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Development of W doped ZnO nanostructure chemoresistor pellet sensors for black tea aroma monitoring

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Abstract

Usually the quality of tea is sensed by tea tasters and classified by smelling and very few devices are available to calibrate the flavour. In this paper, resistance change of W doped ZnO nanostructure chemoresistor pellet sensor was investigated in an environment of different types of tea aroma infusion with an objective to produce a low cost alternative to classify tea by its quality. W doped ZnO nanostructures pellet sensor was fabricated inside the quartz tube along with allied fittings viz. thermocouple, silica gel tube, inlets for vapours and connecting leads. The sensing properties of the pellet sensor were tested for major black tea aroma chemicals (i.e, Linalool Linalool Oxide Geraniol, Trans-2-Hexenal). Sensor material was synthesized through chemical and characterized by XRD, FESEM with EDX, HRTEM with EDX and AFM, etc. which confirm the phase purity, morphology and wurtzite structure. This work shows probable application of doped ZnO nanostructures as one of the sensing elements in a sensor array for monitoring the quality of black tea aroma.

Keywords: *Nanostructures, Pellet Sensor, Linalool, Geraniol, Morphology, Wurtzite.*

1. Introduction

Tea liquor is a really essential factor in identification of quality of black tea because tea is probably the most popular drink in the world. Though the main aromatic ingredients in made tea are same, the quality of made black tea mainly differ from their flavour types, which rely on their trace volatile organic compounds (VOC) like as Linalool, Linalool Oxide, Geraniol and, Trans-2-Hexenal are major aroma chamicals responsible for sweet, floral, fruity and fresh flavor [1] is indicated in table 1. There are several types of tea like black tea, green tea, Oolong tea etc., and out of these, black tea is the most common beverage. Black tea has got two major varieties, viz., (1) orthodox and (2) CTC (Cut–Tear–Curl) operations are performed during production of this type of tea. For measurement of tea quality, unfortunately no instrumental methods are deployed on regular basis in the industry and for the assessment of quality; traditional methods of employing professional tea tasters [2] are still being practiced. These tasters, based on their experience and judgment, assess the quality of tea and the pricing of tea is made accordingly. The tea-tasters give a mark in the range of 1 to 10 each for leaf quality, infusion and liquor of the sample [3]. This method is purely subjective and error-prone. Thus there is a demand in the industry to have low-cost, portable solutions for quality evaluation of black tea. In this regard, electronic nose has been demonstrated to be an appropriate candidate [4] for the same.

Table 1: Aroma chemical responsible for black tea flavour

Volatile Organic Compounds	Flavour
Linalool, Linalool oxide	Sweet
Geraniol, Phenylacetaldehyde	Floral
Nerolidol, Benzaldehyde, Phenyl ethanol,Methyl Salicylate	Fruity
Trans-2-Hexenal, n-Hexanal, Cis-3-Hexenol, Grassy, b-Ionone	Fresh Flavour

The flavour in different commercial organic products like Tea, Coffee, Wine, etc. arises from VOC emitted during infusion. VOCs are commonly used as ingredients in household products or in industrial processes where they normally get vaporized at room temperature and can be breathed, and unfortunately, many VOCs can cause adverse health effects [5]. Other synthetic products such as paints, wax or fuels can release toxic vapors when they are stored; even some foods, such as beverages, fish and meat products, release organic vapours [6]. The most important aspect of the ZnO material is that it is completely an environment-friendly direct band gap material with wide bandgap energy of 3.37 eV and high exciton binding energy of ~ 60 meV. Another attractive feature of ZnO is that its bandgap energy can be engineered by changing dopant materials [7]. Very recently, nanostructure ZnO gas sensors have attracted more interest due to their better properties of detecting pollutants, toxic gases, alcohols and food freshness, especially fish freshness [8], or as gas-sensing films integrated on one chip to make an “electronic nose”[9]. The sensitivities of gas sensors can be greatly improved by doping MnO_2, TiO_2 and Co_2O_3. In some recent paper, identification of flavour components through pattern recognition analysis of Chinese liquors was carried out using doped nano ZnO gas sensor array and different statistical techniques were compared for their classification ability [10]. In our present work, tungsten (W) doped ZnO nanostructures pellet sensor has been developed by chemical synthesis method and characterized by XRD, FESEM with EDX, HRTEM with EDX and AFM, etc. This paper focuses on the evaluation of the selective sensing behaviour of the cadmium doped sensors exclusively

