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Carbon nanotube doped nano-hydroxyapatite sensor matrix for gas sensing application

Rajnedra S. Khairnar, S. R. Anjum, Vanja Kokol and M. P. Mahabole

***Abstract*— Gas sensing behavior of nano composite mixtures of nano-hydroxyapatite (nano-HAp) and multiwall carbon nanotube (MWNT) is investigated by means of electrical characterization using two–probe method. The mixture contains nano-HAp as host material, and MWNT weight concentration ranges between 0.05wtpercent to 0.2wt%. The crystalline phase of nano-HAp and average diameter of MWNT is analyzed from Atomic Force Microscopy (AFM).The phase content and crystal size is estimated by powder X-ray Diffraction (XRD) method. Thermo-Gravimetry Differential Thermal Analysis (TG/DTA) shows good thermal stability of the composite material. Studies reveal that adsorption of Carbon monoxide with MWNT doped nano-HAp thick films results in increase in substrate resistance thereby increasing the gas sensitivity. The study of various gas sensing parameters, reveals that composite containing weight concentration of MWNT (0.05wt %) exhibits good sensing behavior for the detection of 20 ppm CO gas, with rapid response and regenerative capacity.**

***Index Terms*— Multiwall Carbon nanotube, Gas sensor, Nano- hydroxyapatite, Two-probe method.**

I. INTRODUCTION

Ideal sensors matrix material must possess the ability to monitor and detect various chemical gases selectively at low concentrations of the gases. The general criterion for efficient gas sensing is high sensitivity and selectivity, fast response and recovery time, lower operating temperature, and chemical stability [1]. Nano-hydroxyapatite (nano-HAp) in its nano size is a composite material consisting of Ca, P, and OH groups [2][3]. It has porous hexagonal structure with remarkable electronic properties, and good ionic conductivity. Due to its porous nature, its adsorption capacity made nano-HAp a promising material for gas sensing application [3]-[13].The outstanding structural, electrical, chemical, and thermal properties of CNT provide it exciting opportunities to become a promising material for many innovative applications. Because of the one dimensional structure, in CNT, every carbon atom becomes surface atom and makes electron transportation effective. Due to its selective adsorption behavior, CNT is one of the most potential candidates for gas sensing [14][21]. Carbon monoxide is a colorless, odorless, poisonous gas. It is one of the major sources of exposure at work place. The main sources of its emissions are combustion process and mobile sources. It can cause harmful health effect when encountered in higher concentration and also at extremely higher level can cause death. Therefore to reduce the danger of exposure of such poisonous gas, it is necessary to develop CO sensor having sensitivity at low ppm level. In our research work we utilized nano-HAp as a host material and multiwall carbon nanotube (MWNT) is selected as dopant, due to remarkable structural and electrical properties, so that it improves sensitivity and selectivity of the sensor and decreases the operating temperature thus we get an effective sensor which can work at low temperature with high sensitivity even at ppm level of gas concentration.

II. EXPERIMENTAL WORK

A) Preparation of sample material

Nano-HAp is synthesized by chemical precipitation method as reported earlier [4][6][7]. The nano composite materials are prepared by accumulating nano-HAp with various weight concentration of MWNT. Total three composites with different weight concentration of MWNT ranging between 0.05wtpercent, to 0.2wt% are prepared by properly mixing the material in agate and motor. Thick films of these materials are prepared using screen printing method. The nano composite sensor material is deposited on alumina ceramic substrate in the form of paste. The main components of this thick film paste are the functional material, a low temperature glass frit, and organic binder such as butyl carbitol acetate. After screen printing, these films are sintered at 500^0C for 1 hour, for the eradication of these binders.

B) Characterization of sensor material and its thick films

The atomic structure and morphology of the nano-HAp, MWNT, and MWNT doped nano-HAp composite is tested by atomic force microscopy (AFM). The crystalline phase structure and purity of the samples and its thick films are studied by X-ray diffractogram using cukα with incident radiation (λ=1.543 A^0). This pattern is recorded by setting diffraction angle (2θ) from 5^0 to 60^0.The thermal properties of MWNT and MWNT doped nano-HAp composites are measured by thermo-gravimetry differential thermal analysis (TG/DTA).The sample is heated from room temperature to 1000^0C at constant heating rate 10 ^{0}C/min. FTIR is used in the range of 300 cm^{-1} to 2000 cm^{-1} to identify functional groups present in MWNT doped nano-HAp composite.

