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Nanostructured ZnO based Gas Sensors to use in Electronic Nose for Biochemical Compounds in Black Tea

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Abstract: Quantitative evaluation of aroma of black tea is a difficult task as no single sensor has been developed which can quantify the volatile aroma compounds. As an alternative, the array of sensors has been attempted to solve this problem involving the principle of neural-network for analysis of responses. To develop the array we have used nano-structured ZnO doped with various metals. In this presentation we describe the responses of Geraniol, Trans-2-Hexenal, Linalool Oxide & Linalool, the major aroma chemicals of black tea to doped and undoped ZnO with Pt metal. Nanostructured ZnO doped with and without Pt are synthesized through chemical process. The synthesized materials are characterized by XRD and SEM which confirm their nanostructure and phase purity. The synthesized sensors are heated in the temperature range of 200°C to 400°C and their responses towards volatile biochemical compounds like Geraniol, Trans-2-Hexenal, Linalool Oxide and Linalool are studied.

Keywords - Nanostructured; synthesized; Trans-2-Hexenal; Linalool Oxide; Biochemical compounds; Black Tea.

I. INTRODUCTI ON

Tea produced at tea plants is graded by a panel of experts who assign ratings to a particular sample for determination of its market price. But human panel tasting is highly subjective with numerous problems like inaccuracy and non repeatability due to mental status of human-evaluator[1].So the development of technology for Electronic-Nose has become a global challenge for classification of food-products through its' aroma. Quantification of tea quality is very complex because of the presence of innumerable compounds and their multidimensional contribution in determining the final quality of tea [2]. Sensors which can quantify the various compounds in black tea is difficult to develop. The quantification of individual compounds in this complex aroma of black tea is possible only by gas-chromatography and mass-spectrometer. However they cannot be used regularly for classification of industrial tea. The best option lies with the use of array of sensors and analysis of their responses to various oxide based semi-conductor sensors using the principle the principle of neural-network. Nano-structured powders of ZnO doped with and without Pt have been developed as a part of the array and have been synthesized using the principle of thermolysis of triethanolamine (TEA) complex of Zn ion. The response of this oxide based sensor is remarkable to the pure volatile major compounds of tea-aroma.

II. BLACK TEA CHEMISTRY

Black tea processing is done through a series of operations: 1. Plucking; 2. Withering; 3. Preconditioning and Rolling; 4. Cut-tear-curl (CTC); 5.Fermentation and 6.Drying. The various properties of black tea like flavour, odour, colour and taste depends on certain volatile biochemical compounds and aromatic substance which determines tea quality. Critical unit operation of black tea is shown Figure 1 [3]. Black tea compounds responsible different flavour is indicated in Table 1 [4].

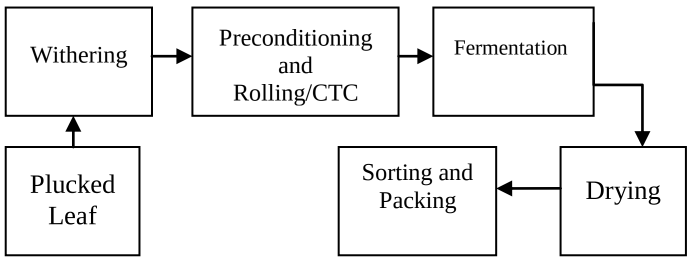

Figure 1: Critical unit operation of Black tea

TABLE I: BIO-CHEMICAL COMPOUNDS PRESENT IN TEARESPONSIBLE FOR FLAVOUR.

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

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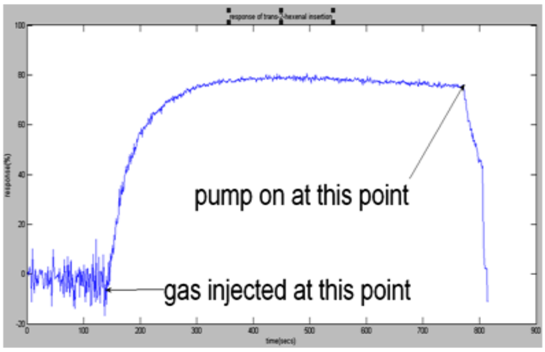


