ARRAY OF NANOSTRUCTURED SENSOR ELEMENTS FOR DETERMINATION OF TEA QUALITY

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Abstract

Detection of Volatile organic compounds is important for identification of flavour in different commercial organic products like Tea, Coffee, Wine, etc. The flavour components are detected through porous nanostructured Zinc Oxide (ZnO) sensing elements. This work shows the potential application of nanostructured gas sensor arrays for monitoring the quality of Indian tea.

In this paper, ZnO nanoparticles were fabricated on a glass substrate by sol-gel technique. The ZnO film possessed a columnar structure consisting of small crystals with an average grain size of around 5 nm. The sensing properties of the ZnO film were tested for two different Tea liquors, namely, Assam CTC Tea and Darjeeling Orthodox Tea. Though the main ingredients in made tea are same, the quality of made tea mainly differ from their flavour types, which rely on their trace components. Flavour type of tea liquors is a very important factor in identification of quality of Indian tea. An obvious change in resistance of the ZnO film was also observed when the sensor was exposed to gas mixture. The nanostructured elements showed higher degree of selectivity than the larger sized grains and pores. The sensing mechanism of the nanostructured ZnO sensor is discussed.

Keywords: Zinc Oxide, nanorod, sensor, tea aroma.

1.Introduction

Tea is probably the most popular drink worldwide. Among all the beverages consumed worldwide, tea is a very popular one and used by all strata of people. 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 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 [1]. 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 [2] for the same.

The flavour in different commercial organic products like Tea, Coffee, Wine, etc. arises from Volatile organic compounds (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 [3]. 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, emit organic vapours [4]. VOCs are also present in some workplaces, especially in the chemical industries; in these cases, it is important to monitor the concentration of the vapors to safeguard the health of the workers, and also to keep atmospheric emissions under control in order to avoid environmental hazards. Finally, other inorganic gases such as hydrogen or oxygen also need to be monitored because of the high risk of explosions if their concentrations surpass safe levels. Therefore, sensing of VOC's has attracted increasing interest focused on their detection, monitoring and analysis.

Porous nanostructured oxide materials like ZnO and SnO_2 have been studied extensively primarily for detection of inorganic gases [5]. Recently, ZnO have been extensively studied for applications in practical gas sensing conversion devices [1-2] ZnO is one of the potential semiconductor materials in sensor due to its fine physical, ch [6,7] emical and optical properties [8-10] 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 ~60meV. Another attractive feature of ZnO is that its bandgap energy can be engineered by changing dopant materials [11]

ZnO is an interesting chemically and thermally stable n-type semiconductor with a large exciton binding energy (60 MeV) and large band gap (3.37 eV) energy. ZnO can be grown at relatively low temperatures as compared to other wide band gap semiconductors. Inexpensive substrate and low-temperature growth make these devices feasible to manufacture at a lower cost. However, these developments, in the meantime, demand a good reproducibility and clear understanding of the stability of thin film based multi-layered structures employed in the devise design. ZnO nanomaterial also appears to be the mostly studied one as it exhibits a wide variety of nanostructures such as nanowires6, nanowalls[7-8] nanobelts [8]nanorod [10], nanosheet [10], and so on. Recent research has demonstrated that the creation of ZnO nanostructures in highly oriented and ordered arrays is of crucial important for the development of novel devices [12]. It has been recognized as one of the promising nanomaterials in a broad range of high technology applications, e.g., surface acoustic wave device6, chemical sensor7, photonic crystals [12], light emitting diodes [13], varistors8, and photoanode films of solar cell. Among its applications, ZnO nanowire is receiving greater interests for use in gas sensors for detecting the VOCs, for example, ethanol. ZnO nanowires prepared by a reactive thermal deposition method were used for ethanol sensing[12]. Very recently, nanocrystalline ZnO gas sensors have attracted more interest due to their better properties of detecting pollutants, toxic gases, alcohols and food freshness, especially fish freshness [14], or as gas-sensing films integrated on one chip to make an “electronic nose [15]. 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 [16,17] of Chinese liquors was carried out using doped nano ZnO gas sensor array and different statistical techniques were compared for their classification ability [18].

In our study, zinc oxide nanorods based sensor has been developedand characterized. The fabricated sensor element was tested for its resistive response for evaluation of quality of two different types of tea infusion Orthodox and CTC. 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 is detected through an appropriate circuit in order to improve its sensitivity. A Whetstone bridge circuit is used with compensation of cross sensitivity due to temperature variation of the sensor element.

