Chapter V

Application of electronic nose systems by array of nanostructured doped ZnO sensing material for assessing tea quality

V.1. Introduction

Application of nanoscience involving the use of various nanomaterials and nanosize components is known as nanotechnology. Nanotechnology is used to design custom made materials, nanoelectronic components, various types of sensors and solar cell systems.[1] There is a tremendous progress in nanotechnology which has been done by researchers in the past few decades. Materials with basic structural units/ grains/ particles/ fibers with particle size smaller than 100 nm in at least one dimension are known as nanomaterials.[2] These nanomaterial found various applications like improvement of conversion efficiency of solar cells, disease prevention, diagnosis and/or treatment. Nanomaterials include nanoclusters, nanotubes, nanocrystals, nanofibers, nanorods, nanowires, nanofilms etc. Various nanofabrication technologies like electro-spinning, phase separation, thin film deposition, self-assembly processes, chemical vapour deposition, nano imprinting, electron beam or nanosphere lithographies etc.[3] These processes help to synthesize various nanomaterials with ordered and/or random nanotopographies. When the material size is decreased into nanoscale, the surface area and surface area to volume ratios can be adjusted leading to superior physiochemical properties such as mechanical, electrical, optical, magnetic, catalytic properties.[4] That is why, nanomaterials have been extensively investigated with wide range of applications, like medicine, electronic devices, solar cells and in particular sensor devices. Thus nanodevices find its huge impact on ability to enhance energy conversion, control pollution and improve human health. The benifits of the applications in sensitivity is due to the presence of large surface area of nanostructured sensing material. Also selectivity of sensors depends upon the nanomaterials used.[5] The present work includes synthesis of ZnO nanorods by sol-gel technique, application of these fabricated nanorods as sensors for the detection of volatile organic component (VOC) for the detection of flavor in orthodox darjeeling tea. A special technology named electronic nose was adopted to detect the organic flavor. An array of sensors are used in the sensing technology of this electronic nose for the simultaneous detection of the signal and analysis of signals, so that the contribution of individual component can be known through sophisticated analysis techniques.

E-nose system is a technology based on sensors. It possess the total headspace full of volatiles and it creates a unique smell print. E-nose does not resolve the volatiles of a sample into individual components, but it responds to the total set of volatiles with a unique digital pattern.

These patterns denote a particular set of aromatic compounds. For each application, a certain database of digitized patterns is created which is called training set. For testing when an unknown sample possessing VOC is exposed to this E-nose sensor system, it digitizes first the volatiles of the sample and then compares the pattern with the existing training set.

From a practical point of view, in the last decade, this E-nose technology has opened a new field which helped to exploit the information related to different application fields. The E-nose ican be used to predict the optimal harvest date by sensing the aroma. Commercially available E-noses consist an array of sensors combined with the pattern recognition software. There are several reports of the application of electronic sensing in the food industry,[6] also in the discrimination of several fruits of different quality and/or ripeness, like oranges,[7] apples,[8-10] tomatoes,[11] grain[12] etc. Few literatures are also available regarding fruit shelf life and quality attribute.[13] The objectives of the present study were to monitor first the flavor in orthodox Darjeeling tea using doped ZnO fabricated electronic-nose sensor and analyze the response by using Principle Component Analysis (PCA); secondly to correlate the analyzed response data with the standard tea testers' scores to generate a calibration system which helps to predict the quality of unknown tea sample.

Zinc oxide (ZnO) is one of the most widely used oxide semiconductor based gas sensing material.[14-17] It is an n-type semiconductor with band gap E_g 3.2 eV. The electrical conductivity of ZnO is due to the intrinsic and extrinsic defects present in the lattice. Pure ZnO has the conductivity due to the former defects such as zinc excess at the interstitial position and oxygen vacancy. ZnO has been alloyed with various 3d transition metal (TM) to explore its applicability as gas sensor.[18-19] The transition metal oxide adhered to the surface of pure ZnO thus widening the depletion layer and increasing the resistance of gas film. The response is increased when test gas comes in contact with the metal oxide particles thereby decreasing the resistance for the wider depletion layer.

Absorption of oxide in the films decrease the electrical conductivity as pure ZnO thin films are sensitive to oxidation. But the electrical properties are enhanced by extrinsic defects in doped ZnO with different dopants and trials have been made in this respect.[20-24] Moreover the electrical properties of ZnO could also be modified by thermal treatment in the reducing atmosphere.[25] Surface morphology mainly affects the optical properties of ZnO and heavy doping changes the optical energy band gap.[26] Thermal treatment in a reducing atmosphere[27] and appropriate doping process also modified surface morphology.[28] Ohyama *et al.* reported that the use of high boiling point solvent 2-methoxyethanol and monoethanolamine (MEA) resulted transparent ZnO films.[29] Further better electrical and optical properties were obtained by 0.5 at.% aluminium doped ZnO thin films treated with heat in reducing atmosphere.[20] Nunes *et al.* found superior electrical and optical properties with doped ZnO, where doping concentrations of Aluminium, Indium and Gallium were 1, 1 and 2 at. %, respectively.[30] The resistive response of the sensing material varies with band gap energy of the substrate. Krylov[31] *et al.* found the activity order of the metal oxide as follows, MnO_2>CoO>Co_3O_4>MnO>CdO>Ag_2O>CuO>NiO>SnO_2>>Cu_2O>Co_2O_3>ZnO>TiO_2>Fe_2O_3>ZrO_2>Cr_2O_3>CeO2>>V_2O_5>>HgO>WO_3>ThO_2>BeO>MgO>Al_2O_3>SiO_2. The potential between the sensor material and the gas molecule depends on the electro negativity difference between them. So variation in the band-gap energy of the sensing material imparts larger cross-sensitivity among various species of gases. When various transition metal ion was doped in ZnO blue and red shifts in band gaps were observed.[32] Thus three transitional elements Iron, Cobalt and Nickel having largest variation in band gap energy were selected.[32] For the preparation of ZnO thin films several deposition techniques, such as pulsed-laser deposition,[33] chemical vapor deposition,[34] RF magnet ron sputtering,[35] spray pyrolysis,[36] sol–gel process[37] etc, it is possible to prepare a small as well as large-area coating of ZnO thin films by the sol–gel technique. X-ray diffraction (XRD) and scanning electron microscopy (SEM) reveals that the ZnO exhibits a hexagonal wurtzite structure. Figure V.1 shows the XRD pattern of the ZnO nanowire growth on an ITO coated glass substrate by using the spin coating sol-gel method and EDX analysis of ZnO, wheras Figure V.2a is the SEM image of undoped ZnO. A dominant diffraction peak for (002) indicates a high degree of orientation with the c-axis vertical to the substrate surface. The hexagonal wurtzite structure of the ZnO nanorods was assured by both XRD and SEM. In this study, we present the growth of ZnO nano rod structures by sol-gel spin coating technique and detection of the tea aroma and their gas sensing properties with the E-nose prepared by doped ZnO nanomaterials . The effects of dopants and their doping concentration on the microstructure and electrical properties of doped ZnO thin films were also investigated.

