Sensors & Transducers, Vol. 206, Issue 11, November 2016, pp. 1-7

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Sensors & Transducers

Published by IFSA Publishing, S. L., 2016
http://www.sensorsportal.com

Integrated Sensing of Alcohols by CNT Blended HAp Nano Ceramics

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Received: 25 July 2016 /Accepted: 30 September 2016 /Published: 30 November 2016

Abstract: The research work reports the application of carbon nanotubes (CNT) blended Hydroxyapatite (HAp) composites as ideal thick film substrates for the detection of hazardous and flammable methanol vapours. The main objective of this work is to improve the temperature-dependent sensitivity of the sensor for the detection of lower methanol concentration. In this study, the sensing ability of native HAp and CNT blended HAp thick films is studied for the detection of methanol vapours present in ambient air individually and in the form of a mixture of methanol, ethanol, and propanol. The sensing parameters are studied using two probe electrical method. The sensor substrate is made by means of doping of different concentrations of CNT in HAp. The sensing of methanol vapours is studied at a fixed concentration of 100 ppm. Native HAp substrate shows good sensitivity for methanol at room temperature; however, its sensing performance is inferior to the CNT blended materials. The blended composites exhibit impressive sensing ability compared with native HAp in terms of sensitivity, response/ recovery time and maximum uptake limit. The sensing mechanism for methanol detection, the role of HAp as a parent material and CNT as an additive, is explained using a suitable sensing mechanism.

Keywords: Alcohol sensor, Carbon nanotubes, Gas sensor, Hydroxyapatite, Methanol sensor.

1. Introduction

Methanol is a liquid petrochemical volatile organic compound. It is one of the most versatile compounds having a variety of applications in various fields. Methanol is a building block for many industrial applications. It is used as an antifreeze, solvent, fuel, and also denaturant for ethanol. This chemical is also a key component of biodiesel production. Like most of the organic volatile chemicals, methanol must be handled, transported and used with great care. It has significant toxic, flammable and reactive properties, producing harmful effects on human health and the environment. Thus, to reduce methanol exposure, one should need a sensor that detects these vapours at their low concentration limits with accuracy and efficiency. The present work elucidates the development of nanomaterial based sensing substrate which works at the lower operating temperatures (almost room temperature) and shows better sensitivity for organic vapours at their lower concentration in ambient. Carbon nanotubes are the most desirable sensor substrate with enhanced surface to volume ratio, small grain size and remarkable electrical characteristics [1-4]. However, the surface of native CNT is not ideal for gas sensing application as it has less number of active reaction sites available for the adsorption of gas molecules [5-6], probably because of the perfect carbon- carbon network. The introduction of defects in carbon network via vacancies, functionalization or dopant, make it a desirable surface for gas sensing application due to creation of many active adsorption reaction sites [7-8]. The presence of defects drastically modifies the structure and electrical properties of this

material, thus creating a potential sensor substrate. The sensors, which are developed using carbon nanotubes as a dopant or functionalized CNT as supportive material, show excellent sensing characteristics. These sensors work at lower operating temperature compared with metal oxide doped material. Also, the response / recovery time for such sensors are found to be less long. Calcium Hydroxyapatite is a well-known material for sensing various gases due to its properties such as porous hexagonal network, nano grain size, and higher specific surface area is utilized as sensing substrate [9-14]. The HAp with chemical compositions as $[Ca_{10}\ (PO_4)_6\ (OH)_2]$ behaves as an ionic conductor. The presence of H^+ and OH^- ions (hydroxyl group) is found to be responsible for its conductivity at elevated temperatures [15-17]. At low temperature, the conductivity is either due to proton transfer among OH^- ions or migration of protons from OH^- to PO_4^{3-} ion [11, 18].

$$OH^- + OH^- \leftrightarrow O^{2-} + H_2O \quad (1)$$

or

$$OH^- + PO_4^{3-} \leftrightarrow O^{2-} + HPO_4^{2-} + OH \leftrightarrow O^{2-} + PO_4^{3-} + H_2O + \text{vacancy OH} \quad (2)$$

The protons (H^+), hydroxyl ions (OH^-), and oxides ions (O^-) control the reactivity when the adsorbed molecules come in contact with the surface. The interaction of volatile organic vapours ($C_xH_yO_z$) like methanol, ethanol and propanol etc. with HAp surface increases its conductivity since these vapours donate a proton to the surface resulting in decreasing the electrical resistance of the material. Thus the surface of HAp acts as a sensing substrate for the detection of organic vapours but like native CNT it also shows poor sensitivity towards the organic vapours. The surface modification is needed to improve its performance. The performance of the material is improved by surface modification. The present study deals with the utilization of sensing ability of HAp and CNT in order to get desirable sensing substrates for the detection of methanol vapor at 30^0C.