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under a new performance index which we call "*rate of response*" to Linalool, Linalool Oxide, Geraniol and Trans-2-Hexenal. The fabricated sensor element was tested for its resistive response for detecting the VOCs, like as Linalool, Linalool Oxide, Geraniol and Trans-2-Hexenal. The performance of the sensor elements was characterized in temperature range of 200 - 500°C for operation of the sensor element and different sensor characteristics were evaluated. Keeping in view of the small variation of the resistivity with changing gas environment, the response is detected through an appropriate circuit in order to improve its sensitivity. Our fabricated instrument setup and software based data acquisition system is used with compensation of cross sensitivity due to temperature variation from 200 - 500°C of the pellet sensor element in the quartz tube [11-12].

2. Nanostructure Material Synthesis

The process of synthesizing ZnO nanostructure doped with tungsten (W) is shown in figure 1.

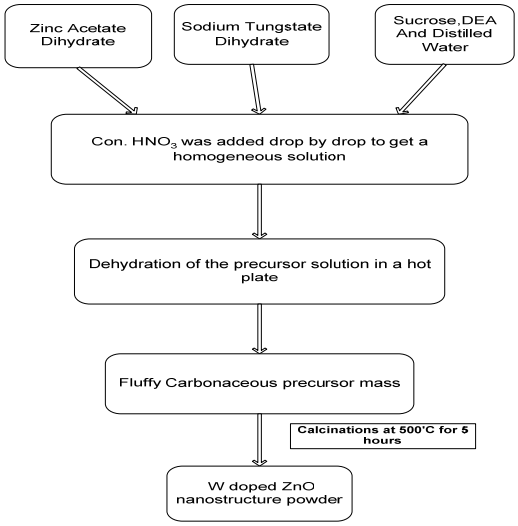

Figure 1. Synthesis process of W doped ZnO nanostructure

For the synthesis of tungsten doped ZnO, an aqueous solution of 10g of zinc acetate dihydrate and 10g of sucrose was prepared initially. Then 4ml of diethanolamine was added under constant stirring to obtain white, highly viscous solution. Concentrated Nitric acid was then added drop wise to obtain a clear solution with pH value close to 2. For W doping, we add calculated mass of sodium tungstate dihydrate (calculated such that molar ratios are W: Zn = 0.05:1, 0.1:1, 0.15:1 and 0.2:1 for 5, 10, 15 and 20 percent doping respectively) to excess conc. nitric acid to obtain bright yellow precipitate of tungsten oxide. Now this ppt. is thoroughly washed and dissolved overnight in 7ml of triethanolamine at 70°C. This clear solution was mixed with the clear solution of zinc acetate and diethanolamine and pH close to 2 was again obtained by adding a few drops of conc.(70%) HNO_3. Now all of this was taken in a beaker and kept on a hotplate at 110^0C. In approximately half an hour dense black fumes emerge the solution burns into a black fluffy mass figure 2(a). This is known as metal-organic complex decomposition.

2.1 Sensor Development

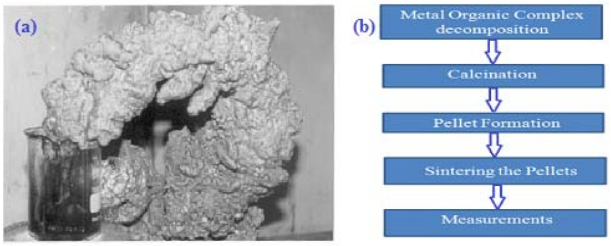

Figure 2: (a) Black floppy mass (b) Flow chart of sensor development and measurement process

***Calcinations*:** The fluffy mass obtained from the above step was calcined at 500°C for 5 hrs in a furnace. On cooling, white powders of doped ZnO nanostructure are obtained. This completes what we call the *calcinations'* stage.

***Pellet Formation*:** In the pellet formation stage, 0.7g of the calcined powder and a drop of poly-vinyl alcohol (PVA) solution are thoroughly mixed in a crucible. The mass is then pressed with 8 tons of pressure using KBr pelletiser for approximately 5 minutes to obtain the sensor pellets.

***Sintering*:** The pellets are sintered at 500°C for 5 hrs. By this process the PVA volatizes off lending some porosity to the pellet as well.