V.2. Background and Objectives

V.2.1. Detection of Tea Aroma

Tea is one of the most most aromatic beverage and popular drink worldwide. Among various types of tea such as green tea, black tea, oolong tea etc black tea is most common beverage. Mainly two types of black teas are there namely Orthodox and CTC tea. The quality of tea is influenced by the amount of time a tea is stored in Almacafe's warehouses. The quality and the purchase price of tea are mainly determined by some protocols. The factors which are important to assess a tea sample are appearance, good condition and proper size of the tea grains. For further assurance tests are done in the cup or by the tasters.

Traditional methods where professional tea tasters were employed are still being practiced for quality of tea measurement. Unfortunately, no instrumental methods are still not in use in the industry. These tasters assess the quality of tea based on their experience and judgment and the price of the tea is fixed accordingly. The tea-tasters give mark ranging from 1 to 10 each for leaf quality, infusion and liquor for a particular sample.[38] This method is very much subjective and error-prone. Thus, industry demands a low-cost and portable instrument for the quality evaluation of the black tea. Electronic nose has been well demonstrated to serve the purpose.[39] To obtain a standard product analysts have developed different types of analysis for CTC, orthodox and green tea. Tea quality index could be correlated well with electronic nose (E-nose) signal. Few literatures illustrates a model using signal of E-nose system which predicts the quality of tea. One of the most important sensory attributes of tea is aroma. The flavor in different organic products like tea, coffee, etc. arises from Volatile organic compounds (VOC) which are emitted during infusion. Sensing of VOC's has attracted much interest focused on several factors like detection, monitoring and analysis. Tea flavor is sensitive due to the compositional alterations of VOCs present in tea. The VOCs which are the cause of tea flavor are produced during ripening, harvest, post-harvest and storage procedures. Many research groups are working now a days on the detection of volatile VOCs that produce aroma in various food products. As a consequence, E-nose technology have been introduced. However, selectivity of sensor material is very much important for the accuracy of the detection procedure. To overcome this problem, various researchers illustrated a number of statistical techniques such as linear multiple regression, principal component analysis (PCA) etc. However to improve the selectivity of the sensors, designing new sensing elements attract much attention. Primarily porous oxide nanomaterials like ZnO and SnO_2 have been studied for detection of inorganic gases.[40] Due to the fine physical, chemical and optical properties ZnO has been used as potential semiconductor materials as sensor.[41-43] ZnO nanowire is much appreciating for fabricating sensors which detects various VOCs.[43] Very recently, ZnO nanomaterial gas sensors have attracted much attention for their capability of detecting pollutants, toxic gases, alcohols etc. Also various food's freshness such as fish freshness[44] can be detected using gas-sensing films integrated on one chip which is known as "electronic nose".[45] The sensitivities of the gas sensors can be greatly enhanced by doping transition metal ions like Fe^{+3}, Co^{+3} and Ni^{+2}. Very recently, identification of various components of the flavour of chinese liquors was carried out by the use of doped nano ZnO gas sensor array and their classification ability were compared using several statistical technique. Some research groups were able to analyse some flavour components by pattern recognition analysis of an E-nose system,[46-48] that possess broadly tuned nonspecific array of sensors. It represents the olfactory sensing mechanism, that has been developed by the use of variety of odour sensitive biological/chemical materials that can be used in food product evaluation. The E-nose system addresses fast and cost effective solution to the problems of tea quality determination which is based on organoleptic study and chemical analysis. The E-nose system consists of an array of gas sensors that record the characteristic response for any particular odour. The pattern recognition methodologies are in the form of software which identify particular odour by sensor response data set.[48] The odour molecules are carried to the sensor array by different sampling techniques like diffusion methods, head space sampling, pre-connectors. The sensing materials suffer some physico-chemical changes when it comes in contact with the odour molecules which leads to the change in their conductivity. Difference in the responses result as different sensor in the array responds to the different odour molecule with varying degree. The total set of responses from all the sensors are used for pattern recognition after transduction into electrical signals.[49-50] Depending upon the chemical composition of the odour/odour mixtures a variety of sensors such as conductivity sensors, intrinsically conducting polymers, conducting polymer composite sensors, metal oxide sensors, surface acoustic wave sensor, piezoelectric sensors, optical sensors, metal-oxide-semiconductor field-effect transistor sensor etc are usually used in the array of modern E-nose systems. Odour gas molecules which contains VOCs interact with thin/thick films of sensor materials by adsorption or chemical reactions and with solid state sensors by absorption process. These changes in the sensing materials of E-nose are measured as electrical signals which are considered to be responses.

