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Material dependent and temperature driven adsorption switching (p- to n-type) using CNT/ZnO composite-based chemiresistive methanol gas sensor

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ABSTRACT

The present study correlates two simultaneous as well as significant observations coming out from a single component concerning the detection of volatile organic compounds (VOCs) by a carbonaceous material based sensor. We have developed a composite based chemiresistive sensor utilizing two different components (carbon nanotube (CNT) and zinc oxide (ZnO)). This reflected in an unique adsorption switching phenomena followed by a ‘p- to n-’ type transition characteristics above a certain operating temperature (150°C) in the VOC detection process. Noticeably, by the virtue of adsorption switching, the CNT/ZnO composite is particularly able to operate as a dual mode sensor, i.e. CNT is dominating in low temperature region ($\leq 150^{\circ}\text{C}$), and ZnO at high temperature region ($>150^{\circ}\text{C}$) with a realistic detection ability. The highly reproducible sensors (29 prototypes) are selective towards methanol (Response, $R \sim 73 \pm 3\%$) and shows 8-fold enhancement in response value compared to neighbouring VOC i.e., ethanol at an operating temperature of 150°C with a very low bias voltage of 10 mV. Finally, the adsorption switching phenomena (physisorption to chemisorption) explained by Fourier Transform Infrared Spectroscopy (FTIR) study and activation energy values along with ‘p- to n-’ type transition is compared qualitatively with a typical full wave rectification process for informal consideration.

Keywords: Carbon nanotubes; ZnO nanostructure; chemiresistive sensor; adsorption switching; p- to n- transition; VOC detection.

1. Introduction

Over the past few decades the rapid advancement of the modern and technology embedded lifestyle undoubtedly takes part to enhance environmental pollution especially by the emission of hazardous gases of different origin. In recent years, a compact and reliable gas monitoring system is of paramount demand considering the toxic components and its effects on human health are under intense investigation [1]. Among the toxic components, volatile organic compounds (VOCs) like, ethanol, methanol and many others are key contributors to the health hazards. The endless toxic effects of these VOCs is the fundamental cause for many critical diseases, such as asthma, cancer, emphysema etc. [2,3]. These necessitates timely and precise detection of these toxic component that are one of the unavoidable requirements in present day devices[4]. Over the past few decades metal oxide semiconductors (MOS) are the first and foremost choice as a gas sensing material due to its faithful and promising characteristics such as low cost, small size, simplest detection technique, high stability, wide range of gas sensing applications etc., [5–9]. Among the MOS, zinc oxide (ZnO) is the most widely investigated material as a gas sensor due to its high efficiency[10–13].

However, in spite of, ease of fabrication and other favourable parameters; its inability of low temperature gas sensing makes it difficult to be used in room temperature or low temperature sensors [14]. A minimum operating temperature of 200°C is required to be able to sense the presence of a particular gas/vapor in a typical MOS sensor. Researches around the world are actively working in this area to minimize or completely eliminate the difficulty of room temperature gas sensing. Also the use of additional heating element to achieve the elevated operating temperature, which effects the power consumption as well as the thermal safety of the gas monitoring system [15–17]. In order to facilitate a wide temperature range (from low to high) to address this challenging issue on gas sensing, composites are promising material due to its uniquely developed sensing characteristics as compared to a single component [18,19]. In particular low cost carbon based systems such as carbon nanotube (CNT), graphene or highly oriented pyrolytic graphite (HOPG) for making a composite material with MOS in nano domain offers a great solution to this challenge [20]. Among, the various carbonaceous materials, CNTs are considered as a key member for making gas sensors due to its unique properties like, large effective surface area, porous structures and available sites for gas adsorption [21,22]. In addition, its high sensitivity to any kind of change in

chemical environment and its ability to work at relatively low temperature makes them as an unconditional choice for gas sensing material [23,24]. On the other hand, graphene or HOPG, a chemically stable sensor can also be formulated which operates at room temperature without any auxiliary heating.