2. Experimental

2.1 Synthesis of ZnO nanorod

Spin-coating is a simple method for preparing ZnO nanoseed 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 hr and then the resultant paste was dropped over a glass plate and the solution spun at 1000 rpm for 30s using a spin coater. Thus the nano layer of Zinc acetate solution is spread uniformly on a rotating substrate [19-20]. 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 [21]. 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 [22]. ZnO nanoseed were spin-coated using zinc acetate solution. In this process, we prepared 5 mM solution of zinc acetate dehydrate, $(CH_3COO)_2$ Zn, $2H_2O$, (98% Merck) with distilled methanol. The solution was spun on clean glass substrates (with heater coil imprinted on back side) at 1000 rpm for 30s using a Programmable Spin Coater (Apex Technologies, Model SCU-2008C). The substrates, now covered with a film of zinc acetate crystallites, were heated to 350^0C in an oven for 30 min to yield layers of ZnO. After evaporation of solvent, a thin ZnO film was formed.

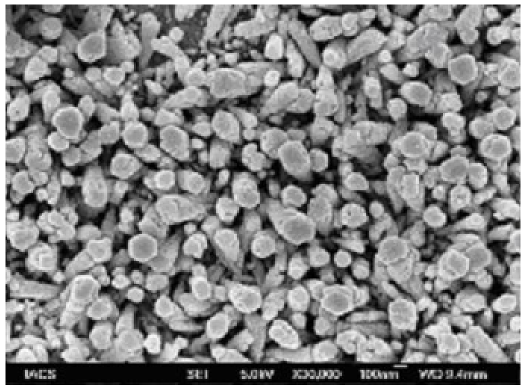

Fig.1: Scanning electron microscope (SEM) picture of ZnO nanorod film grown on glass plate

The formation of phases was 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 (Fig.1) shows clear ZnO nanorods aligned vertically perpendicular to substrate plane.

2.2 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.

Dry tea leaves were weighed (10gms) and placed in a glass flask and appropriate amount (500 ml) of water is added as shown in **Fig.2**. Finally the sample is heated at 100°C while measurement of output voltage of the circuit was carried out.

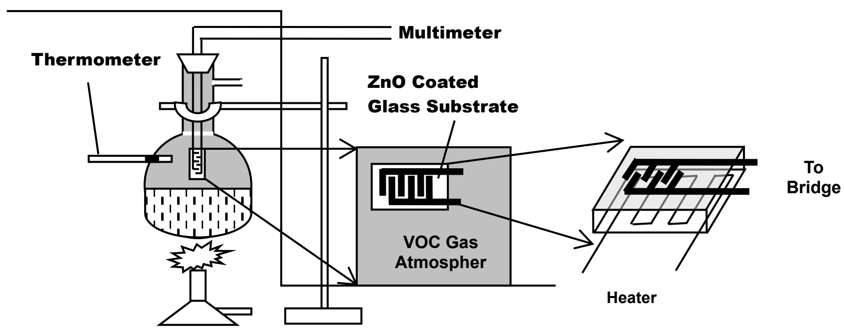

Fig.2: Schematic picture of sample measurement system in static gas environment

The output for the sensor is connected to a Whetstone bridge circuit consisting of a resistance (of same order of resistance of the sensors) a variable resistance (For bridge balancing) and two sensors, one for measurement and one for temperature compensation as shown in **Fig.3.**The resistances are of same order of the sensor elements while the variable resistance is adjusted forbalancing of the bridge. Two exactly similar sensor elements heated simultaneously at same temperature were connected at other two arms of the bridge. One of the element being placed in the gas environment (tea infusion), while the other in open atmosphere (reference). The bridge is powered through a dc power supply (12V).

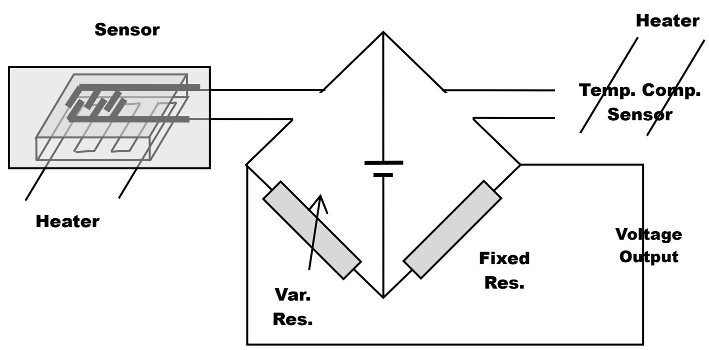

Fig.3: Schematic picture of sample measurement system in static gas environment

3. Results and Discussion

3.1 Response characteristics

The response characteristics of semiconducting ZnO film in the Whetstone bridge circuit showed distinct change in measured off-balance voltage with infused tea leaves of different kinds when compared with the response in plain boiling water. A typical response curve with two different kinds of tea leaves, CTC and Orthodox tea, are presented in **Fig.4**.The difference in response with tea as compared with pure water is quite substantial. This shows that the effect of VOC's on sensor response is quite high. The high response is due to porous nanostructure of ZnO. The pore sizes of the nanostructured sensing element may be close to the organic molecules and so the adsorptions of these molecules are greatly intensified. This also imparts selectivity to some molecules. The molecules whose dimensions matches with that of the pores are adsorbed more resulting in higher response.