Inert gases like nitrogen is flushed through the array of sensors as reference gas in the very first stage of the odour analysis by E-nose system. After that the odour is allowed to reach the sensors. The reference gas is again allowed through the sensors when the data recording is completed. The reference gas is allowed to flush before and after the analysis which is necessary to prepare the base line of the responses. The period of time for which the sensors are exposed to the odour is called response time and the recovery time is the time for which reference gas is passed through the sensor array. After recording the responses, it is then processed for the pattern recognition after base line correction.[49] The basic data analysis techniques for pattern recognition in the E-nose system are,

(i) Graphical analysis: Bar chart, profile, polar and offset polar plots.

(ii) Multivariate data analysis (MDA): Principal component analysis (PCA), canonical discriminate analysis (CDA), featured within (FW) and cluster analysis (CA).

(iii) Network analysis: Artificial neural network (ANN), radial basis function (RBF).

Choice among the abovementioned methods depend on the type of responses obtained and the purpose of its use.[51]

V.2.2. Quality determination of Orthodox Tea by E-nose systems

For quality grading a neural network based E-nose which comprises an array of four SnO_2 gas sensors can assist the monitoring of tea quality. Different aroma profiles were visualised using the Principal Component Analysis (PCA) method.[52] In addition, Kohonen's Self Organising Map (SOM) cluster analysis was also done. Other analytical methods such as, Radial Basis Function (RBF) network, Multi Layer Perceptron (MLP) network and Constructive Probabilistic Neural Network (CPNN) were used for the classification of various aroma.[48-49]

Dutta *et al.* proposed a metal-oxide sensor (MOS) based electronic nose (EN) to analyze five tea samples possessing different qualities viz. over-fermented, overfired, under-fermented, etc using an array of four MOSs, each of which possess electrical resistance having partial sensitivity to the headspace of the tea and a suitable interface circuitry for the signal conditioning.[39] The data obtained were processed by Principal Components Analysis (PCA) and Fuzzy C means algorithm (FCM) method.

Chen *et al.* proposed that a support vector machine algorithm is superior to KNN and ANN model for quality gradation of green tea by E-nose system comprised with MOS sensors. It can also be successfully used in the discrimination of green tea's quality.[53] This study was applied to classify four different grades of green tea. PCA and three different linear or nonlinear classification tools namely, K-nearest neighbors (KNN), support vector machine (SVM) and artificial neural network (ANN) were compared to develop the discrimination model.[53]

Yu *et al*. applied BPNN, PNN and cluster analysis (CA)for the electronic nose (E-nose) analysis which was employed for identification of the quality grades of the green tea.[54] It is evident from the results of CA that the classification of different green tea samples is possible by analysing the response signals obtained from E-nose. BP neural network gives better experimental results. The classification success rates for two neural networks BPNN (back propagation neural network) and PNN (probabilistic neural network) were reported to be 100% and 98.7% for the training sets and 88% and 85.3% for the testing sets respectively. The overall results of the experiment reported that both the neural networks are usable for the identification of different green tea samples.[55]

Tudu *et al.* proposed incremental learning fuzzy model which is a promising one to versatile pattern classification algorithm for the discrimination of black tea grade by using E-nose system.[55] It has been tested in some tea gardens of northeast India and the results obtained were encouraging.[56]

V.3. Present work: Result and Discussion

In our study, doped and un-doped ZnO nanorods based sensor have been developed and characterized. The fabricated sensor element was tested for its resistive response for evaluation of quality of two different types of tea infusion Orthodox. The performance of the sensor elements was characterized in different temperature of 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 was detected through an appropriate circuit in order to improve its sensitivity.

V.3.1. Steps for fabrication of ZnO based devices

Main steps followed to study zinc oxide based materials, both as nanorods and thin films are:

i. Synthesis of ZnO nano-rods using sol-gel spin coating methods.
ii. Coating electrodes by screen printing technique for Sensors.
iii. Fabrication of doped ZnO nanorod sensors for electronic nose.

V.3.2. Fabrication of ZnO Nanorods

Synthesis of ZnO nanorod Spin-coating is a simple method for preparing ZnO nanoparticles from Zinc acetate solution. In this process, we prepared 5mM solution of Zinc acetate dehydrate, $(CH_3COO)_2Zn$, $2H_2O$, (98% Merck) with methanol. The mixture was well mixed using an ultrasonic bath for 1 hour and then the resultant paste was dropped over a glass plate and the solution spun at 1000 rpm for 30s using a Programmable Spin Coater (Apex Technologies, Model SCU-2008C). Thus the nano layer of Zinc acetate solution is spread uniformly on a rotating substrate.[57] The coated substrates were heated to 350 °C in conventional oven for 30 min to yield layers of ZnO islands with their (100) plane parallel to the substrate surface.[57] After evaporation of solvent, a thin ZnO film was formed whose thickness can be controlled by repeating the above process. Concentration of the solution in the spin coater and spinning rate of the substrate also play important roles in adjusting the thickness of the formed seed layer. For preparing ZnO nanorods standard sol-gel protocol was used.[58] ZnO nanoseed were immersed in a solution with Zinc acetate and Hexamine in same proportion and kept at 90 °C for 2 hours for growth of nanorods. This forms an array of vertically aligned ZnO nanorods on the substrate surface. The coated substrate is rinsed and electrode with silver paste for further analysis.

ZnO thin films were prepared by the sol-gel spin coating method. As a starting material, zinc acetate dehydrate $[Zn(CH_3COO)_2, H_2O]$ was used. 2-methoxyethanol and MEA were used as a solvent and stabilizer, respectively. The dopant sources of Fe, Co and Ni were Fe- Acetate, Co-Acetate and Ni-Acetate respectively. Zinc acetate dihydrate and a dopant were first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate was maintained at 1.0 and the concentration of zinc acetate was 0.35 M. The solution was stirred at 60 °C for 2 hours to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The coating was usually made 2 days after the solution was prepared.

The solution was dropped onto glass substrates, which were rotated at 3000 rpm for 30 sec. After depositing by spin coating, the films were dried at 350 °C for 30 min over a conventional furnace to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated six times until the thickness of the sintered films was approximately 200 nm.