Among the various improvement in this field of gas sensors, a typical *p*- to *n*- type transition characteristics is the very recent in the process of gas detection. These two different types of sensors classified on the basis of decrease (*p*-type) or increase (*n*-type) in conductance with respect to the exposure of reducing gases (VOCs). Up and until now, a very few *p*- to *n*- (or *n*- to *p*-) transitions are reported in sensor material [25]. Most of the reported work is related to the measurements of conductance and changes to the work function [26]. Dai *et al.* [27], reported reversible switching from *p*- to *n*- transition while detecting nitrogen dioxide (NO₂) utilizing α -Fe₂O₃ monolayer thin film. In that work, the *p*- to *n*- transition is specific to a particular gas/vapor at a relatively higher transition temperature (250 - 350°C). Jang *et al.* [28], reported in a metal organic framework-template in which a chemiresistor was used to detect acetone. In their work, the so called *p*- to *n*- type transition was achieved by the complex galvanic replacement reaction involving a *p*-type (cobalt oxide) and *n*-type (tin oxide) material associated with the metal organic framework. Furthermore, the enhancement of gas response was achieved at relatively high temperature region (450°C). Hence, there is a need for two tier switching systems takes care of both low and high temperature regime. To the best of our knowledge, we are demonstrating for the first time the switching of gas adsorption process followed by *p*- to *n*-type transition, controlled by the two different component of a single sensing unit (composite in nature). These are as a function of operating temperature (low as well as high).

In our work, the *p*- to *n*- type transition behaviour and its sensing mechanism has been clearly correlated to the temperature and material dependent switching in the VOC adsorption process. ZnO/CNT composites were chosen in our work among the other metal oxides as a key material due to its ease of low temperature synthesis (~ 95°C), wide range of VOC sensing, stability and other favourable parameters.

Even if CNT grabs the limelight for making a composite VOC sensor but, instead of observing the solo performance of CNT attached to ZnO as a composite sensor, we also utilise graphene sheet and HOPG to construct two other prototypes and compare their VOC sensing performance separately with varying temperature (for details, please refer to the supporting information section). The adsorption switching mechanism (physisorption to chemisorption) plays a leading role in determining the response of the sensor for low as well as high

temperature application. Thus, our synthesized prototype (e.g CNT/ZnO composite) will be a wise choice to fulfil the purpose with material dependent, thermally driven adsorption switching will be greater interest to scientific community.

2. Experimental details

2.1. Materials

All analytical grade chemical reagents were used in all our experiments to avoid any purification processes. Zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ ($\geq 98\%$) and hexamethylenetetramine $[(\text{CH}_2)_6\text{N}_4]$ ($\geq 99\%$) were procured from Sigma-Aldrich, USA, CNTs (diameter 30–50 nm and length 40–70 μm , density 1.1 g/cm^3 , purity $> 98\%$) from Nanoshell USA, graphite sheet was received from Kaneka Corporation, Japan and HOPG (Dimensions: $12 \times 12 \times 2 \text{ mm}^3$) was received from NT-MDT Spectrum Instruments, Moscow, Russia. In all our synthesis process we used Ultrapure water (Milli Q, resistivity $> 18.2 \text{ M}\Omega \cdot \text{cm}$).

2.2. Synthesis of CNT/ZnO composite

A mixture of equimolar (50 mM) aqueous solution of zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ and hexamethylenetetramine $[(\text{CH}_2)_6\text{N}_4]$ was prepared under continuous stirring at room temperature (RT). To this aqueous solution, CNT of 0.1 weight percentage (wt%) was taken and continuously stirred for few hours at RT. The prepared solution was heated at a constant temperature of 95°C for about 1 h. The solution was allowed to cool to RT naturally, resulted in a (CNT/ZnO) powder form and, the powder was washed with ultrapure water and then dried for 24 h. in a hot air oven. Using Uniaxial pressing instrument (CARVER, Indiana, USA) was used to compact the CNT/ZnO powder at a compaction pressure of 520 MPa for fabricating circular pellet specimens (diameter: 10 mm and thickness: 7 mm). Gas sensing measurements were carried out by making CNT/ZnO composite pallets

2.3. Synthesis of graphene/ZnO or HOPG/ZnO composite

An equimolar (50 mM) aqueous solution of zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ and hexamethylenetetramine $[(\text{CH}_2)_6\text{N}_4]$ prepared using the similar procedure as above at RT. Graphene sheet or HOPG as substrate were dipped into the solution for 1 h at 95°C to form another composites of graphene/ZnO or HOPG/ZnO. Prior dipping graphite sheet into zinc acetate solution, few graphene layers was exfoliated by chemical treatment reported elsewhere

[29]. Then, graphene/ZnO or HOPG/ZnO composite based microstructures are removed from the solution, rinsed in ultrapure water and finally dried for 24 h in a hot air oven.

