Development of Methanol Sensors: Carbon Nanotubes Blended Hydroxyapatite Nano-Ceramics

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***Abstract*—The experimental study reports the performance of Carbon nanotubes (CNT) blended Hydroxyapatite (HAp) composites as a sensing material for the detection of methanol vapours. The main objective of the work is to improve the temperature dependent sensitivity of the sensor for lower methanol concentration. Moreover, the sensing ability of native HAp and CNT blended HAp thick films is studied in terms of operating temperature, response / recovery time, maximum detection limit. Thick films of the native and blended materials are fabricated via screen printing technique. The sensing parameters are studied using two probe electrical methods. The sensor substrate is made by means of doping of various 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 the 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- Carbon nanotubes; Gas sensor; Hydroxyapatite; Methanol sensor

I. 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. The 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, produces harmful effects on human health and the environment. Thus, to reduce methanol exposure, one should need a sensor that detects these vapours at low detection limit with accuracy and efficiency. The present work elucidates the development of nano material based sensing substrate which works at the low operating temperatures and shows better sensitivity for organic vapours at the lower detection limit. 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]. This is because it has a perfect carbon-carbon network. The introduction of defects via; vacancies, functionalization or dopant, in carbon network, make it a desirable surface for sensing application by providing 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 to metal oxide doped material. Also, the response / recovery time for such sensors are found to be less long. Calcium Hydroxyapatite [Ca_{10} $(PO_4)_6$ (OH) $_2$], having properties such as porous hexagonal network, nano grain size, and higher specific surface area**,** is utilized as sensing substrate [9]-[14]. The surface of HAp is considered as an ionic conductor. The presence of H^+ and OH^- ions (hydroxyl group) is found to be responsible for its conductivity at elevated temperature [15]-[17]. At low temperature, the conductivity is either because of proton transfer among OH^- ions or migration of protons from OH^- to PO_4^{3-} ion [11], [18].

$$OH^- + OH^- \leftrightarrow O^{2-} + H_2O$$

or

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

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. The present study deals with the utilization of sensing ability of HAp and CNT in order

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to get desirable sensing substrates for the detection of methanol vapor at 30^0C.

II. EXPERIMENTAL

Calcium Hydroxyapatite is synthesised by following the path reported in our earlier publications [9]-[10]. In order to achieve the best sensing substrate, CNT in various weight concentrations is blended in HAp via liquid phase reinforce method under similar experimental condition. A known quantity of CNT with nano HAp is dissolved in alcohol is and kept under magnetic stirring followed by sonication and allowed to dry at room temperature. The dried nano powder is sintered at 100^0C for 1h 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), X-Ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface analysis are carried out to analyze the morphological and structural characterization of the material. The prepared composite materials along with native HAp 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 [19]. 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 sensitivity factor (gas response) is calculated by using the equation

$$Gas\ response\ S(\%) = \frac{Rg - Ra}{Ra} \times 100$$

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

III. RESULTS AND DISCUSSION

A. Morphological Analysis

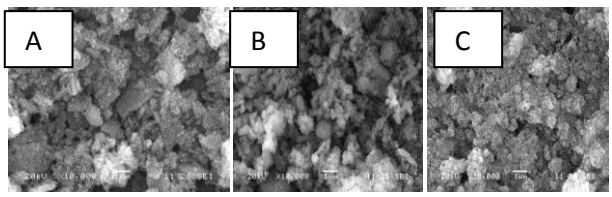

Figure 1. SEM micrographs for (A) Native HAp, (B) 0.5wt% CNT blended HAp, (C) 0.7wt% CNT bended HAp showing variations in surface topography due to the presence of CNT.

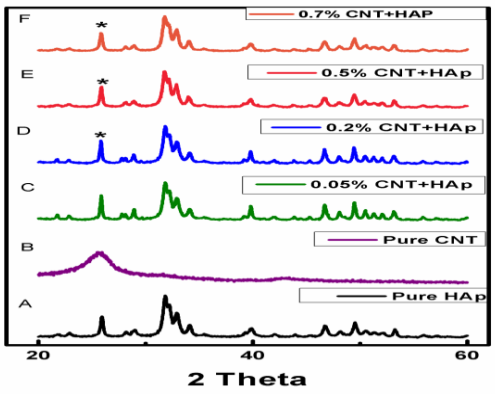

Figure 2. X-ray diffraction pattern of native HAp, CNT and CNT blended HAp material (* represents the peak for CNT): Y-axis has arbitrary units.

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 in a circular pattern over a large area. The presence of CNT in various concentrations significantly affects the surface property. 0.5wt% CNT blended HAp surface shows a porous structure with the small sized particle. 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 0.7wt% CNT, reducing the porosity.

