1C{=}O \longrightarrow RR_1C{=}N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\ (SiOC_2H_5)_3$$

Where ($R= C_6H_5$, $R_1=H$); ($R= C_6H_5$, $R_1=CH_3$) ; ($R=CH_3\text{-}(CH_2)_5\text{-}$, $R_1= H$) and $RR_1C{=}O \longrightarrow$ Camphor

The cleaned quartz crystals were coated with polymer solutions and the excess solutions were evaporated at room temperature in an open atmosphere followed by heating at 90 °C for 2 h in hot air oven. Polymer coated QCM surfaces were not subjected to any further chemical or physical modifications before carrying the experiments.

2.3. Instrumentation

A syringe pump of model no-LPM 50DN was used for the injection of vapor to the sensor chamber at a constant force for 30 s. A Fourier transform infrared spectrum of polymer sample was recorded in the range of 400–4000 cm^{-1} (model Paragon-500 FTIR of PerkinElmer spectrometer). The polymer coated QCM surface before and after adsorption of analytes were scanned by AFM (Veeco, di-Innova) in tapping mode using the nanoprobe cantilever made up of silicon nitride with a spring constant of 49 Nm.$^{-1}$ The study of the surface morphology of the polymer film was carried out using JEOL JEM6700F field emission scanning electron microscope (FESEM).

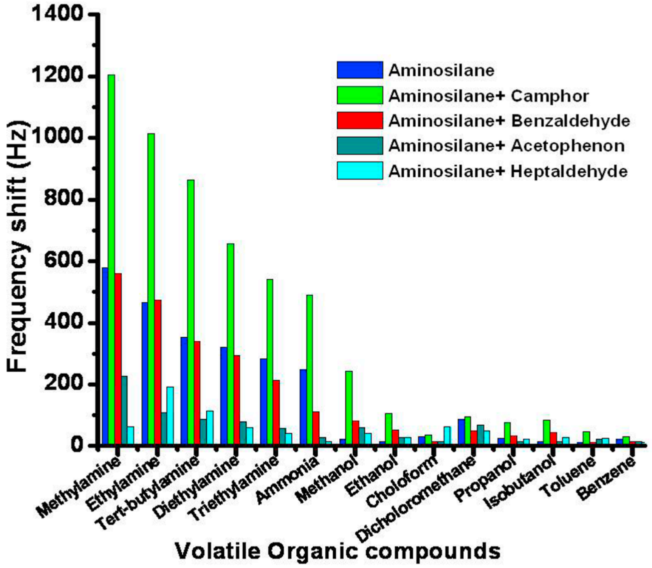

Fig. 1. Comparison of sensor response of five sensors to common volatile organic compounds.

3. Results and discussion

3.1. Preparation of sensing film

Initially, the amino group of APTES reacts with ketone group of camphor/organic ketone/organic aldehyde to form Schiff base polymer. Then the polysiloxane solution is prepared by hydrolysis of silicate ester groups and it is coated on the QCM surface by dip coating method. After the deposition of the polymer film on QCM surface, the frequency is measured and then the responses of the sensor after injection of different analytes are recorded separately. For adsorption of small volatile organic molecules, the polymer should have reasonable and flexible free volume with specific molecular pore for selectivity. The bulky head group of Schiff base attached to polysiloxane introduces molecular pores to accommodate small molecules of amines and is stabilized through the formation of H-bonds and dipole-dipole interaction. The effect is noticeable from the Schiff base produced by camphor and APTES. It is because of globular structure of camphor molecule. Hence, it is explored the details study using the polymeric siloxane film produced from APTES and camphor. Four different polymer solutions with variation of compositions of camphor are prepared for optimization of sensitivity. The four sets of polysiloxane solutions are prepared by keeping the concentration of APTES (20 μl) and ethanol (5 ml) as constant and varying the concentration of camphor as 0.05 mg, 0.25 mg, 0.50 mg and 0.75 mg respectively.

After the siloxane film is deposited on the QCM surface the sensor is placed in the sensor chamber with a rigid base. Then the experiment is carried out by injecting the target gas into the sensor chamber through the glass syringe having the concentration range from 10 ppm to 250 ppm. The vacuum pump is off at the beginning and the particular concentration of VOC is injected into the chamber. The change in frequency is recorded after the equilibrium reached. It is observed that the frequency shift value is proportional to the analyte concentration. The