2.4. Characterizations of composites and measurement of gas-sensing properties

The phase formation of the synthesized composites was studied by the X-ray diffraction (XRD) pattern (X' Pert PRO, PANalytical) using a Cu K α 1 radiation (wavelength, $\lambda=1.5406$ Å). Data were collected in the range of 20-70° with a step width of 0.02° and a scan rate of 0.2° min⁻¹. All the powder diffraction data were collected by applying a tube voltage of 40 kV and a tube current of 30 mA. A field emission electron microscope (FESEM) (evo 60, Carl Zeiss, Switzerland) was used to investigate the surface morphology of the as-synthesized composites. The micro-structural analysis was carried out using a transmission electron microscope (TEM) (JEM-2100, JEOL, Japan). The Fourier Transform Infrared Spectroscopic (FTIR) (IRPrestige-21, Shimadzu, Japan) was carried out with and without the presence of respective VOC vapors to investigate the interaction between sensing materials and target VOC. The gas sensing measurements were carried out using an indigenously developed gas sensing measurement system shown in [Fig. S4 \(Supporting Information\)](#). The electrometer unit (6517A, Keithley Instruments, USA) equipped with a data collection system was used for current-voltage measurements. A set of 29 similar types of samples was used to record the sensing behaviour for reproducibility of CNT/ZnO composite and the average value of the change in conductance is utilized to represent the conductive transient curves. In a primary stage, the transient current was measured for a low fixed bias voltage (10 mV) at different operating temperature through periodically testing the sensor in air. The target VOC (desired concentration in form of liquids were injected by a microliter syringe with a volume precision of < 2.5% into the stainless steel chamber) using a fixed concentration (about 25 parts per million (ppm)). The details for calculating VOC concentration in ppm is shown in supporting information ([Table S2](#)). To control the relative humidity (RH) for sensing, a pumping system along with a humidity controller (E-14009384, ZORBES) is used that connects the water bath to the gas sensing chamber to transfer required RH air to the test chamber. To control the RH at low values, silica gels are used to absorb excess humidity of the test chamber and to keep RH at desired low level. The temperature of water bath controlled by using a high precession temperature controller to get the desired RH level in the test chamber. A similar protocol has been used in FTIR test to maintain a constant RH to 26%. Finally, the response (R) to a particular VOC expressed in terms of the change in conductance by the equation: $R = (\Delta G/G_a) \times 100\%$ where, $\Delta G (= G_g - G_a)$ represents change in conductance of the sensing

material when it is exposed to the VOC from air. For the p -type sensing behavior $\Delta G = (G_a - G_g)$ and for n -type sensing it becomes $(G_g - G_a)$. Again, G_g is the conductance measured in the presence of the gas being sensed and G_a is the conductance measured in air (i.e., in the absence of the vapor being tested).

3. Results and discussion

3.1. Structural study and gas sensing

Fig. 1 shows the XRD pattern of the as synthesized composites. The observed XRD patterns of CNT/ZnO along with other carbonaceous based composites (graphene/ZnO and HOPG/ZnO) are found to be matched with standard crystallographic data (ZnO: Joint Committee on Powder Diffraction Standards (JCPDS) 01-076-0704, Carbon: JCPDS 00-026-1080). It confirms hexagonal wurtzite structure of ZnO. A detailed structural analysis has been performed using Rietveld refinement technique (Fig. S1) (Supporting Information) and the refined parameters are shown in Table S1 (Supporting Information). The extracted refined parameters for CNT/ZnO, graphene/ZnO and HOPG/ZnO reflects the fact that there is no significant change in the crystal structure of ZnO due to the incorporation of different carbonaceous materials (CNT, graphene and HOPG) which in turn consistent with other similar reports [30–31].