Figure 2: General reponse of nanostructured ZnO sensor to tea compounds

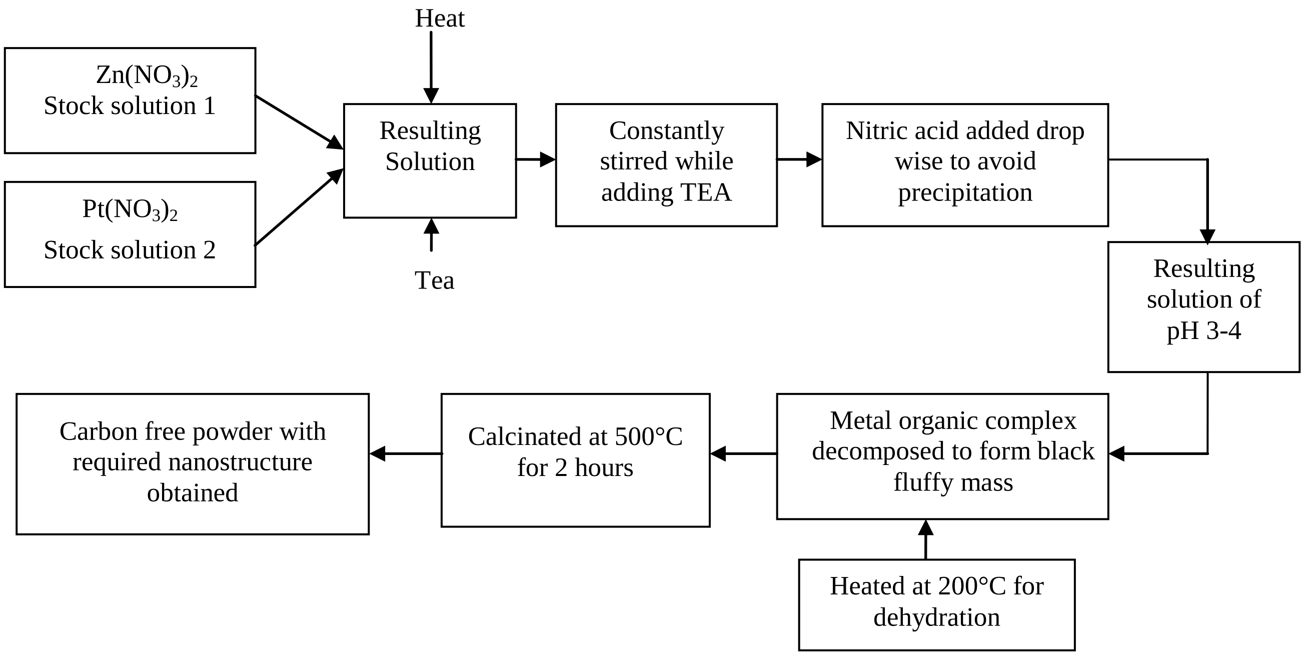


Figure 3: Synthesis of Nanostructured Sensor

III. EXPERIMENTAL

A. *Raw Materials*

The chemical used Zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], Diethanolamine(DEA), Platinum Tetrachloride [$PtCl_4$], Triethanolamine[$C_6H_{15}NO_3$] and Nitric Acid [HNO_3] (70%). All the materials were procured from Sigma Aldrich (USA).

B. *Nanostructured Material Syntheses*

The method of synthesizing nanostructured ZnO doped with Pt is shown in Figure.3.

C. *Characterization of Synthesized Material*

The synthesized materials were characterized to confirm their phase purity and nanostructure. XRD analysis was done using *Rigaku X-Ray Diffractometer* operated at 40 kV and 30 mA with Cu radiation and K-β Filter and is shown in Fig- 4,5. The data was collected over 2θ angle range of $20° \leq 2\theta \leq 80°$ with step size of 0.02°. Phase identification was done using JCPDS database [5]. The crystallite size (D) of the synthesized material was calculated using Scherer's equation as follows:

$$D = \frac{0.9*\lambda}{\beta * \cos(\theta)} \quad (1)$$

Where λ= wavelength of the target material (1.5406 Å), β= Full Width at Half Maximum of the diffraction peak of the material, θ = incident angle of X-ray. SEM analysis was done using JEOL JSM 6360 equipped with an EDX analyzer.

D. *Result Obtained from Characterization of Synthesized Material*

The synthesized wurtzite structured ZnO (pure) and also doped the same with metals like Ni, Pt, Pd and Co. The average crystallite size (D) calculated from the XRD report for the synthesized materials are tabulated below in Table II using equation (2).