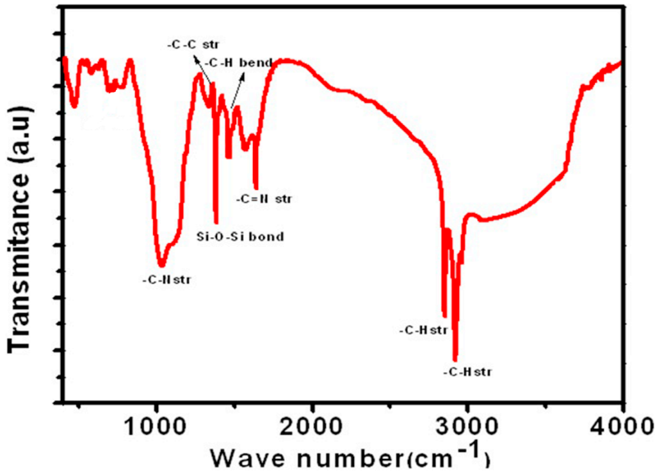

Fig. 2. FTIR spectra of Schiff based siloxane film prepared from APTES and camphor.

sensor has excellent reversibility, fast response. The slight drift in baseline is negligible during the experiment. Each experiment is repeated for 5 times and the average data is taken for final analysis. The five sets of sensors such as AS, AC, AB, AA and AH are tested with a saturated concentration of volatile organic compounds. These sensors are more sensitive to aliphatic amine vapors than other VOCs; however, the sensor prepared from camphor and APTES has higher sensitivity than other sensors. Fig. 1 shows the comparison of sensor response of five sensors to common volatile organic compounds. The details study of the AS sensor is explained in this work.

3.2. Characterizations of sensing film

The FTIR spectrum of the AS polymer film is presented in Fig. 2. The –C-H stretching vibrational band appears at 2848 cm^{-1} and 2915 cm^{-1}. The band at 1659 cm^{-1} is corresponds to the presence of –C=N- stretching of the Schiff base group. The band obtained at 1340 cm^{-1} and 1470 cm^{-1} are responsible for –C-C stretching and –C-H bending vibration respectively. The Si-O-Si bond shows the absorption band at 1388 cm^{-1}. The –CH=N stretching band is appeared at 1029 cm^{-1} [40].

The morphology of the Schiff base siloxane (AS) is characterized by FESEM and is presented in Fig. 3. It is observed that the irregular shaped particles are agglomerated and the small pores are uniformly distributed throughout the matrix. The formation of pores is responsible for adsorption of analytes. The polymer coated QCM sensor is immediately heated for the homogeneous spreading of polymer film on the surface with less agglomeration. Therefore; the bulky head with uniformly distributed pores are formed on the QCM surface which provides a large surface area with reasonable molecular pores for the adsorption of analyte molecules. On exposure of the analytes to the sensor, frequency of the QCM sensor is changed which is proportional to the mass adsorbed on the sensitive polymer film. Analytes are injected into the sensor chamber through a syringe pump. The sensitivity of the sensor towards VOC (Hz/ppm) is calculated from the slope of the graph plotted between the concentrations of analytes with the change in frequency with time. When vapors are adsorbed on the QCM surface, the frequency of the oscillating crystal decreases and comes to baseline after removal of analyte by purging with nitrogen. The measurement procedure is consistent, which confirms the physical adsorption of analyte takes place on the sensor surface. The response of the developed sensors increases linearly with an increase in vapor concentration. The calibration curve is obtained by plotting the vapor concentration of all the analytes such as methylamine, ethylamine, tert-butylamine, diethylamine and ammonia from 10 ppm to 250 ppm with the frequency shift. The density and purity of individual analytes along with the volume of the sensor chamber are considered for the calculation of the concentration of organic vapor in ppm. The sensitivity values and the correlation coefficient of the sensor for VOCs in the concentration range of 10 ppm–250 ppm are presented in Table 2.

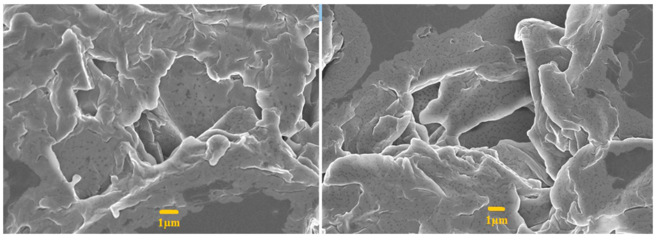

Fig. 3. FESEM images of Schiff base polymer prepared from APTES and camphor.

Table 2
Analytical characteristic parameters of sensor for aliphatic amine vapor.

Analytes	Sensitivity (Hz/ppm)	Correlation coefficient (R^2)	LLD mg/L
Methylamine	2.59	0.99	1.022
Ethylamine	2.17	0.98	1.201
Diethylamine	1.97	0.98	2.365
Triethylamine	1.72	0.99	0.952
Tert-butylamine	1.63	0.98	2.978
Ammonia	1.20	0.98	0.829

It seems from Table 2 that the correlation coefficient of the sensor ranges from 0.98 to 0.99 for all the analytes. The sensitivity of the sensor is higher for methylamine (2.59 Hz/ppm). The 2D and 3D AFM images of the sensors before and after adsorption of the analytes are presented in Fig. 4. It is seen that the crystal surfaces are smooth before the adsorption of VOC but after adsorption the peaks are not in the same height and the RMS surface roughness values are increased. The calculated average RMS surface roughness values before and after adsorption of analytes are 88 nm and 137 nm respectively. This is due to the evaporation of analyte from the sensor surface and the small void spaces are produced during purging of the sensor chamber by nitrogen gas.