The crystallinity of each ZnO film was measured using an X-ray diffractometer with CuKα radiation. The surface and cross-section of the films were observed with a scanning electron microscope (SEM). The electrical resistance was measured by a four-point probe method. Optical transmittance measurements were carried out using a UV–VIS spectrophotometer.

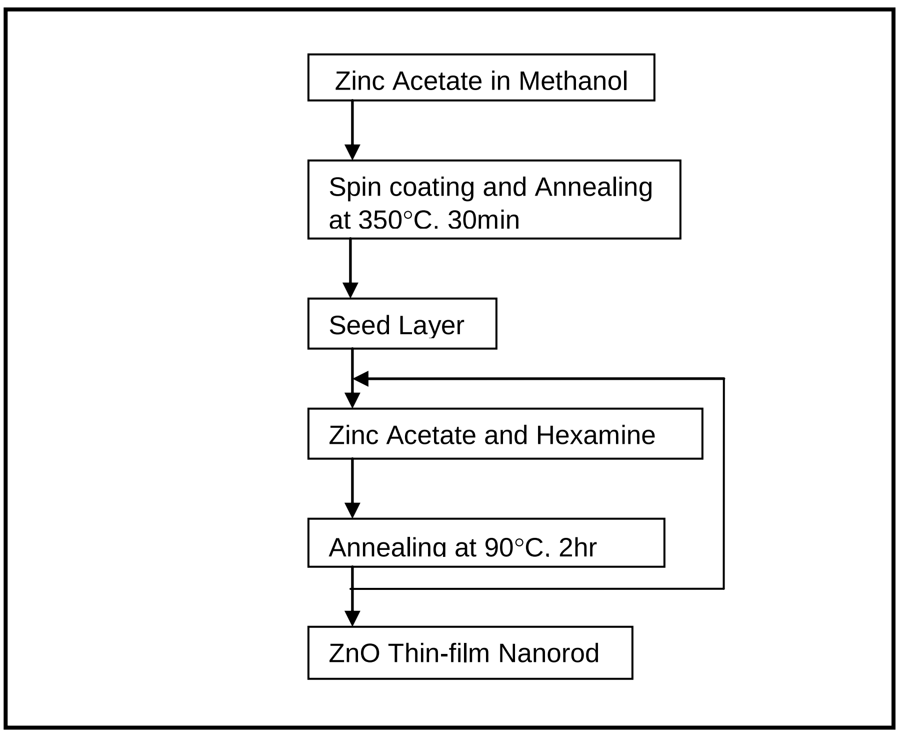


Figure V.1. Flow chart for preparation of ZnO nano layer.

A flow diagram of total synthesis process of ZnO nanolayer as presented in Figure V.1. The formation of phases were ascertained through study of X-ray diffraction pattern of the film calcined at various temperatures. Results showed pure ZnO phase formed at 350 °C and above.

For proper microstructure of sensor element, 350 °C was taken as optimum sintering temperature. The fabricate sensor material is characterized through SEM and the picture Figure V.4 shows clear ZnO nano rods aligned vertically perpendicular to substrate plane. Fabrication of device structure and measurement two interpenetrating comb like electrode structures were made with silver paste on the deposited film and was cured at 150 °C. Finally, two electrodes were soldered with copper wires for connecting with Whetstone Bridge circuit for measurement of off-balance voltage due to resistance change of the element.

For preparation of doped ZnO, Fe-Acetate, Co-Acetate and Ni-Acetate were added with Zinc acetate with appropriate proportion with further steps being identical to fabrication of the undoped one. The resulting nano-layer produced in this method over the substrate was electrode and connected to a digital multimeter for measureing the simultaneous resistance change in an atmosphere whose flavour (VOC composition) has to be determined.

V.3.3. Sensor Array and its Responses in Tea Infusion Vapour

For fabrication of E-nose, four such sensor measurement units, one of pure ZnO, one doped with iron, one doped with cobalt and one doped with nickel were incorporated at the same time in tea infusion vapour and the change of resistances of individual sensor were detected simultaneously. Four major grades of Orthodox black tea samples, Leaf, Broken, Fannings and Dust, were collected from fourteen Darjeeling tea gardens.

V.3.4. E-Nose measurements

This includes investigation on various sensors and sensor arrays useful for detection of smell and visual appearance of black tea liquor by electronic means using the system. Four similar systems pure ZnO, one doped with iron, one doped with cobalt and one doped with nickel were inserted in infusion vapour for simultaneous measurement. These E-Nose sensor responses of Volatile Organic Components (VOC) emitted from heated tea samples were analyzed through a Principle Component Analysis as presented in details in the results section.

V.3.5. Correlating sensor signals with Tea-tasters scores

The made tea samples were sent to selected professional tea tasters for organoleptic evaluation, and scores (between 1 to 10) were obtained for strength, aroma, and colour of the liquors. The evaluation included estimation of following parameters: Colour with milk, Colour without milk, Colour of Infused Leaf, Strength, Flavour and Price/Kg. The calibration of sensing parameters and the scores of tea taster are outlined by the flowchart given as Figure V.2.