TABLE II : CRYSTALLITE SIZE OF SYNTHESIZED ZNO (PURE AND DOPED)

Material	Crystallite size
ZnO(pure)	40 nm
ZnO(doped with Ni)	45 nm
ZnO(doped with Pt)	42 nm
ZnO(doped with Pd)	50 nm
ZnO(doped with Co)	52 nm

The SEM analysis reveals a porous morphology and XRD confirms the nanostructure of the synthesized material. From the characterization report it may concluded that a potentially good sensing material has been synthesized. The analysis of XRD data was done using JCPDS database [5] and confirmed the presence of pure wurtzite phase of ZnO. XRD of Pt doped ZnO was similar and did not affect the crystal structure nose images revealed a highly porous surface morphology which implied a high surface to volume ratio. This meant a greater surface area and thus enhanced sensor performance. The crystallite size calculated from XRD analysis and surface morphology as observed from SEM (Figures 6 to 9) confirmed the materials as nanostructured.

E. Gas Sensing Studies and Discussion

The synthesized ZnO is shaped into a cylindrical pellet having a diameter of 20 mm and thickness of 2 mm. When a reducing gas is allowed to come in contact with the sensor surface, it is oxidized and the surface is reduced leading to release of electrons. The resistance of the sensor decreases due to this release of electrons .This property of the synthesized material is exploited for the sensing of the vapor of organic aroma Geraniol, Trans-2-hexenal, Linalool Oxide and Linalool have been selected from Table-1 for testing the performance of sensor. The sensor is placed in an airtight chamber and is heated at a fixed temperature in a range of 200-400°C.Then the sensor resistance is measured in presence of the injected gas and its response is evaluated [6-7]. Fig.-2 shows general response of nanostructured ZnO sensor to the above mentioned tea-aroma compounds.

The response of the sensor is calculated as in equation (2).

$$\text{Response (\%)} = \left[\frac{(Ra-Rg)}{Ra}\right]*100\% \qquad (2)$$

This procedure is repeated at different temperatures between the range 200°C-400°C at an interval of 50 °C for the three sensors and each sensor is tested with the all the black tea compounds mentioned above.

F. Electrical Measurement and Discussion

The electrical conduction of the sensor in dry air is observed in a temperature range of 200°C to 400°C. Conductivity of the sensors is seen to follow Arrhenius law given by

$$\sigma = \sigma_0 * e^{-E/kT} \qquad (3.1)$$

$$\text{or } \ln(\sigma) = \ln(\sigma_0 * e^{-E/kT}) \qquad (3.2)$$

A plot of **ln(σ)** vs **1/T** gives a straight line whose slope gives us the activation energy E. Activation energy is calculated for all the sensors and given in Table III.

TABLE III: ACTIVATION ENERGY FOR SYNTHESIZED SENSORS

Sensor type	Activation energy in eV
ZnO (pure)	0.6
ZnO (Pt doped)	0.55
ZnO (Pd doped)	0.58
ZnO (Ni doped)	0.6
ZnO (Co doped)	0.65

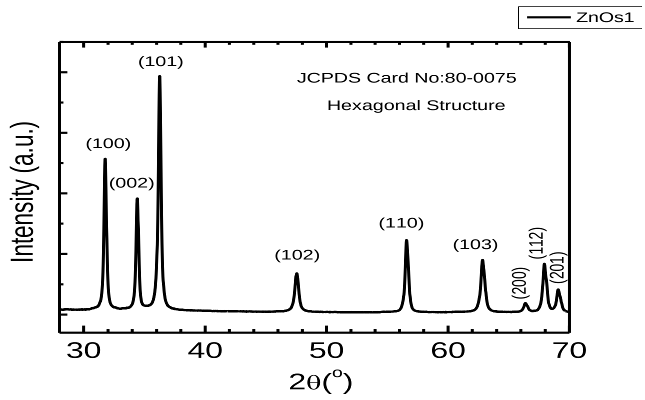


Figure 4: XRD Image of ZnO (Pt Doped)

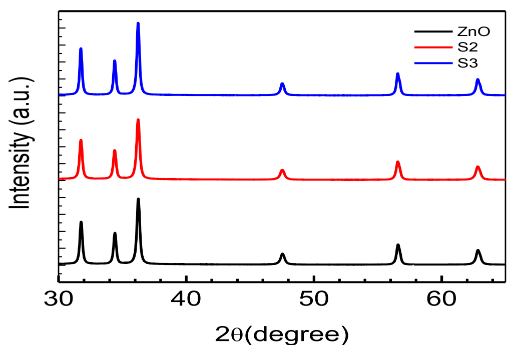


Figure 5: XRD Image of ZnO (Pd doped)