2. Materials and Methods

Calcium Hydroxyapatite is synthesized by following the path reported in our earlier publications [9-10]. In order to achieve the best blended sensing substrate, carbon nanotubes (CNT) in different weight concentrations is blended in HAp via liquid phase reinforce method under similar experimental condition [19]. A known quantity of CNT with nano HAp is dissolved in alcohol. The solution is kept under magnetic stirring followed by sonication. The mixture is allowed to dry at room temperature. The dried nano powder is sintered at 100 ^{0}C for 1 h in a programmable furnace to remove volatile compounds and water vapours. The powder is then mixed mechanically in an agate mortar continually for 4-5 hours. Scanning Electron Microscopy (SEM) is performed to analyze the morphological and structural characterization of the material. The crystallinity and purity of the material are tested by X-Ray Diffraction (XRD). Brunauer-Emmett-Teller (BET) surface analysis is carried out for the determination of surface area and pore size (volume and diameter). The prepared composite materials is deposited in the form of thick films by screen printing technique. The area for each prepared film is kept constant. A schematic sensing setup is employed to examine the sensing ability of the material [20]. The variation in resistance in the presence of atmospheric air and tested vapours is measured for a preset concentration of methanol under similar experimental conditions. The selective performance is tested by injecting a mixture of organic vapours into the chamber in a single stroke. The sensitivity factor (gas response) is calculated by using the equation

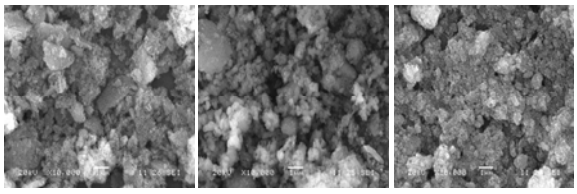
$$\text{Gas response } S(\%) = \frac{R_g - R_a}{R_a} \times 100, \quad (3)$$

where Ra and R_g represent the sensor resistance in the presence of atmospheric air and test gas respectively.

3. Results and Discussions

3.1. Morphological Analysis

The surface morphology for native HAp and CNT blended HAp is shown in Fig. 1. The surface of HAp is covered with a large number of small grain sized particles. These small grains are closely arranged over a large area. Such surface increases the possibility of interaction between organic vapours and the sensing substrate. It seems that there is more compactness on the surface for 0.7 wt% CNT, reducing the porosity.



(a) (b) (c)

Fig. 1. SEM micrographs for native HAp and CNT blended HAp (a) Native HAp, (b) 0.5 wt% CNT blended HAp, (c) 0.7 wt% CNT blended HAp.

3.2. Structural Analysis

X-ray diffraction pattern of native HAp, CNT and CNT blended HAp material is recorded for 2θ value between 20 to 60 degree with a scan rate 2 ^{0}/min with Rigaku diffractometer having Cu $K\alpha_1$ radiation (λ = 1.54 À). The X-rd profile of native HAp

synthesized by weight chemical precipitation method is depicted in Fig. 2(a). The planes of native HAp, (2 1 1), (3 0 0), (0 0 2), (2 1 3), (2 2 2) are clearly observed in the diffraction pattern. The major peaks of HAp present in the diffractogram exhibit hexagonal phase structure of HAp (JCPDS card No. 00-009-0432) [9-11, 14-15, 17]. The CNT blended HAp material also exhibits similar diffraction patterns. The peak for CNT with the plane (0 0 2) at 26^0 is not clearly discerned by diffraction pattern may be due to the small weight concentration of CNT in the composite material or presence HAp peak at the same plane.

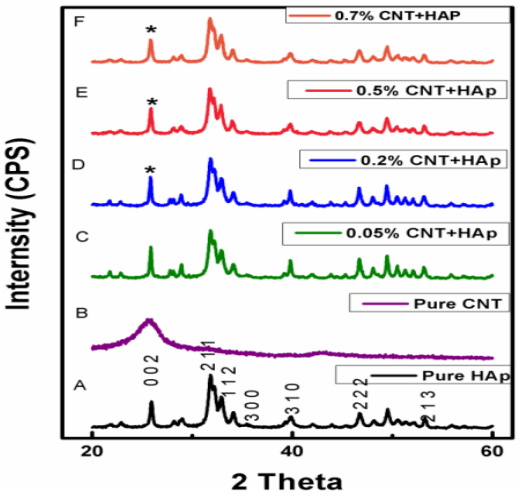


Fig. 2. X-ray diffraction pattern of native HAp, CNT and CNT blended HAp material (* represents the peak for CNT): Y-axis has arbitrary units.