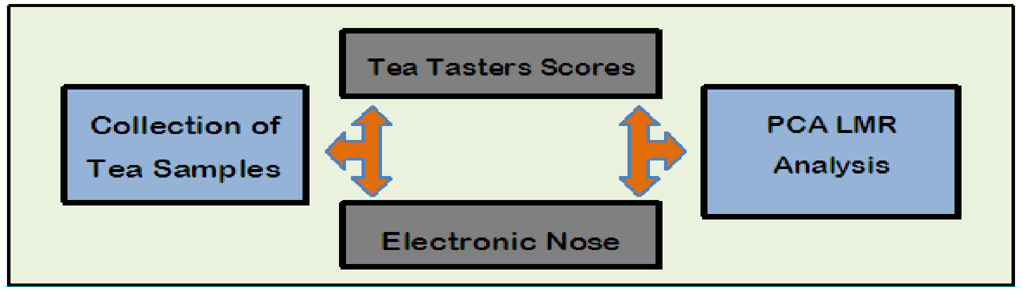
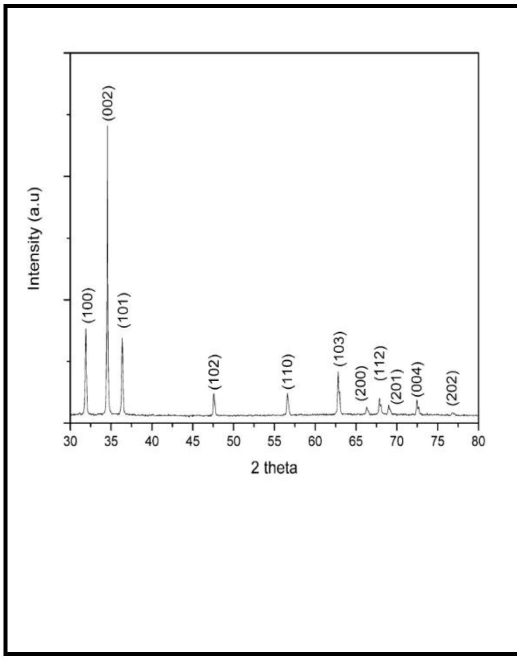


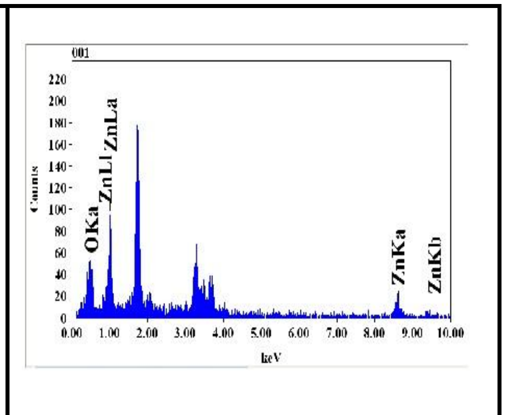
Figure V.2. Sketch of the Electronic Nose system used for the study.

V.3.6. Characterization of ZnO

V.3.6.1. X-ray Diffraction Analysis

The ZnO thin film crystal structure was investigated by X-ray diffraction analysis (Philips X'Pert Pro Alpha1 MPD diffractometer), utilizing Cu-Kα_1 radiation (λ=0.15406 nm). Figure V.3. shows the X-ray diffraction patterns of ZnO thin film. The EDAX analysis of selected area of SEM image was also studied for analysis of purity and identification of phases. Analysis shows a little impurity containing La ions. X-ray diffractrogram of ZnO films doped with iron, cobalt and nickel were also studied. However, no significant departure in the diffractogram from that of pure ZnO was noticed.





Ele...	Cl...	(keV)	mass%	Error%
O K*		0.525	28.98	3.53
Zn K*		8.630	71.02	11.02
Total			100.00	

Figure V.3.(a) X-ray diffraction patterns of ZnO thin film and (b) EDX analysis of ZnO Sample

V.3.6.2. Effect of Dopant Concentration

The surface morphology of the films and its dependency on the type and concentration of the dopant are displayed in Figure V.4. A particular structure was observed in SEM images of doped and un-doped ZnO thin films on glass substrates for all films. The particle size of films doped with 1 at.% for all dopants was somewhat larger than that of the un-doped film. In the case of Co doping, the film doped with 1 at.% exhibited a porous structure and had grain sizes of 150 nm on the average. The microstructure of the films consisted of many round shaped particles. In addition, the films had a smooth surface morphology.

For the Fe doped films, the film have even larger grains. The grain size of the 1 at.% Fe doped film reduced a little, but the packing density of the film increased due to disappearing gaps between particles. The grains are more flaky in nature reducing the overall surface area.

For Co-doped films, particles with different shapes and sizes were mixed. Additionally, a microstructure with a larger difference in size between the large and small particles, similar to the case of Ni-doped film was observed. In the cases of films doped with Co and Ni with a smaller ionic radius than zinc, particles forming a matrix became smaller with increased doping concentration because grain growth was disturbed by compression stresses due to the difference in ionic radii between zinc and Co or Ni. The change in particle size with an increase in doping concentration was observed more in the Co-doped films than in the Ni doped films. This is due to a higher difference in ionic radius between zinc and Co than that of the radii of zinc and Ni. However, since the ionic radius of Fe was larger than that of zinc, the change in particle size with an increased dopant concentration for Fe was less than that for the other dopants.