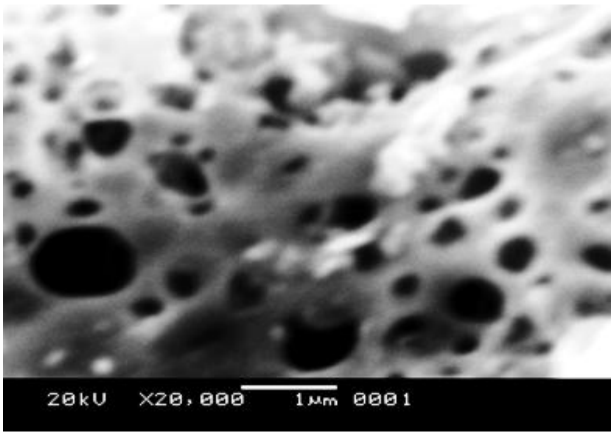


Figure 6: SEM Image of ZnO (pure)

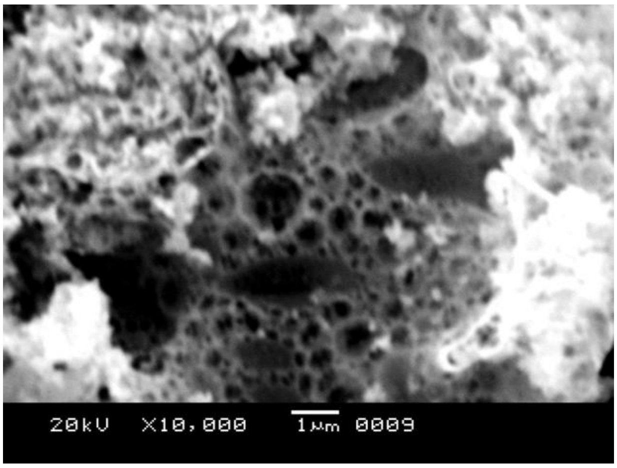


Figure 7: SEM Image of ZnO (Pt doped)

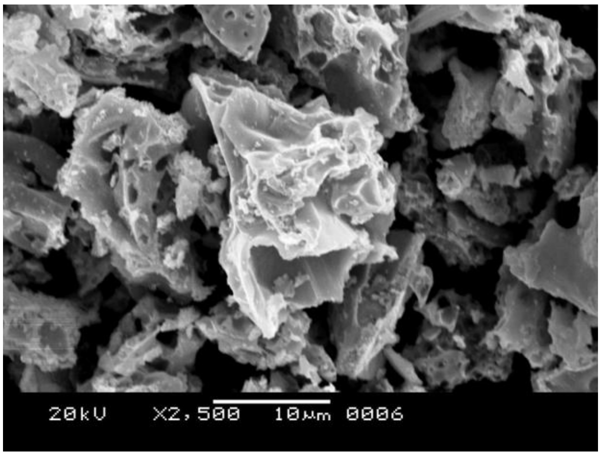


Figure 8: SEM Image of ZnO (Pd doped)

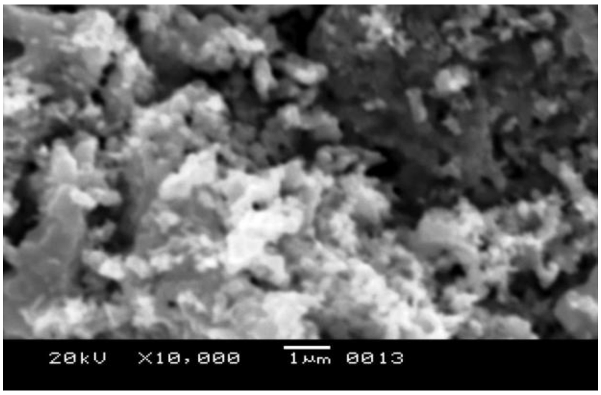
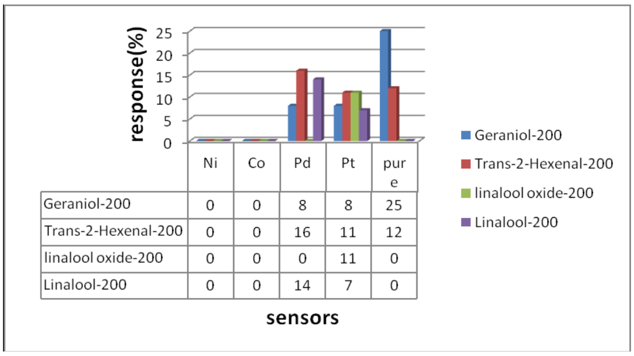


Figure 9: SEM Image of ZnO (Co doped)