C) Gas sensing setup and mechanism

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Rajnedra S. Khairnar, professor in physics at SRTMU Nanded, India,
S. R. Anjum, post-graduate degree from SRTMU Nanded
Vanja Kokol, Associate Professor at Institute of engineering material and design
M. P. Mahabole, Ph.D. in 2005 from SRTM University, Nanded, India

A specially designed gas sensing setup is used to study the gas sensing properties of these nano-HAp and MWNT doped nano-HAp composite thick films. To characterize the performance of the thick films as CO sensor, we measure its charge transfer property upon exposure to test gas. For this purpose, the sensor substrate is placed in a closed chamber with a constant supply of 90 V. The electrode of the sensor is connected to the substrate material to enable electrical measurements. The resistance of the sensor substrate (R_{air}) is measured by varying its temperature from 350^0C to room temperature. Once the resistance in presence of atmospheric air is measured the test gas carbon monoxide with a set concentration of 20 ppm is introduced in to the chamber. Again the change in resistance (R_{gas}) is measured by varying its temperature from 350^0C to room temperature. The interaction of CO gas molecule with the surface of the thick film causes the transfer of electron between the sensor substrate and the adsorbents. CO acts as a reducing gas therefore after interaction it reduces the negative charge carrier on the surface. This process decrease the conductance of the material hence increases the resistance.

Thus the sensitivity of the material is the ratio of (R_{gas}-R_{air}/R_{air}) and can be determined by using equation

$$Gas\ response\ \ S(\%) = \frac{R_{gas} - R_{air}}{R_{air}} \times 100$$

III. RESULTS AND DISCUSSION

A) Characterization of sensor material

The atomic force microscopic (AFM) images shown in Fig.1 confirm that MWNT doped nano-HAp composite is nano structural material. Fig. 1(a) displays micrographs for nano-HAp. The surface of nano-HAp shows the appearance of nanosize grains. From Fig. 1(b) showing the micrographs for MWNT, it is concluded that the diameter of the material is approximately 50 nm. The micrographs shown in Fig. 1(c) are of MWNT doped nano-HAp composite showing nano grain size of the material.

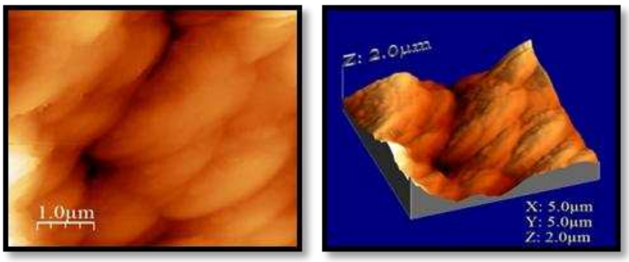
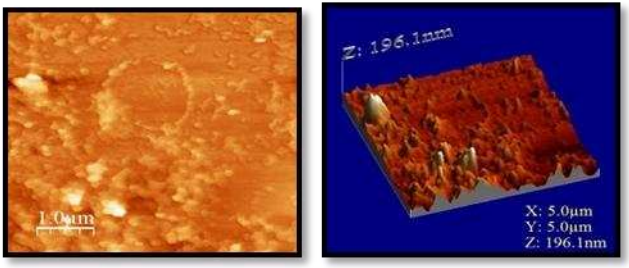


Fig. 1(a)



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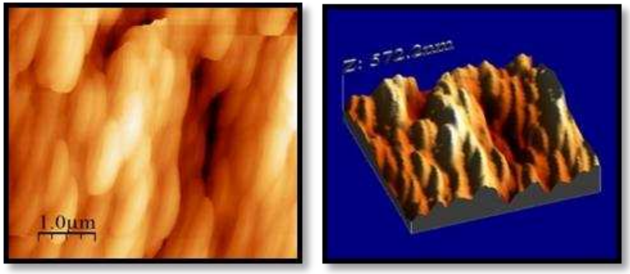


Fig. 1(c)

Fig. 1.1 1-D and 3-D AFM micrographs of (a) nano-HAp, (b) MWNT, and (c) MWNT doped nano-HAp composite material displaying nanosize grain and approximate average diameter 50 nm for MWNT.