3.2. Morphological study

The morphologies of CNT/ZnO composite have been observed from SEM image as shown in Fig. 2(a). Please refer to Fig. S2(a–b) (Supporting Information) for morphologies of graphene/ZnO and HOPG/ZnO. It is seen from the Fig. 2(a) that the CNT is attached to the wall of ZnO micronuts. Fig. S2(a) (Supporting Information) shows the SEM image of ZnO grown on graphite sheet where graphene is chemically exfoliated from graphite [29]. Fig. S2(b) (Supporting Information) shows the SEM image of ZnO micronuts grown on HOPG, where graphene layers from HOPG are exfoliated during ZnO growth and well attached with ZnO micronuts. The distribution of diameter of ZnO in the composite is about 120 nm – 3 μ m. The insight structures and crystallinity of ZnO micronuts was confirmed by TEM, as shown in Fig. 2(b). It is certainly observed that CNTs are dispersed and wrapped on the surface of ZnO indicating the attachment between them and is strongly affects their sensing properties. The selected area electron diffraction (SAED) pattern (Fig. 2(c)) indicates that each ZnO micronuts is a hexagonal single crystal. The diameter and length variation of as synthesized ZnO micronuts in CNT/ZnO, graphene/ZnO and HOPG/ZnO composite is shown in Fig. S3(a–b)

(Supporting Information). The width of ZnO micronuts in CNT/ZnO composite is in the range of 100 nm – 3.2 μ m whereas, the maximum length for ZnO micronuts in CNT/ZnO, graphene/ZnO and HOPG/ZnO composites is within 5.5 μ m.

3.3. Gas sensing performance

The VOC detection characteristics of the as prepared composite prototype has been explored by utilizing a number of volatiles in a wide range of working temperature (50 – 250°C) for a fixed amount of the target VOCs about 25 ppm. A set of 29 similar kinds of samples (synthesized following the same protocol) has been utilized for the gas sensing measurements and the conductive transient curve shows same type of sensing characteristics with a negligible deviation which in turn reflects the reproducibility of the material. The prototype also proves its device forming capability for practical application as shown in Fig. 3(a–c). A very simple and low cost sensing device has been developed by using low cost and easily available components utilizing a pellet (diameter: ~1 cm) of CNT/ZnO composite. Fig. 3(a) shows the overall view of the compact sensing device and Fig. 3(b) reflects the closer image of the same. The inset image of Fig. 3(b) shows the actual dimension of the pellet. The circuit and its connections for two probe measurement sensing device is shown in Fig. 3(c). The material in device form shows similar kind of sensing characteristics in the laboratory using experimental setup (Fig. S4) (Supporting Information). Fig. 3(d) shows the pulse like temperature dependence conductance transient characteristics of the CNT/ZnO sensor for methanol. In the conductance transient curves a typical ‘*p*- to *n*-’ type transition characteristics was observed as a function of operating temperature. The highest response ($R = \Delta G/G_a \times 100$) of $73 \pm 3\%$ has been achieved at an optimum temperature of 150°C for 25 ppm exposure of the methanol vapor. The other selected volatiles (ethanol, formaldehyde, ethylene glycol and 1-propanol) have also been tested to compare the sensitivity and selectivity, and the corresponding conductance transient is shown in Fig. 4(a–d) using a fixed amount of 25 ppm targeted VOCs. For better visualization of the conductance transient observed at 50°C for 25 ppm exposure of ethylene glycol (Fig. 4(c)), shown in Fig. S5 (Supporting Information). In all conductance transient curves, particularly in the *p*-type region, the conductance of the material decreases upon exposure to different volatiles (reducing gases) whereas it increases in case of *n*-type region (>150°C). It is also undoubtedly observed that the sensor response decreases beyond 150°C (for most of the target volatiles). This might be due to the amount of adsorbed gas on the surface of the material decreases, while the desorption process becomes dominant

with increasing operating temperature, leading to a reduction in response. When the desorption rate of the gas becomes equal to that of adsorption, the maximum loading of chemisorbed ions reaches the optimum temperature accelerating the reduction of VOCs molecules, resulting in the highest response. However, for some specific VOCs (like ethanol), the response decreases with increasing temperature. This effect may be attributed to the difference in diffusion character of the different VOCs with temperature. A '*p*- to *n*-' transition has been observed in all the conductance transient characteristics above an operating temperature of 150 °C irrespective of the tested VOCs.