***Measurements*:** Each pellet is contacted with silver paste was used to complete the circuit and clamped to a brass holder in self fabricated inside the quartz tube along with allied fittings viz. thermocouple, silica gel tube, inlets for vapours and connecting leads as anode and cathode for measurements.

3. Characterization of Synthesize Material

3.1. *Structural analysis by XRD*

The X-ray diffraction (XRD) analysis of the synthesized ZnO nanoparticles was done using Rigaku X-ray diffractometer operated at 40kV and 30mA with Cu radiation and K- α filter. The data is collected over 2θ angle range of $20^0 \leq 2\theta \leq 80^0$ with step size of 0.02^0. The phase identification is done using JCPDS data base (072-1464, 024-1470 and 041-1445) respectively [13] and presence of synthesized zinc oxide and tungstate (W) in wurzite phases are confirmed. Figures 3: (a-b) illustrates the XRD of the calcined and sintered nanocrystals which are used as sensors in our present study. Applying scherrer's equation we evaluate the crystallite as approximately 20 nm in figure 3 (a) while it is approximately 20 nm in figure 3(b).

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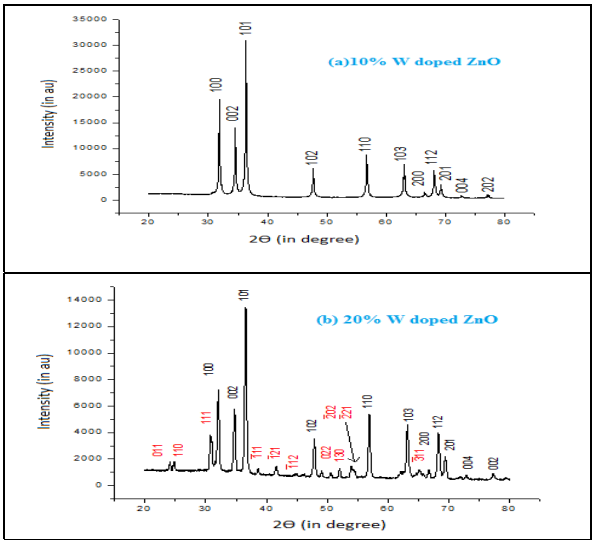

Figure **3(a-b)**: XRD image of nanostructure **(a)** 10% W doped and **(b)** 20% W doped ZnO sintered at 500^{0}C for 3 hours

In figure 3(a) observe that there is a shifting in 110 and 101 plane by a 2θ 0.12° and 0.16° from the nominal value (31.728° for 100 plane) while the shift is 0.19°. In figure 3(b) it is observed that separate crystals of zinc tungstate ($ZnWO_4$) as monoclinic crystals with a primitive lattice. Sensor studies with the last sensor material were erratic and are hence not presented.

3.2. *Surface morphological Compositional studies by FESEM with EDX*

The field emission scanning electron microscopy (FESEM) analysis of the tungsten (W) doped nanostructure pellet sensor was done using *JEOL JSM 6360* equipped with an Energy-dispersive X-ray (EDX) analyzer of the actual sensor surface under test. The potential applied was 15kV. The image is around a pore on the pellet. We observe that the grains are more or less hexagonal in figure 4(a) nature of around 50nm.

3.3. *Nano-structural and Compositional analysis by HRTEM with EDX*

The high resolution transmission electron microscopy (HRTEM) of the tungsten (W) doped nanostructure sensor was performed with JEOL JEM 2100 equipped with an energy-dispersive X-ray (EDX) analyser. Hexagonal nanoparticles of around 50 nm are observed from the micrograph and the EDX confirm the presence of tungsten in figure 5(b) along with oxygen and zinc.

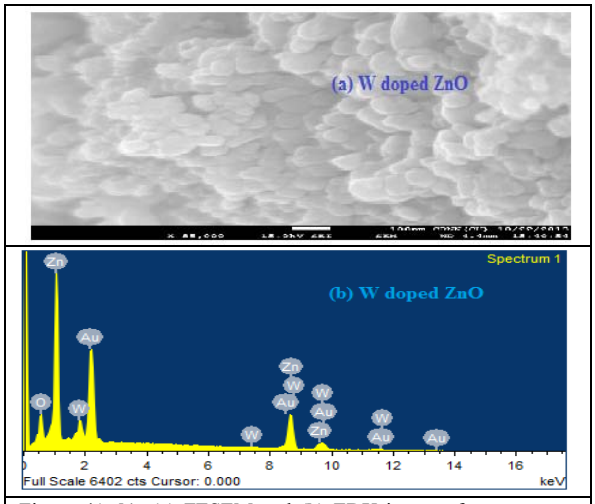

Figure **4(a-b)**: **(a)** FESEM and **(b)** EDX image of nanostructure W doped ZnO sintered at 500^{0}C for 3 hours