IV. Results and Discussion

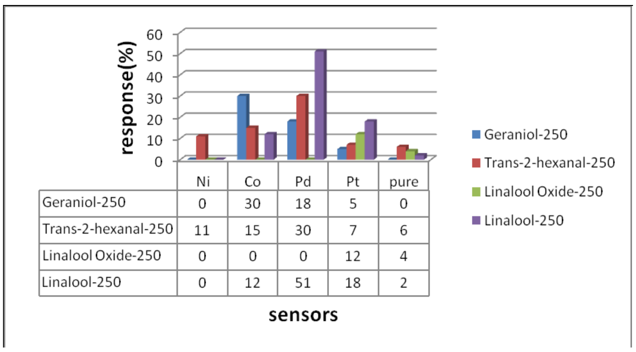
Response for the five sensors has been represented in bar graphs in Figures 10 to13. Each bar-graph corresponds to the performance of a single sensor over a temperature range of 200°C-400°C towards each of the 4 gases indicated by different colours as follows:

(a)Geraniol-blue, (b) Trans-2-hexenal-red, (c) Linalool Oxide-green and (d) Linalool-violet



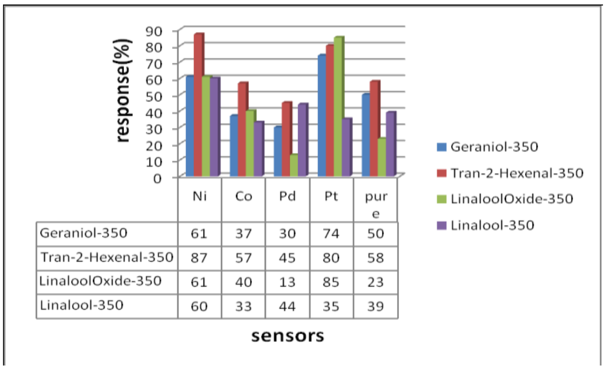
	Ni	Co	Pd	Pt	pure
Geraniol-200	0	0	8	8	25
Trans-2-Hexenal-200	0	0	16	11	12
linalool oxide-200	0	0	0	11	0
Linalool-200	0	0	14	7	0

Figure 10: Performance of ZnO (doped and undoped) towards all compounds at 200°C



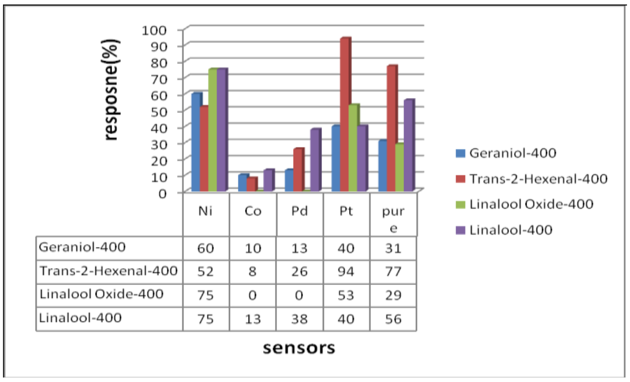
	Ni	Co	Pd	Pt	pure
Geraniol-250	0	30	18	5	0
Trans-2-hexanal-250	11	15	30	7	6
Linalool Oxide-250	0	0	0	12	4
Linalool-250	0	12	51	18	2

Figure11: Performance of ZnO (doped and undoped) towards all compounds at 250°C



	Ni	Co	Pd	Pt	pure
Geraniol-350	61	37	30	74	50
Tran-2-Hexenal-350	87	57	45	80	58
LinaloolOxide-350	61	40	13	85	23
Linalool-350	60	33	44	35	39

Figure 12: Performance of ZnO (doped and undoped) towards all compounds at 350°C



	Ni	Co	Pd	Pt	pure
Geraniol-400	60	10	13	40	31
Trans-2-Hexenal-400	52	8	26	94	77
Linalool Oxide-400	75	0	0	53	29
Linalool-400	75	13	38	40	56

Figure 13: Performance of ZnO (doped and undoped) towards all compounds at 400°C

V. CONCLUSION

Nanostructered ZnO pure and doped with Pt has been synthesized to be used as gas sensor material. XRD and SEM has been done and crystallite size found to be for ZnO (pure) and doped with Pt respectively. The sensors have been tested with Geraniol, Trans-2-hexenal, Linalool Oxide and Linalool in a temperature range of 200°C to 400°C and response has been found to be high at *300°C, 350°C and 400°C Ni doped sensor, at 300°C and 350°C for Co doped and at 350°C for Pt doped* while decreasing at other temperatures.

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