Comparing the results found in Fig. 3(d) and Fig. 4, there is an 8-fold increase in gas response toward methanol as compared to ethanol vapor ($R \sim 9.2\%$) at 150°C, suggesting the high selectivity of the CNT/ZnO composite toward methanol. Fig. 5(a) compares the response in % of the sensing material as a function of operating temperature (50–250°C) for different VOCs. The transition diagram of the sensor response of detecting 25 ppm methanol vapor is shown in Fig. 5(b) which clearly indicates that the temperature controlled *p*- to *n*-type switching character ($>150^\circ\text{C}$) possessed by the composite sensing device. For confirmation of *p*- to *n*-type transition, we have also tested VOC detection using other prototypes of graphene/ZnO and HOPG/ZnO composite based sensors and it behaves similar *p*- to *n*-type transition to the CNT/ZnO. Moreover, graphene/ZnO is selective towards methanol (Fig. S6) (Supporting Information), whereas HOPG/ZnO shows highest response for 1-propanol at 150 °C (Fig. S7) (Supporting Information). The variation of sensor response (*R*) with increasing vapor concentration (*C*) also tested for CNT/ZnO sensor. Fig. 6(a-b) shows the variation of CNT/ZnO sensor response with increasing methanol concentration (1-100 ppm) for low (150°C) and high (250°C) operating temperature. The inset images of Fig. 6(a) and (b) shows the fitting of sensing response towards the said concentrations of methanol to Freundlich isotherm equation [32]: $\log R = \log \alpha + \beta \log C$ with linear regression. Where, *R* is the response of the sensor, α is proportionality factor, β is the exponent and *C* is the concentration of methanol. The as obtained β values particularly for high temperature region is very close to unity ($\beta=0.96$) as compared to low temperature region ($\beta=0.82$). This increase in β value towards unity (01) clearly indicates the possibility of chemisorption in high thermal region ($>150^\circ\text{C}$) and physisorption in low thermal region ($\leq 150^\circ\text{C}$) [32]. Furthermore, it seems Freundlich isotherm equation is not good enough (correlation coefficient, Adjust $R^2 = 0.8945$) for linear fitting especially in Fig. 6 (a). So, the same data was fitted (Fig. S8) (Supporting Information) using Langmuir isotherm equation [32]: $R = \frac{\beta R_{\max} C}{1 + \beta C}$ with linear regression. Where, *R* is the response

of the sensor, β is the Langmuir isotherm constant, C is the concentration of methanol and R_{max} is the maximum response. As shown in Fig. S8(a) and (b) (Supporting Information), the Langmuir isotherm equation in linear form are well fitted with the experimental data, where the correlation coefficients (Adjust R^2) are 0.9814 and 0.9864 for 150°C and 250°C operating temperature, respectively. These Adjust R^2 values indicating that the Langmuir isotherm is appropriate for describing the detection ability towards methanol. The selective detection of methanol among other four tested VOCs was further confirmed by the principal component analysis (PCA) as shown in Fig. 7. The PCA analysis reveals that, 1-propanol, ethylene glycol and formaldehyde belong to the negative quadrant of the PCA curve among the five targeted volatiles. Furthermore, ethanol and methanol is related to the positive quadrant, whereas methanol is very closer to the origin indicates a strong correlation and thus proves the selectivity towards this particular VOC for the sensor.

The solo components (i.e., ZnO and CNT) of the CNT/ZnO composite detect the target volatiles either in high temperature region (for ZnO only) or in comparatively low temperature region (for CNT only) separately. Table 1 compares the detection ability of these two constituents depending on the required operating temperature as per the previous reported works. It is clear from the intense information of Table 1 that a single component (i.e., either ZnO or CNT) is not enough to serve the purpose of full thermal range gas sensing. So, we combine the both to get a composite sensing material which can remove its inability of low temperature gas sensing of ZnO by the blessings of detection ability of CNT in low thermal domain. On the other hand, a very low bias voltage (1–10 mV) is required to observe the gas sensing behaviour which also enhances the importance of the material as a potential choice for making a self-powered sensing device in future.