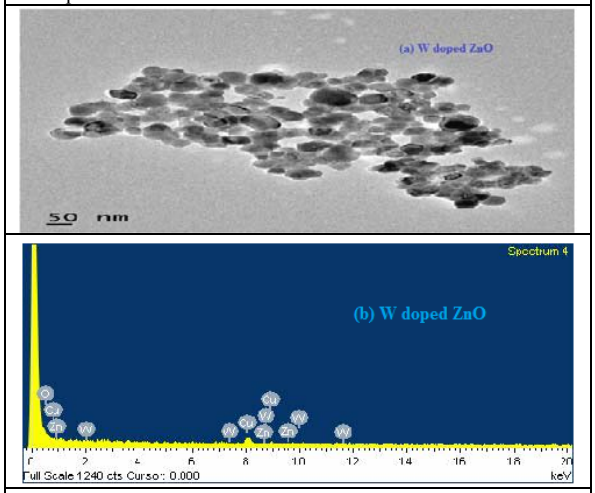

Figure **5(a-b)**: **(a)** HRTEM and **(b)** EDX image of nanostructure W doped ZnO sintered at 500^{0}C for 3 hours

4. Instrument Setup

4.1. *Measurement system*

Our designed instrumentation setup is primarily a Static System. The setup has different assemblies as discussed below. Though bulky, the system is extremely rugged. An ON-OFF type auto heating assembly is used to heat the sensors to 200-500°C. The sensor to be tested is contacted with gold and put in to a spring system made of brass which holds the sensor firmly on a ceramic base [12]. This enables the transmission of potential change in the sensor material in presence of injected gas to the data acquisition system through connecting wires. The ceramic base with the sensor is placed in a temperature resistant airtight quartz tube which is placed in a tube-furnace to be operated up to a maximum 500°C as shown in figures 6 and 7.

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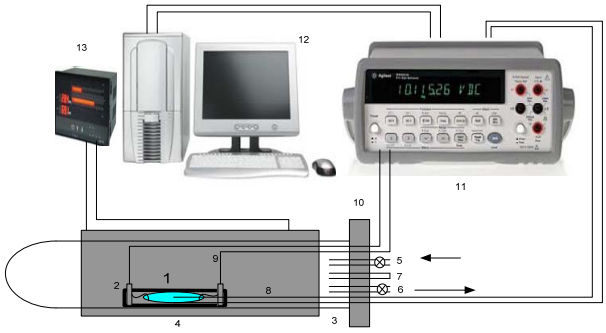

Figure 6 : Setup equipment for in-situ resistance measurements: 1) Pellet sample; 2) Two probe sample holder;3) Quartz test chamber; 4) Furnace; 5) Gas inlet; 6) Gas outlet; 7) Gas injection port; 8) Thermocouple; 9) Platinum wires; 10) Flung; 11) Digital multimeter; 12) Personal computer; 13) Temperature controller (PID controller).

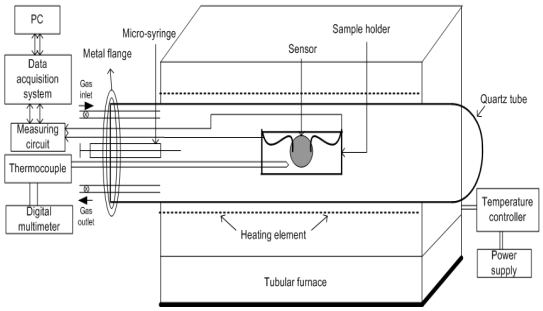

Figure 7: Sensor assembly inside the quartz tube alongwith allied fittings viz. thermocouple, silica gel tube, inlets for vapours and connecting leads: Schematic diagram of instrument setup with experimental sensor in quartz tube.

4.2. *Lab-View based Data Acquisition System (DAS)*

The data acquisition system typically converts analog waveforms into digital values for processing and collection of information to document or analyze phenomenon to be measured show in figure 8.