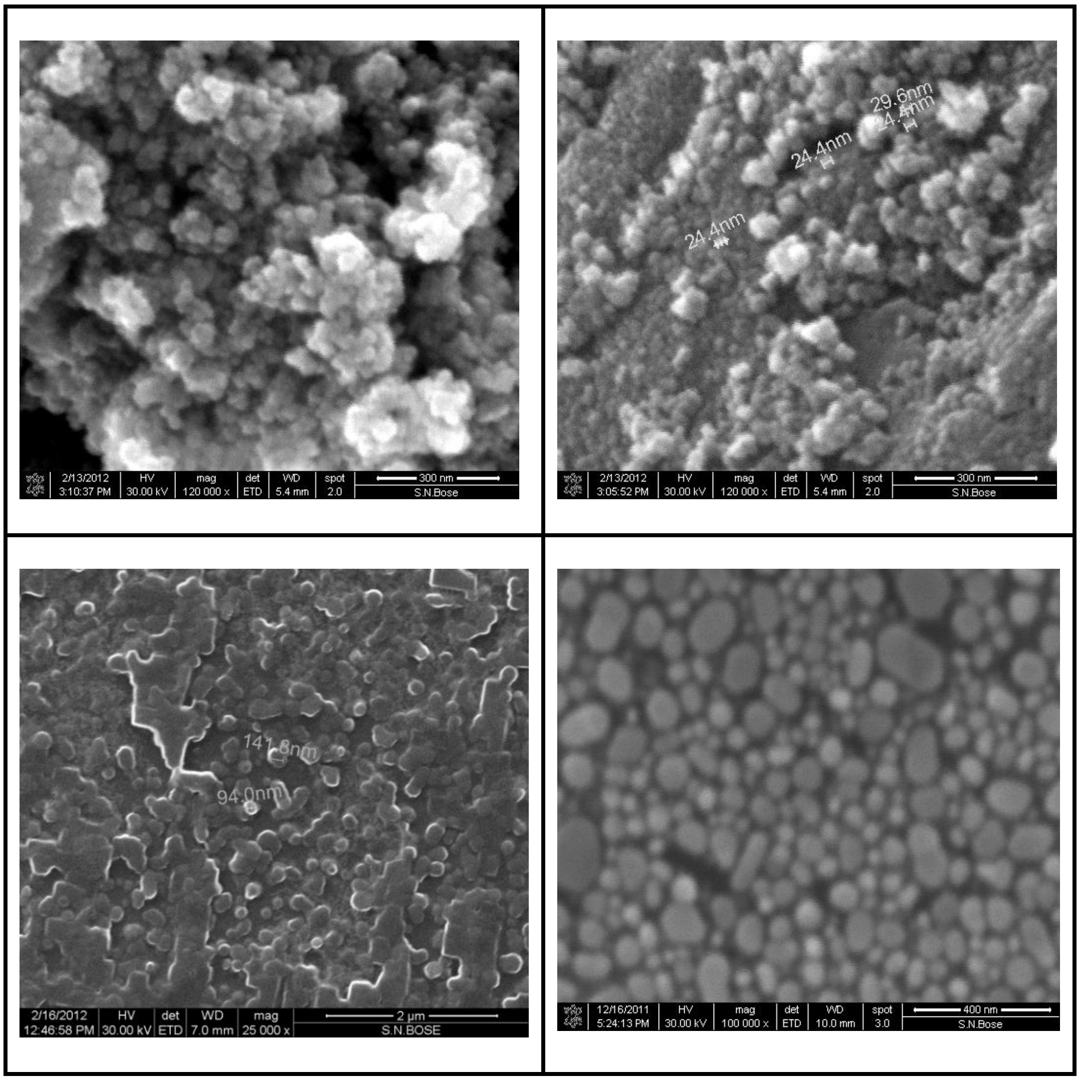


Figure V.4. SEM images of (a) un-doped and doped ZnO thin films with (b) Fe doped ZnO (c) Co doped ZnO and (d) Ni doped ZnO

The electrical resistivity of doped films was decreased by an increase in the carrier concentration. The lowest electrical resistivity values of the doped films were found out to be 1.1

x 10^{-1}, 4.8 x 10^{-1} and 5.6 x 10^{-1}Ωcm for Fe, Co and Ni, respectively. However, the increase in the electrical resistivity of doped films with increasing doping concentration may be due to a decrease in mobility of carriers caused by segregation of dopants at the grain boundary. Doped materials were acting as an electrical dopant at initial doping concentration but as an impurity at more doping concentrations having the lowest electrical resistivity values. Additionally, the electrical resistivity value of film was inversely proportional to a (0 0 2) preferred orientation of film. The resistance was measured using a Keithley 2400 multimeter configured in the two-wire mode. The main electrical characteristics: conductivity, carrier concentration, and mobility were derived from Hall measurements.[59]

Table V.1. Properties of doped and undoped sensing elements

	ZnO Film	**Fe doped ZnO**	**Co doped ZnO**	**Ni doped ZnO**
Average Grain Size (nm**)**	120	120	200	150
SurfaceResistivity(Ω-cm)	2.4 x 10^{-1}	1.1 x 10^{-1}	4.8 x 10^{-1}	5.6 x 10^{-1}
Electronmobility(cm^2/V s)	17.1	14.3	12.1	11.2
Conductivity$(\Omega\ cm)^{-1}$	0.015	21.981	1.651	0.001
Electron concentration (cm^{-3})	5.8×10^{15}	9.1×10^{18}	8.6×10^{17}	9.73×10^{14}
Semiconductor Band Gap (from UV-Vizabs. spectra) (eV)	3.31	3.27	3.29	3.27

The UV-Vis absorprion spectra, carried out between wavelengths from 300 to 800 nm, of the un-doped and doped ZnO thin films. The band gap were measured through the general formula given by Davis and Mott[60] for optical band gap E_g is

$$\alpha h\nu = [\ B(h\nu - E_g)\ ]r \qquad 5.1$$

where, r = index taking different values depending on the mechanism of the interband transition (usually 2 for ceramic system), B = constant called band tailing parameter and hν = incident photon energy.

Therefore for undoped and doped ZnO equation 5.1 becomes

$$\alpha h\nu = [\ B(h\nu - E_g)\ ]^2$$

or, $$(\alpha h\nu)^{1/2} = Bh\nu - BE_g$$

Variation of $(\alpha h\nu)^{1/2}$ with hν will be straight line with slope m = B and intercept c = BE_g

Therefore, $E_g = BE_g / B = c/m$ = intercept/ slope

The results of Hall measurements band gap studies were presented in Table V.1.

V.3.7. Measurement of sensor characteristics

The sensitivity of ZnO based nanosensor is defined as:

$$S = \frac{(R_g - R_a)}{R_a} = \frac{\Delta R}{R_a} \qquad 5.2$$

where R_a and R_g are the resistance of the sensing film in the atmosphere to be measured and the atmosphere that are referenced, respectively. In our case percentage change in output voltage can give an indication of sensitivity of the sensing system. Response time is the time taken by the sensing element to reach 90% of the final stable value of the response while the Signal-to-noise ratio was measured by the signal response divided by the mean fluctuation of results from its average value.