‘Reversibility’ is one of the principal features of a successful gas sensor for its device forming capability and long term application. A reversible gas sensor that completely regain its initial state (a stabilized conductance in presence of air/before exposing to target vapor) when it is re-exposed to air (at the time of recovery) after the application of a target vapor/gas for a desired interval of time [12, 33]. In simple words, if we observe the total change in signal (i.e. changes in conductance/resistance/current) upon exposure to a target gas/vapor (response) is exactly or nearly equal to the total change in signal at the time of recovery (in presence of air) is an indication of sensing material as a reversible one. In our case, most of the conductance transient characteristics shows a reversible type behaviour except a very few (in Fig. 3(d) @ 100°C, Fig. 4(a) @ 50°C and 100°C etc.) in the low temperature domain. These few

conductance transients, irreversible in nature might be understood by considering a slow desorption rate of the target analytes due to the lack of thermal energy in this region.

On the other hand, response and recovery time are the key features for a particular gas sensor when timely detection of gas/vapors are concerned. Response (τ_{res}) and recovery (τ_{rec}) time was calculated on the basis of time taken to reach the 90% of the total signal change [90% of ($G_g \sim G_a$)] after the introduction of VOCs and the time involved to recover up to 90% of the same after re-exposing to air as shown in Fig. 8(a). The variation of response time with the operating temperature for CNT/ZnO sensor is shown in the Fig. 8(b). The lowest response time ($\tau_{\text{res}} = 3.15$ s) has been observed for 1-propanol at 250 °C. The variation of recovery time shows similar decrement in nature as a function of operating temperature, where the lowest recovery time ($\tau_{\text{rec}} = 3.45$ s) has been achieved with 25 ppm formaldehyde at 250 °C. The gradual decrease in response and recovery time with increasing operating temperature can be attributed to faster reaction of the VOC molecules with the adsorbed (ionized) oxygen on the surface of composite. So, a fast response and recovery character is associated with the present sensor especially at high temperature region.

The long term stability is a necessary feature for commercial application of any gas/VOC sensor. In view of this, Fig. 9(a) delineates the variation of response as a function of duration of use as long as for 300 days. The as prepared CNT/ZnO composite sensor shows a little deviation (3%) in response value with 25 ppm methanol vapor at 150 °C which in turn reflects the long term stability of the sensor. The inset of Fig. 9(a) shows the variation of baseline conductance value with duration of use in same operating condition. It can be noted that the deviation of the baseline conductance value is very less for CNT/ZnO composite sensor. Furthermore, to observe the humidity variation on the response of the sensor, it was tested for 25 ppm methanol vapor operating at 150 °C (for highest response) with various percentage of RH (10 – 90%) as shown in Fig. 9 (b). It is very obvious that, the humidity will block the active sites of the sensing material which in turn decrease the response of the sensor. In region-I (RH = 10 – 50%) the response of the sensor was quite stable, whereas the response was highly affected by the presence of humidity in region-II (RH > 50%) (Fig.9(b)). As the prepared prototype may be principally used to detect various biomarkers through analysing exhaled breath (with RH $\approx$ 34%) so, the present prototype can be used to detect methanol in region-I (RH = 10 – 50%) without any remarkable deviation in response value. The inset of Fig. 9 (b) shows the variation of baseline conductance with the RH (10 – 90%). At low values of RH (10

– 50%) the baseline conductance shows less deviation as compared to in high RH values (RH > 50%).

Activation energy values both in high and low temperature region are considered to be very important and useful to evaluate the mechanism of sensing. From the response characteristics, activation energy for different VOCs with different temperature range can be calculated by using Arrhenius equation [34–35], $\tau_{res} = \tau_0 \exp(E_a/2kT)$, where, E_a is the necessary activation energy for the conductive response to the respective VOC vapors, k is the Boltzmann constant and T is the operating temperature of the sensor at absolute scale. Depending on the linear relationship between $\ln\tau_{res}$ with $1/T$ the activation energy can be estimated from the slope of the curve relating $\ln\tau_{res}$ and $1000/T$. In this present study, the activation energies calculated for individual VOCs considering two different temperature regions, i.e., up to 150 °C as a low and above this as high temperature region. From the slope of the curves shown in Fig. 10 the activation energy for two different thermal regions are extracted for the detection of methanol and also for other vapors in a similar way. The as calculated E_a values (shown in Table 2) are relatively higher at high temperature region indicating a strong probability of switching to chemisorption from physisorption, i.e., adsorption switching associated with the VOC detection process which is already reveals from the calculated β values by Freundlich isotherm [32].