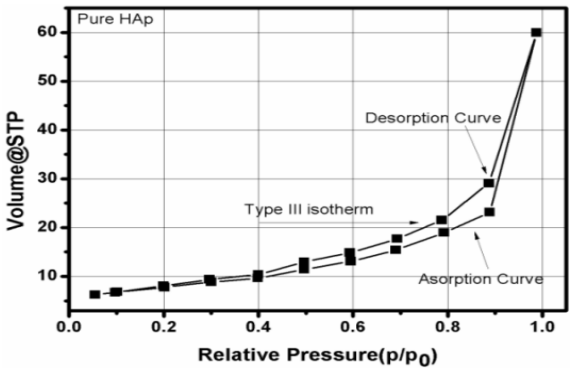
3.3. Surface area Analysis

The adsorption-desorption isotherm along with the pore size distribution is displayed in Fig. 3. The isotherms for both native HAp and 0.5 wt% CNT blended HAp are identified as type III showing weak interaction between adsorbent and adsorbate. The BJH pore distribution suggests the mesoporous nature of the material. The measured specific surface area of native HAp is 22.069 m^2/g, while that of 0.5 % CNT blended HAp is found to be 49.99 m^2/g which is more than twice the surface area of HAp.

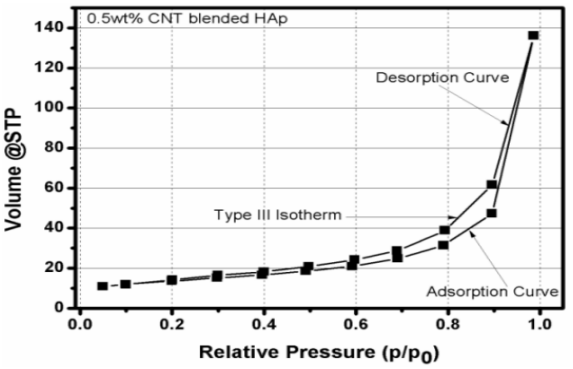
3.4. Methanol Sensing Properties

The response of the sensing substrate is tested at various elevated temperature in order to determine the operating temperature.

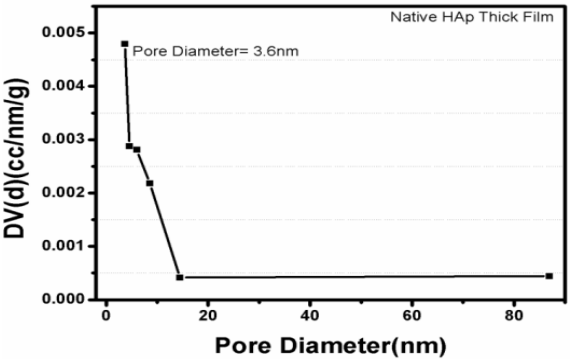
The operating temperature is defined as the temperature at which the sensor has a maximum gas response. A profile of gas response as a function of temperature for a fixed concentration of methanol is plotted in Fig. 4(a). Both the native HAp and CNT blended HAp materials show maximum sensitivity at 30ºC in the presence of 100 ppm methanol vapours.



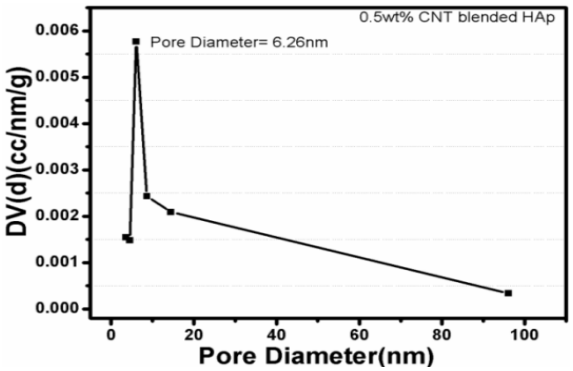
(a)



(b)



(c)



(d)

Fig. 3. N_2 adsorption/desorption isotherms (a) native HAp, (b) 0.5wt% CNT blended HAp and BJH pore size distribution curve (c) native HAp, (d) 0.5wt% CNT blended HAp.