V.3.8. Doped ZnO Materials for Four Different Sensors

Tea is a non-alcoholic beverage consumed worldwide with an endlessly extending market. Like other food items, it also needs to be passed through the food safety and quality criteria.[61] Professional tea tasters have been traditionally assessing the physical quality attributes of tea by visual and nose approximations, which suffer from inconsistency and variability. So, there is a need for more accurate quality evaluation system.[62] Bio-chemical methods are available for assessment of tea quality applying modern analytical tools like high-performance liquid chromatography, gas chromatography, etc which are more accurate than human assessments, but these are time-consuming, and the results are often inconsistent with sensory evaluation. An application of electronic nose and vision coupled with multivariate data analysis in the analysis of foodstuffs has been increasing in last few years. The electronic testing devices are comprised of three principal components, sensor array, the equipment receiving signals and pattern recognition. In place of a single sensor, an array of sensors is solving the purpose more efficiently.

This is done by using array of sensors with partially overlapping selectivity and treating the data obtained by multivariate methods. E-noses have been used for identification of tea grade, prediction of tea quality, and monitoring of black tea fermentation process.[63] E-nose devices have also been successfully applied to different fields particularly in food and beverage industries, such as tomato, and coffee.[64] Computer vision systems are also gaining significant popularity in food industry because of their cost effectiveness, consistency, superior speed and accuracy. Also, the methods used so far for estimation of tea quality parameters have their own merits and demerits as they have been developed independently.[62] In the present study, an attempt has been made to integrate the three types of tea quality measurement techniques viz., taster's scoring, biochemical analysis and electronic sensor based studies, to find a correlation between them. This would be used to standardize the electronic sensor based study of Darjeeling Orthodox black tea quality, to contribute to the process of simplification as well as enhancing accuracy in determination of tea quality.

V.3.9. E-nose Application of Doped ZnO Sensors for Tea Quality Estimation

The E-nose was developed in order to mimic human olfaction that functions as a non-separative mechanism: i.e. an odor / flavor is perceived as a global fingerprint. Essentially the instrument consists of headspace sampling, sensor array, and pattern recognition modules, to generate signal pattern that are used for characterizing odors.

Electronic noses include three major parts: a sample delivery system, a detection system, a computing system.The sample delivery system enables the generation of the headspace (volatile compounds) of a sample, which is the fraction analyzed. The system then injects this headspace into the detection system of the electronic nose. The sample delivery system is essential to guarantee constant operating conditions.

The detection system, which consists of a sensor set, is the "reactive" part of the instrument. When in contact with volatile compounds, the sensors react, which means they experience a change of electrical properties.

In most electronic noses, each sensor is sensitive to all volatile molecules but each in their specific way. However, in bio-electronic noses, receptor proteins which respond to specific odor molecules are used. Most electronic noses use sensor arrays that react to volatile compounds on contact: the adsorption of volatile compounds on the sensor surface causes a physical change of the sensor. A specific response is recorded by the electronic interface transforming the signal into a digital value. Recorded data are then computed based on statistical models.[65]

In our case, there are four sensors and there are various Volatile Organic Components arising in tea infusion has to be detected. The contribution to individual gas component can be isolated through Principal Component Analysis (PCA).

V.3.10. Principal Component Analysis

PCA reduces the data dimension to some principal components and enables the extraction of the differences between samples and the main variables. The data of 51 samples were analyzed by PCA. PCA is a linear method that has been proved to be effective for discriminating the response of gas sensor array to simple and complex odours. Considering the differences of sensitivities of gas sensors, all data have been normalized before analyzed by PCA. Figure V.5 shows PCA results of training data set projected onto their first two principle components.

Table V.2. Covariant Matrix formed from responses of four different sensor and its Eigen values

(a) The Covariant Matrix

0.0025	0.0013	0.0087	0.0141
0.0013	0.0011	0.0035	0.0056
0.0087	0.0035	0.0455	0.0669
0.0141	0.0056	0.0669	0.1170

(b) Eigen values of Covariant Matrix

Eigen value-1	**Eigen value-2**	**Eigen value-3**	**Eigen value-4**
0.1592	0.0054	0.0014	0.0002

Four eigen values of covariance matrix are listed in Table V.2b. It was found that the first eigen value appears to be the largest and other eigen values are smaller by an order of 10^2.

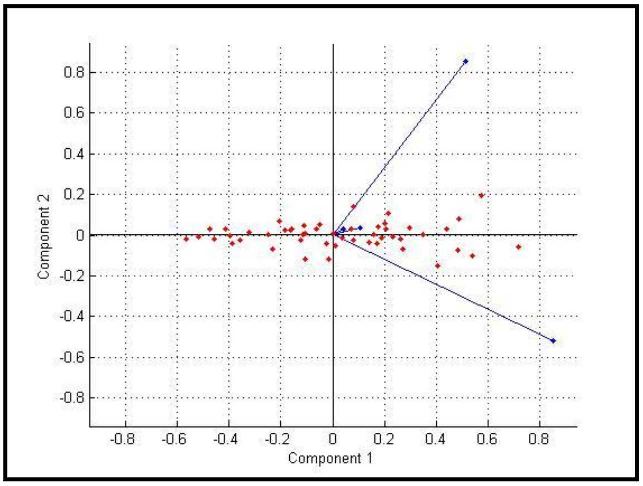
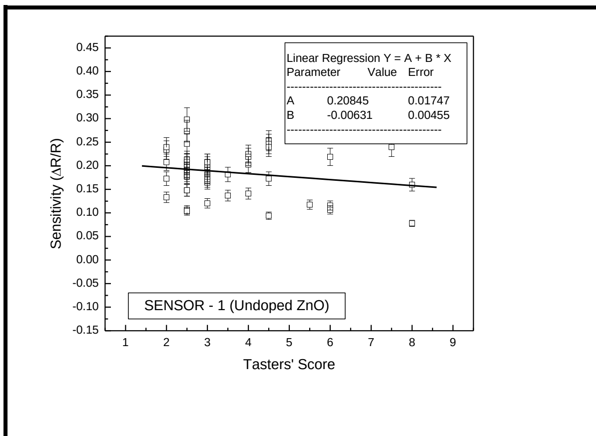
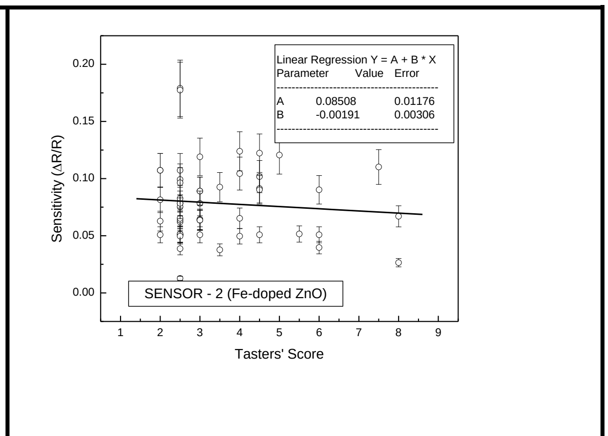