A series of amine vapors such as methylamine, ethylamine, diethylamine, tri-ethylamine, tert-butylamine and ammonia are more efficiently detected by the Schiff base coated QCM sensor. The diffusion coefficients of the analytes are related to the molecular volume the

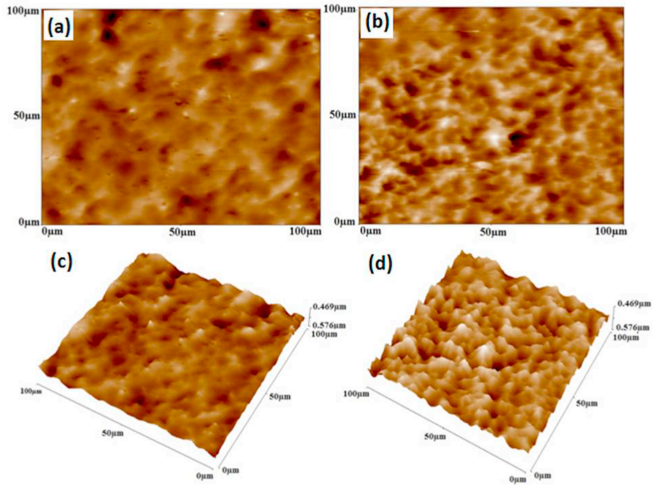

Fig. 4. AFM images of AC3 sensor surface (a) 2D, (c) 3D before and (b) 2D, (d) 3Dafter absorption of analytes.

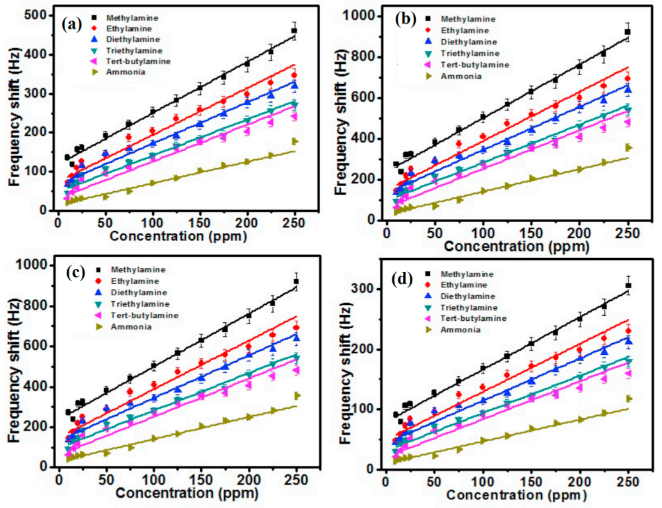

Fig. 5. Calibration curves of the AC1, AC2, AC3 and AC4 sensors for aliphatic amine vapors (10–250 ppm).

polymer matrix. The developed sensor is more sensitive to methylamine vapor due to its smaller molecular volume compared to other amine vapors. We have optimized the sensitivity of the sensor by varying the concentration of camphor (0.05 mg, 0.25 mg, 0.50 mg and 0.75 mg) in APTES with ethanol and the sensors are named as AC1, AC2, AC3 and AC4 respectively. The calibration curve of the four sensors with different camphor concentration in polymer solution is obtained by plotting frequency shift values vs concentrations of the analytes from 10 to 250 ppm and is presented in Fig. 5. It is found that the sensitivity values increases linearly with increase in concentration of analytes. The response of AC3 sensor towards aliphatic amine vapors is higher than other sensors under optimum condition.

The sensor has fast response time as the diffusion coefficient is inversely proportional to the molecular volume according to Stokes–Einstein equation. The sensor shows reproducible result for all the analytes and the response is obtained for the repeated (about 10 times) exposure of analytes with respect to time. Fig. 6 shows the reproducibility of the AC3 sensor for 50 ppm of methylamine vapor. Other sensors also show reproducible result for individual vapors. It is observed that the response is rapid and sensitivity is quite high to all the analytes which indicates the coated polymer film has good sensing properties. Fast response and fast recovery time of the film is due to weak intermolecular force of interaction (i.e. -H bonding and Vander Wall force of attraction) between the polymer film and amine molecules. Fig. 7 represents the real time sensor response of the AC3 sensor with the concentration of 50 ppm, 25 ppm, 20 ppm and 15 ppm of methylamine vapor.