The interaction of methanol molecules with HAp surface increases the sensitivity of the device by forming hydrogen bonding with HAp molecules. The methanol molecules interact with CNT via electrostatic interaction. It is believed that this interaction assists the unidirectional flow of electric current flowing through the tube (See Fig. 4(b)) increasing the sensitivity of the device.

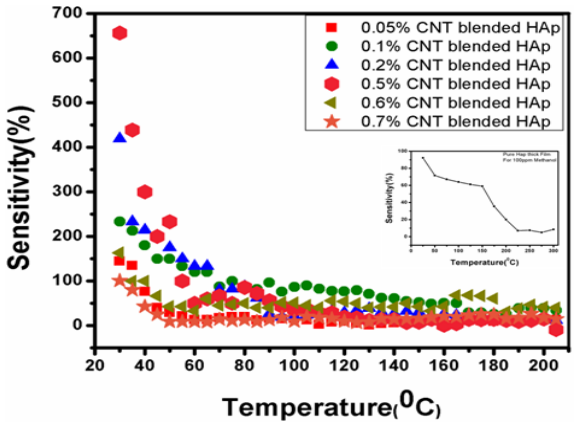


Fig. 4(a). Sensor sensitivity (response) of native HAp and CNT blended HAp at variable temperature for 100 ppm concentration of methanol.

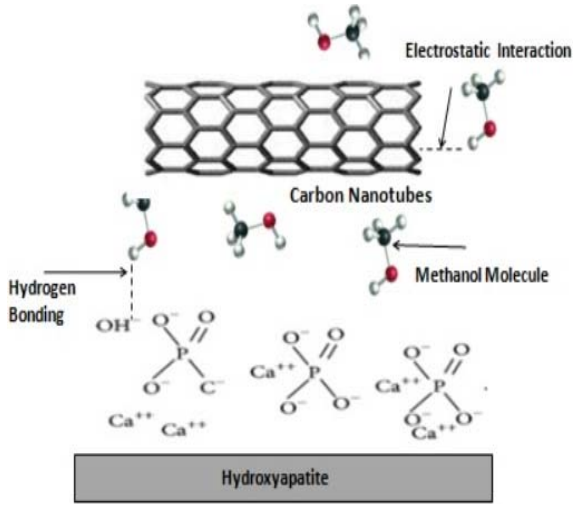


Fig. 4(b). Formation of hydrogen bonding, due to dipole-dipole interaction between polar methanol molecule and hydroxyl ions on HAp surface. Electrostatic interaction between methanol and CNT molecules leads to enhancement in the sensing property of the substrate material.

The variation in sensitivity as a function of CNT concentration in composite at room temperature (30°C) for 100 ppm methanol is shown in Fig. 5. The response varies linearly with CNT concentration, attains peak value for 0.5 wt% of CNT concentration, and afterwards, it decreases with increase in concentration. It shows that each composite material has its own impact on the sensitivity of the material. However, the response of 0.5 wt% of CNT concentration is superior with a magnitude approximately 600 %, when exposed to methanol at room temperature (30°C). This particular concentration leads to provide a balanced sensing layer for the gas sensing application. For higher concentrations, the surface modification doesn't support the effective sensing phenomenon.

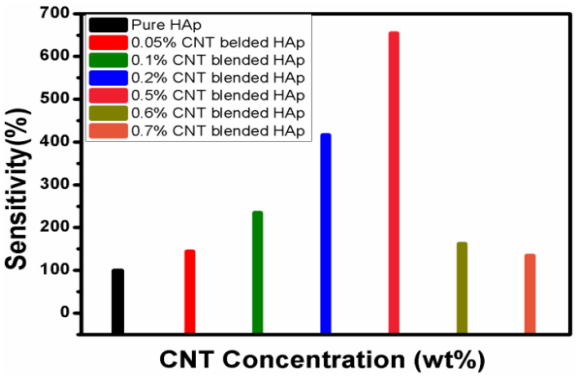
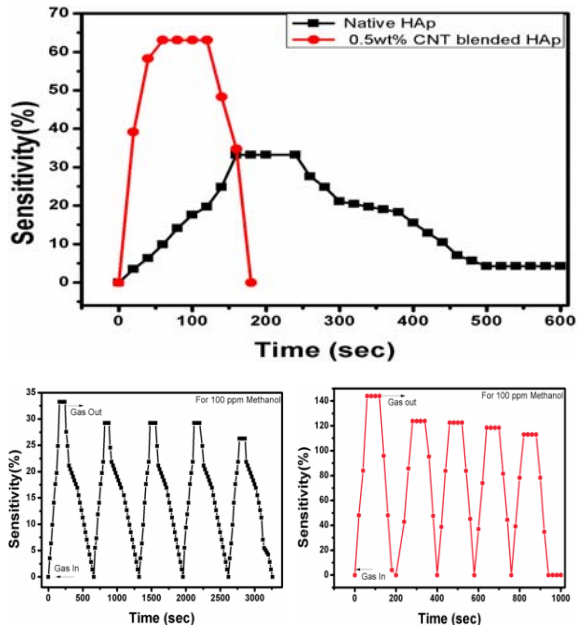