3.4. Gas sensing mechanism

Now it is essential to uncover the mechanism of sensing related to the material. Two different aspects are involved in the detection of VOC phenomenon related to the present study, i.e., ‘adsorption switching’ and ‘*p*- to *n*- type transition’. In the low temperature region ($T \leq 150^\circ\text{C}$), *p*-type sensing behaviour is observed which can be enlightened by considering the physisorption process occurring on the surface of CNTs attached to ZnO micronuts [36–38]. The thermal energy is not sufficient to trigger the chemisorption as suggested by the lower activation energy (E_a) values obtained in this region. One of the dominating factors related to physisorption phenomena is the high effective surface area. In this regards CNTs can act as a functional material for sequential surface reactions with adsorbed oxygen ions and VOC molecules by providing high surface area to facilitate the physisorption process in the low temperature domain as compared to ZnO. As a result, in the low temperature region CNTs contributes more for sensing the VOCs rather than ZnO and the composite sensor behaves like a *p*-type (reduction of holes due to recombination to free electrons). Beyond 150 °C (considered as a high temperature region) the sensing behaviour changes to *n*-type in nature due to the

switching of the adsorption process followed by the switching of the sensing component (from CNT to ZnO). The thermal energy associated within this region is high enough to activate the chemisorption phenomena (high activation energy). In this region of temperature, ZnO plays the dominating role in determining the response as the sequential chemisorption reaction occurs on the surface of ZnO rather than CNT. The thermal chaos associated with the high temperature on the surface of CNT decreases the possibility of occurrence of physisorption process [37, 39–40]. Therefore, the sensing mechanism is actually similar to the pure ZnO with the addition of the bridge electron existence from the CNTs [41–42].

For evaluating the fact of adsorption switching and also the possible gas sensing mechanism, FTIR study was carried out for CNT/ZnO composite in absence and presence of methanol vapor (25 ppm) in low (150 °C) as well as in high temperature (250 °C) region. The observed FTIR spectra for both the thermal region is as shown in Fig. 11(a) and (b) respectively. It can be clearly observed from both the FTIR spectrum (without VOCs) that the peak very near to at 547 cm^{-1} is designated as the stretching vibrations of Zn–O [43]. The peak very near to 1650 cm^{-1} is responsible for stretching vibrations of –C=C– in CNT [43]. An additional peak at 3435 cm^{-1} indicates the –OH groups absorbed on the surface of CNT/ZnO composite [43]. At low temperature region (Fig. 11(a)) in presence of methanol vapor there was no remarkable shift in peak positions except a change in the peak (from 1650 – 1658 cm^{-1}) for stretching vibrations of –C=C– in CNT which indicates the interaction of VOCs mainly on the surface of CNTs. An additional peak appears near to 1030 cm^{-1} , which belongs to single characteristics methanol band provides a direct evidence of the physisorption of the species on the sensor surface [44]. On the other hand, the observed FTIR spectrum (Fig. 11(b)) at high temperature region shows a significant change in the peak position related to the stretching vibrations of Zn – O (from 552 – 584 cm^{-1}) in presence of methanol vapor. All the other peaks were almost unaffected (or partially affected) in this condition. Summarizing these two observations it was very obvious that, at low temperature region, VOCs interact mostly with the CNT surface rather than ZnO preferably through the process of physisorption (no significant peak shift) as there is no additional peaks appear in the spectrum except the peak for methanol [45]. On the other side, considering high temperature region, the VOCs preferably interact with the surface of ZnO rather than CNTs may be through chemisorption process (significant change in shape and position of peak). These two cumulative effects provide the ‘p- to n- type’ transition in the sensing of VOCs by CNT/ZnO composite sensor.

Furthermore, a *p-n* heterojunction is expected to form on the interface of CNT and ZnO in every contact point. This will also affect the sensing properties of the composite sensor. Due

to the interaction of a p-type (CNT) and n-type (ZnO) material a built in potential was generated. So, there should be a decrease in this potential when VOCs are adsorbed on the surface of the composite sensor [14]. This decrease in junction potential also gives contribution to the overall sensing process. A schematic illustration with electron transfer mechanism is given in Fig. 12 related to the phenomena.