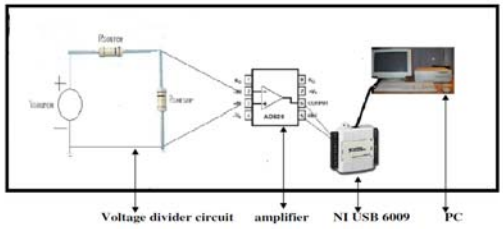

Figure 8: Schematic of Data Acquisition System (DAS)

The components of data acquisition systems are:

i. Sensors that convert physical parameters to electrical signals.
ii. Signal conditioning circuitry to convert sensor signals into a form that can be converted to digital values.
iii. Recording and processing of conditioned sensor signals to extract information

5. Results and discussions

5.1. Mechanism of nanostructure gas sensor

Nanostructured gas sensor is synthesized from nanocrystalline material having dimensions within 100 nanometer. The unique properties of nanocrystalline material (nanostructured gas sensor) is attributed to its high surface to volume ratio and is therefore characterized by

(i) large fraction of surface atoms and large number of grain boundaries,
(ii) high surface energy and
(iii) spatial confinement which do not exist in other gas sensors.

Metal oxides like ZnO is n-type semiconductor have wide band gap of 3.37 eV. It possesses an electron depleted surface under normal atmospheric condition and in the typical operational temperature range of 200 °C- 450 °C. The electron depleted surface forms due to absorption of atmospheric oxygen which gets dissociated in to O_2^- or O^- species (Morrison, 1978) by accepting electronic carrier from semiconductor oxides [12]. This chemisorbed oxide ion (O_2^- or O^-) participates in the reaction with the reducing gas (test gas) like Linalool, Linalool Oxide, Geraniol and Trans-2-hexenal different aroma compounds chemical structures are shown in figure 9, present in black tea responsible for flavour and release electrons in the process.

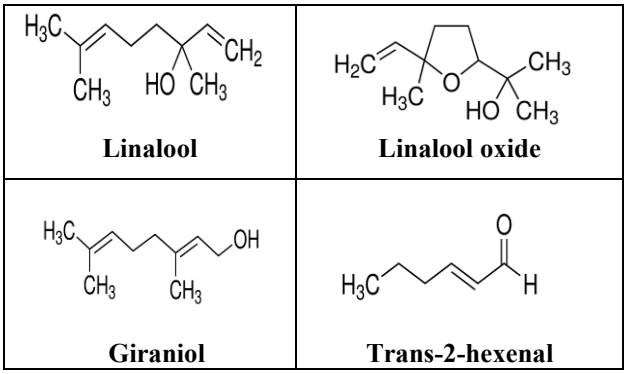

Figure 9: Chemical structures of black tea major aroma

The electron produced in the reaction process, goes in to the conduction band of the sensor material and hence the n-type semiconductor gas sensor exhibit a decrease in the resistance due to presence of a reducing gas. The reaction mechanism involved in the sensor is outlined below [9,12].

$$O_2(air) \leftrightarrow O_2(ads)\ ;\ O_2(ads) + e^- \leftrightarrow O_2^-(ads)$$

$$O_2^-(ads) + e^- \leftrightarrow 2O^-(ads);\ R + O^-(ads) \leftrightarrow 2O + e^-$$

Where, R denotes the reducing gas.

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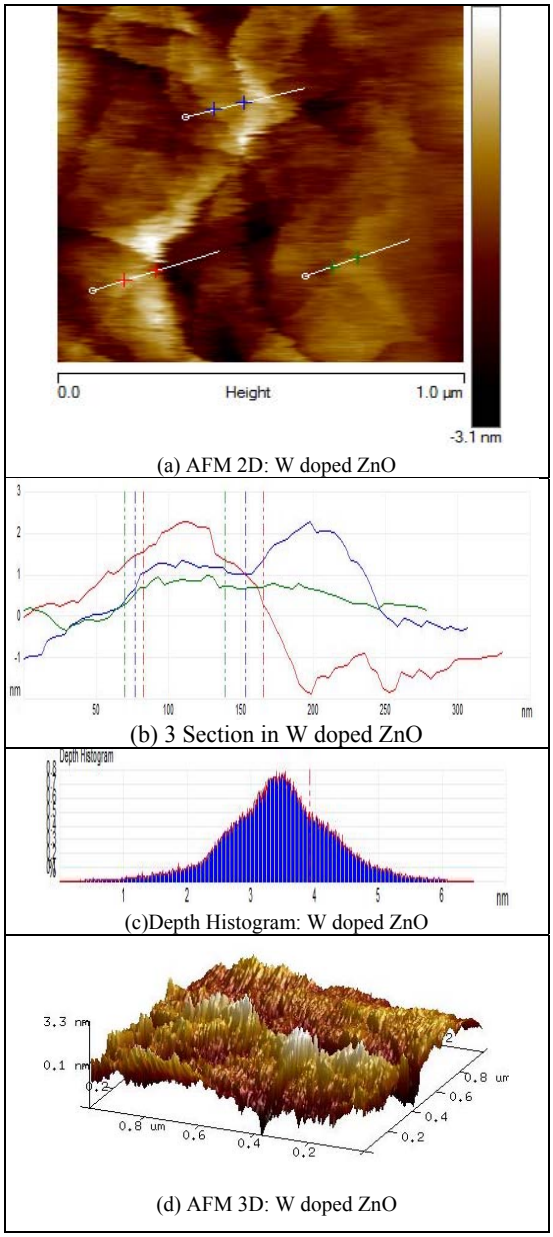