Fig. 5. Variation in sensitivity of methanol vapours for different CNT concentrations in HAp, at room temperature (30°C) for 100 ppm methanol.

A comparative study of the response/ recovery time characteristics of native HAp and 0.5 % CNT blended HAp material at room temperature (30°C) is carried out. The response of the material as a function of time is recorded by exposing the sample to detecting vapours and atmospheric air, respectively as shown in Fig. 6.



(a) (d)

Fig. 6. Response / recovery time plot for native HAp and 0.5 wt% CNT blended HAp thick films in the presence of 100 ppm methanol; Continuous repeated cycles for response / recovery time at room temperature (30°C), (a) native HAp, (b) 0.5 % CNT blended HAp.

The response time is 160 sec for native HAp substrate and 60 sec for 0.5 wt% of CNT concentration respectively. The material recovers more than 90 % of its initial value after exposing to atmospheric air. Native HAp shows sluggish desorption rate due to the polar affinity (hydrogen bonding between methanol molecules and HAp surface). In the case of CNT blended HAp composite material two possible types of physisorption may occur upon exposure to target molecule. One is a weak physisorption (van der Waals dispersion forces) between CNT molecules and target molecules. This force being weak, easily desorbed after exposing to atmospheric air at room temperature without any need for extra heat or energy resulting in faster recovery time. The other is the formation of hydrogen bonding (stronger than van der Waals dispersion forces) due to the dipole-dipole attraction between polar methanol molecule and hydroxyl ions on HAp surface. It requires few minutes to recover its original state when the sensor is exposed to atmospheric air.

The sensitivity of native HAp and 0.5 % CNT blended HAp material to different methanol concentrations is also studied to compare the maximum methanol detecting limit of the materials. The sensor is held at room temperature (30°C) and exposed to various concentrations of methanol ranging from 100 ppm to 6500 ppm. The nature of the graph in Fig. 7 depicts significant changes with increasing methanol concentration. The surface area and available active reacting sites of the HAp and CNT play an important role in the deposition of methanol. Sensitivity depends on adsorption of the gas molecule at the available adsorption sites. Therefore, 0.5 % CNT blended HAp shows much higher uptake capacity than HAp. Saturation occurs due to lack of vacant adsorption sites with increasing concentration since the surface is covered with methanol vapours.

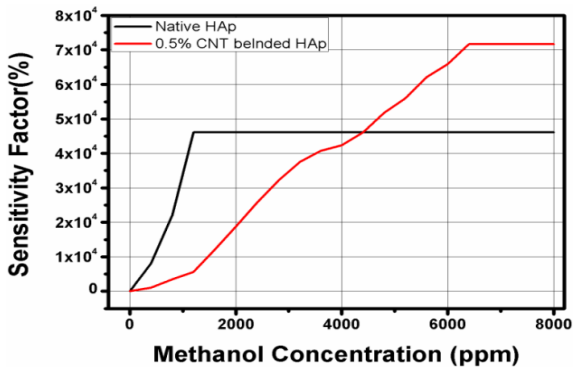


Fig. 7. The sensitivity of native HAp and 0.5 % CNT blended HAp thick films for various concentrations of methanol vapours at room temperature (30^{0}C).

To access the faithfulness and selectivity of these thick films in respect to gas/ vapour sensing, a novel experiment is performed wherein such sensor films are exposed to a mixture of gases/ vapours of methanol, ethanol, and propanol in their equal proportion. Thus three different types of organic vapours namely methanol, ethanol, and propanol of concentration 50 ppm each is injected into the chamber in a single stroke. The sensor substrate shows separate response to the individual analyte (methanol, ethanol, and propanol) as shown in Fig. 8 and Fig. 9.