From Table 1 that any one of the two components (either CNT or ZnO) of the composite takes active participation to detect the target analytes for one particular thermal region. Interestingly, this typical VOC sensing behavior is hypothetically similar to the working principle of a ‘full wave rectifier’ where alternatively two diodes are in ON and OFF condition for one half cycle of the full signal to achieve a full wave rectification. In this study, for the low temperature region, CNT is said to be in ON condition (i.e ZnO: OFF) to detect the volatiles whereas, ZnO becomes ON (i.e CNT: OFF) for the detection of the same in comparatively high temperature region providing the wide (or full) thermal range (low to high) VOC detection capability of the as prepared CNT/ZnO composite sensor. The comparative phenomenon is shown in Fig.13 clearly where we compare the ‘CNT/ZnO Composite sensor’ with a ‘full wave rectifier’ to understand the sensing mechanism in a better way.

4. Conclusions

We have successfully developed and demonstrated a hybrid sensing prototype for detection of toxic VOCs by synthesizing a composite of ZnO and CNT. It is able to operate within a wide temperature range. Switching of VOC adsorption process as a function of operating temperature and composite material, provides a distinguishable property to this sensor and able the material to operate in high as well as low temperature region. The as mentioned adsorption switching mechanism is further confirmed by the typical *p*- to *n*-type transition behaviour observed above 150 °C in all the conductive transient curves irrespective of tested VOCs. FTIR study provides the evidence for the physisorption and chemisorption in low and high temperature region, respectively. Among the other four interfering vapors the present prototype can selectively detect methanol with a response of $\sim 73 \pm 3\%$ at an optimum operating temperature of 150 °C. Requirement of very low bias voltage (≤ 10 mV) to drive the VOC detection process confirms applicability of the material for a low as well as self-powered device in future. Device formation using the prototype provides its direct commercial application ability in different fields. So, the as synthesized sensing prototype reflects the parameters depending on which it can be used as a viable VOC sensor with ability to operate in a wide thermal region in addition to very low power consumption characteristics.

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Figure Captions

Fig. 1. XRD pattern of CNT/ZnO, graphene/ZnO and HOPG/ZnO composites.

Fig. 2. (a) FESEM image of CNT/ZnO composite. Inset image shows pellet with diameter 1 cm. (b) TEM image of ZnO micronuts attached with CNTs. (c) SAED pattern of ZnO indicates hexagonal single crystal.

Fig. 3. Actual picture of the device formed by CNT/ZnO composite: (a) full view, (b) close side view (inset shows the actual dimension of the sample), (c) two probe connection with the sample and (d) the conductance transient curve for methanol (25 ppm).

Fig. 4. Conductance transient curve of CNT/ZnO composite sensor using 25 ppm of selected four VOCs: (a) ethanol, (b) formaldehyde, (c) ethylene glycol, (d) 1-propanol.

Fig. 5. (a) A bar diagram showing all response of CNT/ZnO composite sensor for different operating temperature and targeted VOCs at fixed concentration of 25 ppm, (b) Transition diagram of CNT/ZnO sensor for a particular VOC (methanol) with a concentration of 25 ppm.

Fig. 6. Variation of CNT/ZnO composite sensor response with methanol concentration (1-100 ppm) at operating temperature (a) 150°C and (b) 250°C. Inset images shoes the linear fitted curve using Freundlich isotherm.

Fig. 7. PCA for five tested VOCs using CNT/ZnO composite sensor.

Fig. 8. (a) Response and recovery characteristics at operating temperature of 150°C and (b) Variation of response time with temperature.

Fig. 9. (a) Long-term stability and (b) Variation of response with relative humidity (RH=10 – 90%) for CNT/ZnO composite sensor operating at a temperature of 150°C for 25 ppm methanol vapor.

Fig. 10. Linear fitted curve for calculating the activation energy of CNT/ZnO composite sensor for methanol.

Fig. 11. FTIR spectra for CNT/ZnO composite in absence and presence of methanol vapor (25 ppm) at (a) 150°C and (b) 250°C.

Fig. 12. VOC detection scheme by CNT/ZnO composite sensor in low and high temperature region.

Fig. 13. Comparison between (a) full wave rectifier and (b) CNT/ZnO chemiresistive sensor.

Table Captions

Table 1. Comparison of operating temperature, response using ZnO and CNT based sensors for VOC detection.

Table 2. Activation energy values for different VOCs at different thermal region.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13