(a) AFM 2D: W doped ZnO

(b) 3 Section in W doped ZnO

(c)Depth Histogram: W doped ZnO

(d) AFM 3D: W doped ZnO

Figure 10 (a-d): AFM surface morphology (a) 2D planer view (b) Section on planer (c) Depth Histogram and (d) 3D image with 60°C rotation.

The atomic force microscopy (AFM) non contact mode was used to record the topography of the W doped ZnO nanostructure chemoresistive pellet sensor annealed at 500°C. The surface morphologies of the doped ZnO nanostructure exhibit notable features. The surface roughness of the nanostructure a 10 µm x 10 µm area was measured by AFM shown in figures 10(a-d).

The in depth investigation of the morphological feature of the electropolished nanostructure surfaces have been carried out by AFM. The studies indicate that for all the nanostructure powder solution positioned on glass strip electropolished at 40, 50 and 60 V for the time duration of 20, 40 and 60s, generates self-ordered nanostripe pattern on the metal surface. The average distance between the stripes and the average height of the ridges was found to be in between 25-30 nm and 4.5 nm, respectively.

The sensitivity of metal oxide sensors to the test gases is intimately related to the grain size, surface morphology, surface area and internal porosity of the sensor material. Nanostructures mixed oxide based gas sensor material exhibit improved sensitivity due to their small particle size, high surface to volume ratio and a high density of low-coordinated surface sites compared to the corresponding other gas sensors. The gas sensing phenomenon is a sort of surface catalyzed combustion [14].

5.2. *Electrical measurement and discussion*

The electrical conduction of the sensor in dry air is observed in a temperature range of 200°C to 450°C. Conductivity of the sensors is seen to follow Arrhenius law given by

$$\sigma = \sigma_0 * e^{-E/kT} \quad (1)$$

$$\text{or, } \ln(\sigma) = \ln(\sigma_0 * e^{-E/kT}) \quad (2)$$

A plot of **ln(σ)** vs **1/T** gives a straight line whose slope gives us the activation energy E. Activation energy is calculated (which is 0.55 to 0.65 eV).The electrical resistance of nanostructure W doped ZnO chemoresistor pellet sensor in air (R_a) and in the presence of test gas (R_g) was measured to evaluate the gas response, *S*, defined as follows[15]:

$$S = \frac{R_a - R_g}{R_a} \times 100\% \quad (3)$$

The performance of any chemorestive pellet sensor should not be judged merely by the maximum deviation of its conductance from its baseline value. A transient response analysis is also desirable to judge its merit. We thus define a performance index (PI) for our sensor as its "Rate of Response" which incorporates time that the sensor takes to respond as using equation (4).

Rate of Response=Response (%)/ saturating time;.... (4)

Saturating time refers to the time taken for voltage across the sensor to change from its baseline to minimum (saturated) value upon the injection of the tea aroma vapours as test gas [16].

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This procedure is repeated between the range 200°C - 450°C at an interval of 50°C for each set of sensors and is illustrated in figure 11.