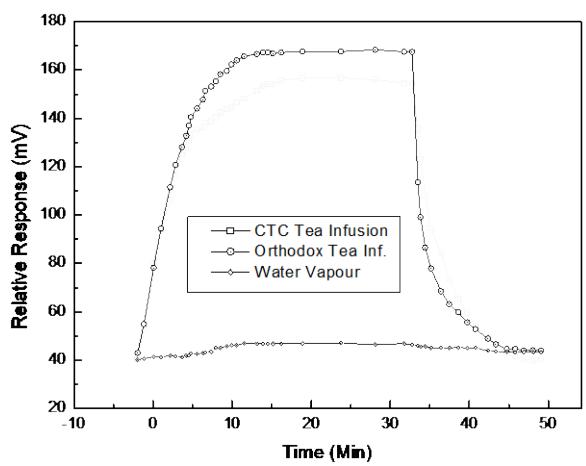

Fig.4: Response of the ZnO nanowire gas sensors measured at temperature 200□C with Orthodox tea and CTC tea infusion (at 100□C) and compared with response in plain water vapour.

Results shows slightly lower concentration of VOC is detected for CTC compared to Orthodox tea which is in accordance toTea tasters reports that indicates Orthodox tea has superior flavour characteristics. The difference may be due to the presence of less VOC's in CTC leaves.

3.2 Variation of response sensitivity with operating temperature

The sensor operating temperature is varied by controlling the heater current in the coil attached to the substrate. Results are presented in **Fig.5**for two kinds of two infusion. It shows that while the tea infusion temperature being the boiling point of water (100□C), that maximum sensitivity is obtained at around 100-200□C.

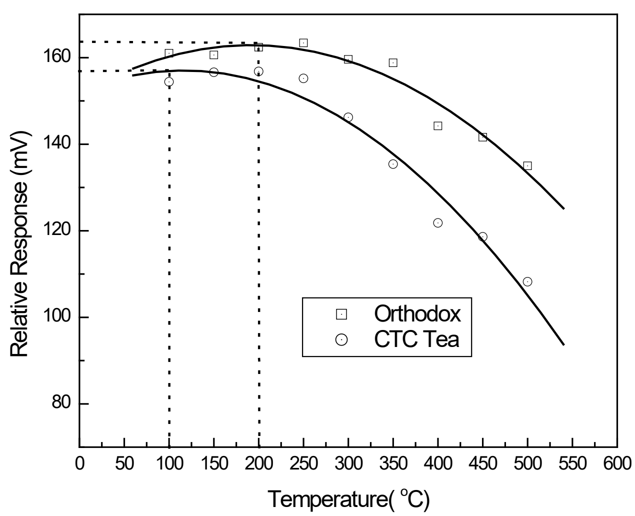

Fig.5: Response of the ZnO nanowire gas sensors are measured with Orthodox tea and CTC with varying temperature.

Lowering of sensitivity with higher temperature could be explained due to following fact that adsorbtion of VOC molecules over nano-porous sensor substrate is reduced at elevated temperatures. The little rise in response for the range 100□C to 200□C can be due to higher mobility of VOC components.

3.3 Measurement of sensor characteristics

The sensitivity, response time and signal-to-noise ratio of two kinds of teainfusion are presented in **Table-I**. The sensitivity of ZnO based nanosensor is defined as

$$\%S = (R_g - R_a)/R_a = \Delta R/R_a \qquad (1)$$

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 is measured by the signal response divided by the mean fluctuation of results from its average value.

Table-I: Response characteristics of semiconducting ZnO film sensing devices when exposed with Darjeeling Orthodox tea and CTC tea.

Type of tea	Sensitivity (%)	Response time (Sec)	Signal-to-Noise (S/N) Ratio
Orthodox	0.12	540	127
CTC	0.10	600	64

It is observed that sensitivity of CTC tea is higher than that of Orthodox tea. However the orthodox tea has got faster response. The signal-to-noise ratio for Orthodox tea leaves has got higher value than that of CTC tea. The differences in sensitivity are due to different types of organic molecules vaporized for different types of tea leaves. The response time is related to the vapourization rate of organic molecules concerned. At same temperature, different organic molecules vaporize at different time. As the VOC compositions of different types of tea are different, the vaporization rates of VOC's are different, resulting in differences in response time.

4. Conclusion

Nanostructured sensing element of ZnO was fabricated on glass substrate. The microstructure shows neat columnar structure with uniform porosity. X-ray diffractogram shows formation of pure ZnO phase. The nanostructured ZnO film showed distinct change in their resistivity with infused tea leaves of different types. Due to its characteristic pore structure organic gas molecules are adsorbed over sensing surface resulting in selective response with different types of tea. Sensitivity of CTC tea is found to be lower than that of Orthodox tea which may be due to the more number of flavoury VOC's in Orthodox tea infusion. The response time and signal-to-noise ratio in Orthodox tea are also better than CTC tea. Further investigation is under progress to fine tune the response of the two types of tea leaves by changing the size of the microstructures and also by doping ZnO film with appropriate materials.

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