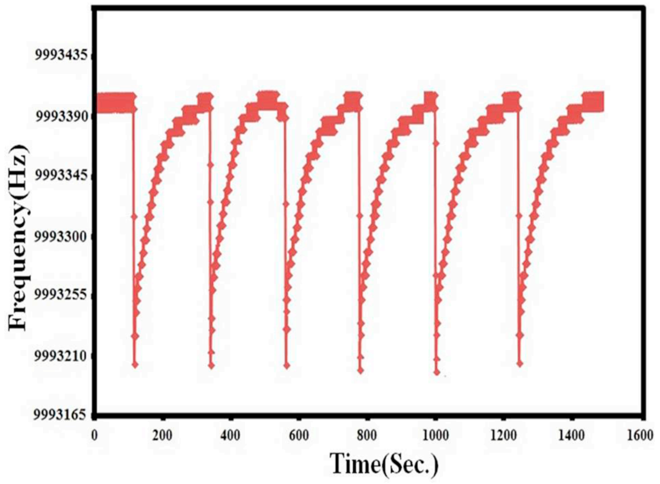

Fig. 6. Reproducibility of AC3 sensor when exposed to 50 ppm of methylamine vapor.

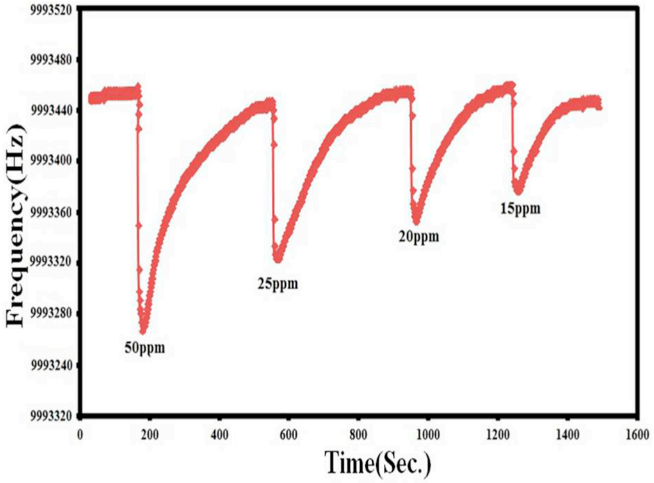

Fig. 7. Real time sensor response of the polymer AC3 sensor with different concentration of methylamine vapor.

It is observed that the frequency shift value increases with increase in vapor concentration which indicates that analyte dissolves or absorbed is directly proportional to analyte concentration. It is expected that the diffusion of gas is quite slow in the deposited polymer film. The fast response and quick recovery of the sensing film is possibly due to the presence of largely distributed pores which is obtained from the free volume of the polymer. As the siloxane based bulky Schiff base polymer has a porous structure, it provides the desired molecular pores for efficient sensing of amine vapors. Here, in this work we have produced various Schiff-base compounds from APTES and organic aldehyde or keto compounds such as benzaldehyde, acetophenon, heptaldehyde and camphor. It is observed that more the bulky aldehyde or ketonic compound better is the sensitivity. Camphor has globular structure and thus it generates globular head in Schiff base for which it shows high molecular porosity (or free volume) introducing highest sensitivity. Further, it is noted that the APTES was treated with camphor to prepare the Schiff base with head tail structure. When Schiff base is used as a coating material during polymerization the head part of the Schiff base are stereo regulated the head part of the Schiff base are stereo regulated with a systematic way in the surface of the sensor creating more space. As a result of which porous structures are created. It provides sufficient space for adsorption of vapor by which sensor performance of the material was improved.

4. Conclusions

QCM sensor coated with stereo-regulated siloxane film containing Schiff base with the bulky head group as a sensing film is developed for the detection of aliphatic amine vapors in ppm level. Bulky Schiff base is synthesized using 3-(aminopropyl)triethoxysilane (APTES) and ketone or aldehyde group containing compounds by simple condensation reaction. It is expected that polysiloxane tail is attached to the quartz surface with a bulky head generated by organic keto or aldehyde compounds. The formation of porous or cage like structured polymer film provides sufficient molecular space for easier accommodation of analyte molecules. The more the bulky aldehyde or ketonic compound better is the sensitivity. Camphor has globular structure and thus it generates globular head in Schiff base producing sufficient molecular pores for its highest sensitivity. The sensor is tested for six aliphatic amine vapors such as methylamine, ethylamine, tert-butylamine, diethylamine, triethylamine and ammonia at room temperature in a concentration range of 10 ppm–250 ppm. The developed sensor is efficient for the detection of amine vapors than other volatile organic compounds. The detection limit is low and the response time is very fast which indicates the sensor can be used as a device for both indoor and outdoor monitoring and the quality estimation of fish and shellfish as methylamine vapors are generated from putrid fish. Also amines vapor is a biomarker of certain disease detection.

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