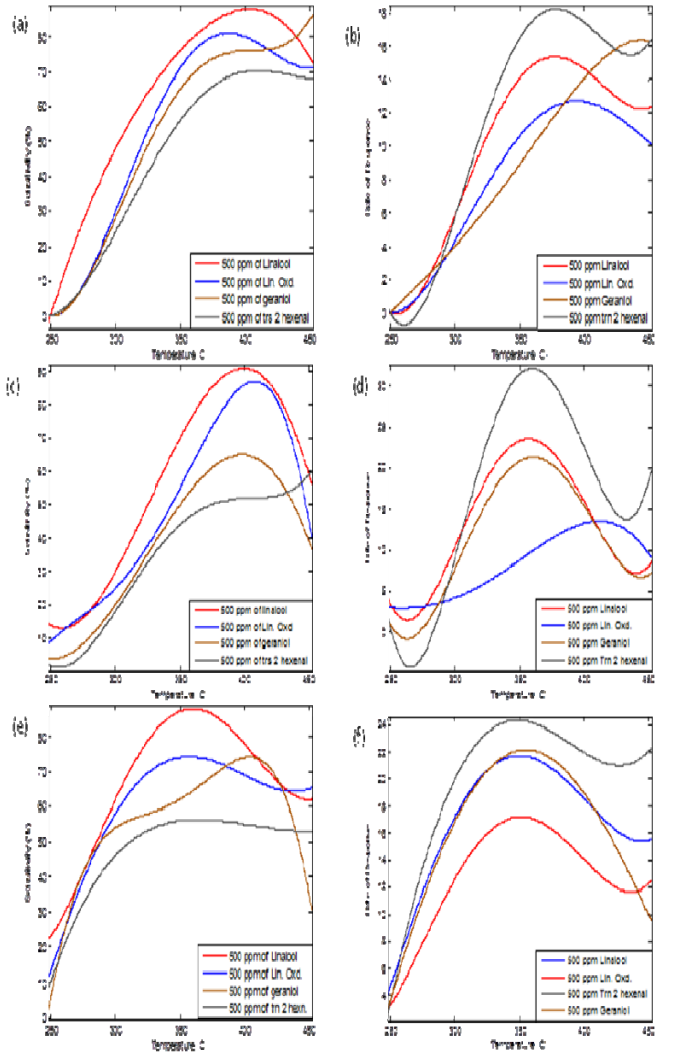

Figure 11: Sensitivity vs. temperature (a, c and e) and Rate of response vs. temperature (b, d and f) at 500ppm of each of the four major black tea bio-chemicals.

The interesting feature to be observed that in all cases linalool exhibits the maximum and trans 2-hexenal the minimum sensitivity but Trans 2-hexenal exhibits the maximum rate of response. In figure 10 (a) and (b) are of the 5% W doped ZnO nanostructure pellet sensor, 10 (c) and (d) are of 10% W doped nanostructure pellet sensor and similarly10 (e) and (f) are of 15% W doped nanostructure pellet sensor.

The trans-2-hexenal responds fastest with minimum sensitivity is clearly justified as it is the smallest molecule. Linalool and geraniol have the same molecular weight but though linalool is a tertiary alcohol, it is evident from its structure that it is more unstable than geraniol and hence though the rate of response of both linalool and geraniol are near about the same, sensitivity to linalool is more than geraniol. Lastly Linalool oxide is the most stable of all of the above compounds and hence the slowest to respond. The major achievement with tungsten doping is that saturating time which was around 40-50 seconds in case of Mo doped sensors is now down to 5-6 seconds. Also the sensors are very stable repeated temperature recycling hardly affects its performance. Also the same sensor may be used for all analysts as forecaster under study which is not the case in Mo doped ZnO. However for real time applicability, speed of response is still not small.

6. Conclusions

Nanostructured doped ZnO chemoresistive pellet sensors were prepared by low-cost chemical synthesis technique exhibit hexagonal wurtzite structure. Nanostructural analysis revealed uniform, smooth surface morphology with an average size of ~50 nm. The test gas (tea bio-chemicals) sensing studies were carried out at concentrations of like Linalool, Linalool Oxide, Geraniol and Trans-2-hexenal 500 ppm. The selectivity study showed that nanostructured pellet sensors were most sensitivity to linalool is more than geraniol. Lastly linalool oxide is the most stable of all of the above compounds and hence the slowest to respond. The maximum gas response of 25.3% was achieved with 87.3% stability for nanostructured pellet sensors upon exposure of 500 pmm linalool at operating temperature 400°C. The stability study indicates that ZnO nanostructured is potential material to be used as an effective black tea aroma sensor.

Acknowledgments

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