B. Structural Analysis

X-ray diffraction pattern of native HAp, CNT and CNT blended HAp material is recorded for 2θ value 20 to 60 degree with a scan rate 2^0/min on Rigaku diffractometer with Cu $K\alpha_1$ radiation (λ=1.54Å). Fig. 2(A) shows X-rd diffractogram of native HAp synthesized by weight chemical precipitation method. The (2 1 1), (3 0 0), ((0 0 2), (2 1 3), (2 2 2) planes of HAp are clearly observed in the diffraction pattern. All peaks 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 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.

C. Surface area Analysis

The adsorption-desorption isotherm along with the pore size distribution is displayed in Fig.3. The isotherm for both native HAp and 0.5wt% CNT blended HAp is identified as type III as it exhibits type III hysteresis loop having weak interaction between adsorbent and adsorbate.

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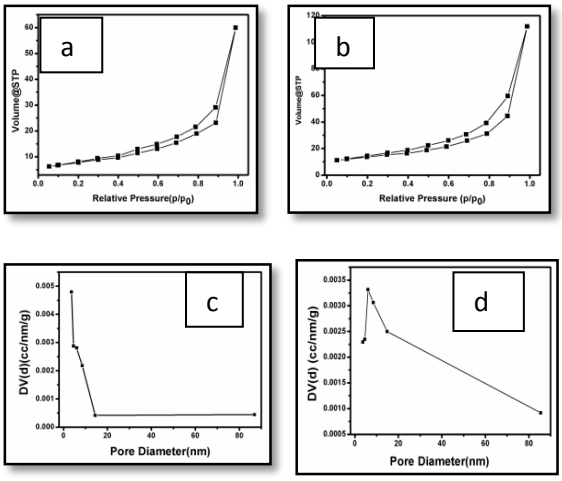

Figure 3. N_2 adsorption/desorption isotherm (a) native HAp, (b) 0.5wt% CNT blended HAp and BJH pore size distribution curve (c) native HAp, (d) 0.5wt% CNT blended HAp.

The 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 twice the surface area of HAp.

D. Methanol Sensing Properties

The response of the sensing substrate is tested at elevated temperature in order to select 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).

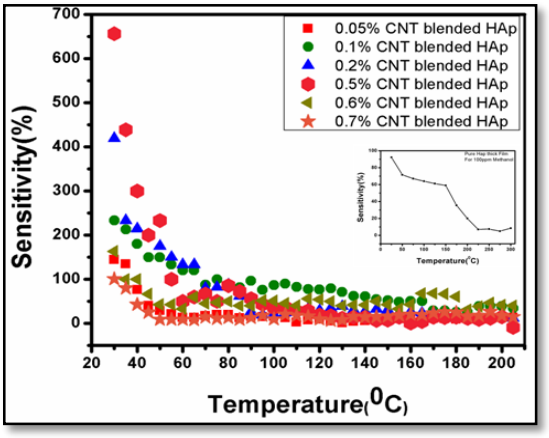

Figure 4(A). Sensor sensitivity (response) of native HAp and CNT blended HAp at variable temperature for 100 ppm concentration of methanol

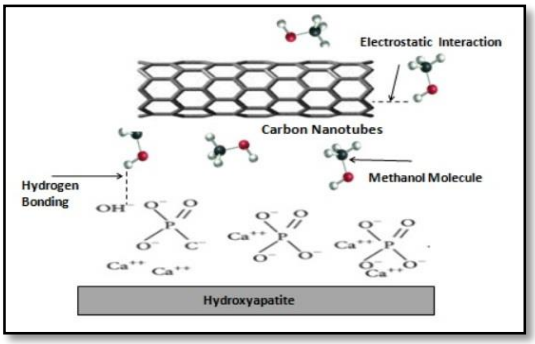

Figure 4(B). Formation of hydrogen bonding, due to dipole- dipole interaction between polar methanol molecule and hydroxyl ions on HAp surface. Electrostatic interaction between methanol and CNT molecules leads to enhance the sensing property of the substrate material

Both the native HAp and CNT blended HAp materials show the same substrate temperature of 30 ^oC for getting maximum sensitivity in presence of 100 ppm methanol. 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. The alteration in sensitivity as a function of CNT concentration in composite at room temperature (30 ^oC) for 100ppm methanol is shown in Fig 5. The response varies linearly with CNT concentration, attains peak value for 0.5wt% 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~ 600%, when exposed to methanol at room temperature (30 ^oC). 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.