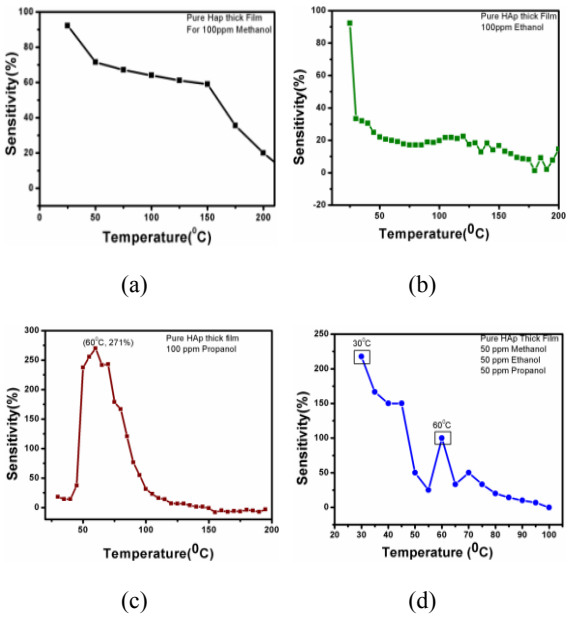


Fig. 8. Sensor sensitivity at different temperature of native HAp sensor substrate (a) in the presence 100 ppm methanol (b) in the presence 100 ppm ethanol (c) in the presence 100 ppm propanol and (d) in the presence of a mixture of organic vapors (methanol, ethanol, and propanol) to obtain the operating temperature.

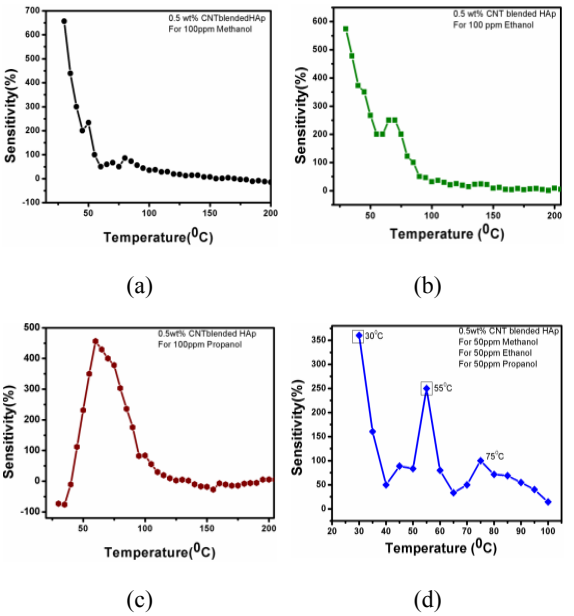


Fig. 9. Sensor sensitivity at different temperature of 0.5 wt% CNT blended HAp sensor substrate (a) in the presence 100 ppm methanol (b) in the presence 100 ppm ethanol (c) in the presence 100 ppm propanol and (d) in presence of mixture of organic vapors (methanol, ethanol, and propanol) to obtain the operating temperature.

The results imply the interesting fact that the sensor substrate is sensitive to each of these organic vapours at their unique temperature.

In case of native HAp it is noted that, the sensitivity for methanol and ethanol in mixed quantity is more than the sensitivity when sensed separately. However, the sensitivity is found to be less for propanol at 60^0C because of less concentration of propanol. The comparative study also reveals that native HAp and 0.5 wt% CNT blended HAp thick films shows selectivity of vapours/ gas and ability to detect them at their unique temperatures.

4. Conclusions

The influence of CNT blending on HAp surface, for enhancement in sensing properties of methanol, has been studied. The sensing performance of the native HAp thick film and 0.5 wt% CNT blended HAp thick film are compared in terms of sensitivity (maximum response), response time and reproducibility for a fixed concentration of methanol. The response of the material in the presence of various concentrations of methanol is recorded to find out its maximum detection limit. The results corroborate that addition of CNT in small weight concentration dramatically ameliorates the sensing property of native HAp. The enhancement is attributed to increment in surface area and possible immobilization of methanol molecules on the peripheral end corners of CNTs. The study indicates the potential use of such blended matrix in practical sensing devices operating at around room temperature (30^oC). Thus such sensors when exposed to mixed vapours in ambient and ramped with heating at various temperatures would prove to be dynamic sensor devices for the detection of individual vapour species out of mixed vapours in ambient.

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