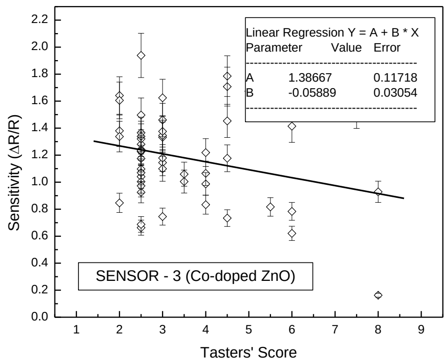
Figure V.5. PCA results of training data obtained from sensor array.

Therefore, the response data were greatly aligned along first principal component. In other words, the aroma in Darjeeling Orthodox tea liquor arises mostly from a single component. This is also evident from the PCA result shown in Figure V.5. Where all data were mostly aligned in the direction of first principle component.

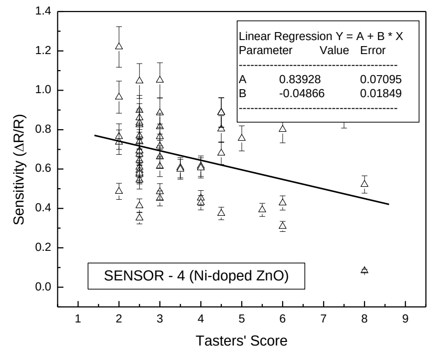
V.3.11. Development of E-Nose response function

Response of individual sensors will have either positive correlation or negative correlation with individual flavour component i.e. some sensors have positive response with a particular flavour component, whereas, some exhibits negative response.

	
(a) Response of Sensor-1 (Undoped ZnO)	**(b) Response of Sensor-2 (Fe-doped ZnO)**



(c) Response of Sensor-3 (Co-doped ZnO)



(d) Response of Sensor-4 (Ni-doped ZnO)

Figure V.6. Calculation of individual response gradient of four different sensor elements

Also, the contribution of individual response due to flavour component will be proportional to the sum for a particular sensor's response.[66] So, a function is constructed for the total sensor response (S) which is a linear sum of individual response multiplied by the individual gradient value of each sensor response.

$$S = \sum_{i=1}^{4} R_i \times \left| M_{Si} \right| \qquad 5.3$$

where, M_{Si} (i = 1 to 4) is the individual response of each attributes factor, and R_i is the weight coefficient corresponding to each attribute. The gradients of individual responses are taken as the weight coefficient of that sensor element.

The response from each sensor is plotted with tasters flavour score and the gradient is noted and presented in Table V.3.

Table V.3. Gradient of each sensor calculated from individual response.

Sensors	Un-doped	Fe-doped	Co-doped	Ni-doped

Response (R_i)	R_1	R_2	R_3	R_4
Gradient (M_{Si})	-0.00631	-0.00191	-0.04866	-0.05889

The resulting function is plotted with the Taster's scores obtained for orthodox tea. Figure V.7 shows the calibration of the sensors using a new function built appropriately from individual sensor responses as presented in Equation 5.2 where the weight coefficient of four individual sensing elements was built through multiple regression equation of four sensor data versus the tasters flavour score.

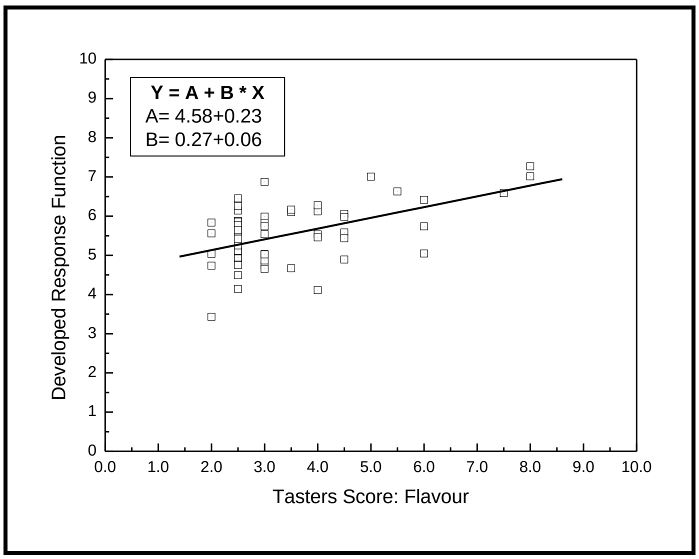


Figure V.7. Calibration of the sensors using a function built from individual sensor responses for Orthodox black tea.

When this newly developed function is plotted with the tasters' flavor score, a very good linear relationship is observed with very small scattered data exhibiting a significantly high value of the gradient as presented in Figure V.7.

V.4. Conclusion

In our study we have prepared various transition metal doped ZnO nanosensing material which have been successfully used to sense the flavor of Orthodox Darjeeling tea collected from various garden by electronic nose system. The application of E-nose system to determine tea quality is a new direction of research to develop better sensing material. Doping is a very good process which can modify the response signal of E-nose system to a better one. Research in this ground will significantly increase the quality of the sensor system which will obviously help to better differentiate the quality of various teas, foods etc.Our research in this ground to develop further sensing material is underprocess.

V.5. Reference

References are given in BIBLIOGRAPHY under chapter V page no. 97-100.