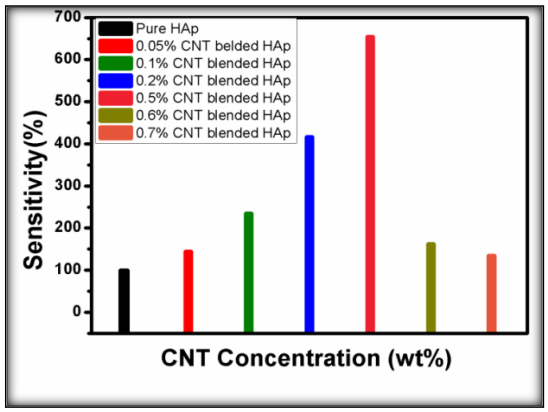

Figure 5. Variation in sensitivity for different CNT concentrations in HAp, at room temperature (30 ^oC) for 100 ppm methanol

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A comparative study of the response/ recovery time characteristics of native HAp and 0.5 %CNT blended HAp material at room temperature (30 ^{o}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. The response time is 160 sec for native HAp substrate and 60 sec for 0.5wt% 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 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. Being weak, forces such adsorption to be easily desorbed after exposing to atmospheric air at room temperature without any need for extra heat or energy resulting 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.

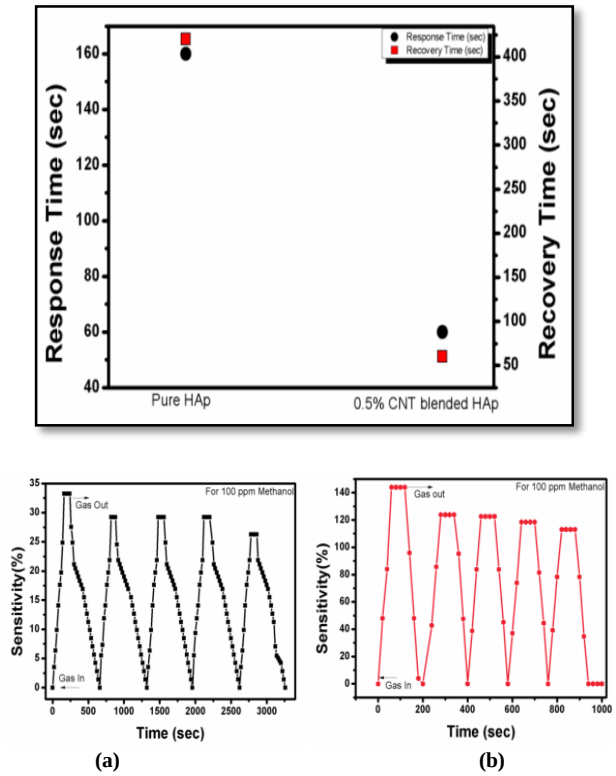

Figure 6. Response/ recovery time plot for native HAp and 0.5wt% CNT blended HAp thick film in the presence of 100 ppm methanol. Continuous repeated cycles for response / recovery time at room temperature (30 ^{0}C), (a) native HAp, (b) 0.5% CNT blended HAp.

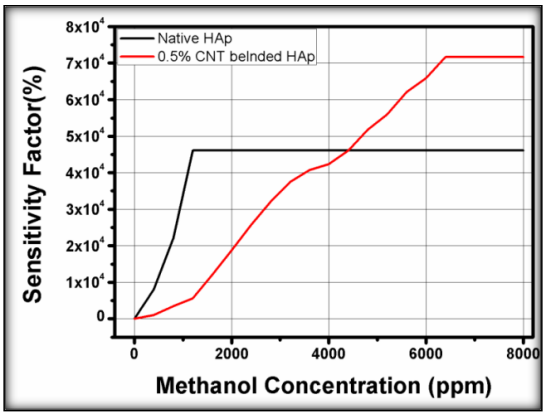

Figure 7. Sensitivity of native HAp and 0.5% CNT blended HAp thick films for various concentrations of methanol vapours at room temperature (30^{0}C).

The sensitivity of native HAp and 0.5% CNT blended HAp material to different methanol concentrations is also recorded to compare the maximum methanol detecting limit of the materials. The sensor is held at room temperature (30 ^{o}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 adsorption sites with increasing concentration since the surface is covered with methanol vapours.

IV. CONCLUSIONS AND FUTURE WORK

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 0.5wt% 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 immobilisation 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 ^{o}C). This work represents the first report in a series of experimentations. This work will be followed by the sensing studies for higher alcohols such as ethanol, propanol, and butanol. In addition to this, oriented deposition of the CNT on HAp surface may be

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carried out in the future for the enhancement of sensitivity and detecting the lowest concentration of organic vapours.

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