From X-ray diffractogram displayed in Fig. 2(a), it is seen that the XRD pattern of MWNT consisting of few broad peaks located at (0 0 2) and (1 0 0) with 2θ value of 26^0 and 43^0. The dominant peak at 26^0 is attributed to carbon and other attributed to graphite structure [22]-[24]. The XRD pattern in Fig. 2(b) is taken after annealing the nano material at 500^0C for 2 hours. It shows that as an effect of annealing, MWNT peaks are relatively constant with a slight decrease in their intensity.

The diffractograms of nano-HAp and MWNT doped nano-HAp composites for various weight concentrations of MWNT are shown in Fig.3. The major peaks associated with hexagonal phase of nano-HAp are observed at 26^0, 31^0 and 33^0 with orientation (0 0 2), (2 1 1), and (3 0 0) [13][25]. The diffractograms also show that the presence of MWNT does not cause any structural detrimental change in nano-HAp matrix, as the phase of nano-HAp is stable over a large range of temperature even after doping. Again in the diffractogram of 0.1wt% MWNT doped nano HAp, the major peak of MWNT at 26^0 with orientation (0 0 2) may overlap or diminished because the less intensive presence of MWNT due to its concentration (only 0.1wt %) in the nano composite sample. But the diffractogram of 0.2wt% MWNT doped nano HAp shows presence of this peak with more intensity.

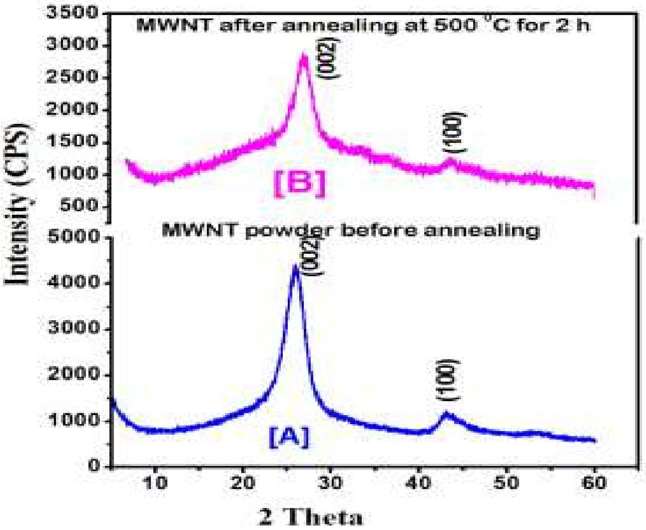


Fig. 2 XRD pattern for MWNT powder [a] before and [b] after annealing the material at 500^0C for 2 h showing the

intensity of diffracted X-ray from various planes as a function of 2θ value. Two major peaks are appearing at 26^0 and 43^0. The dominant peak at 26^0 is attributed to carbon and other at 43^0 attributed to graphite structure.

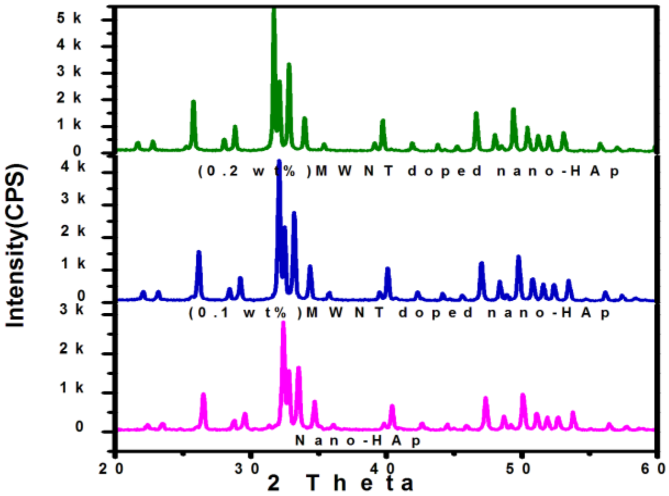
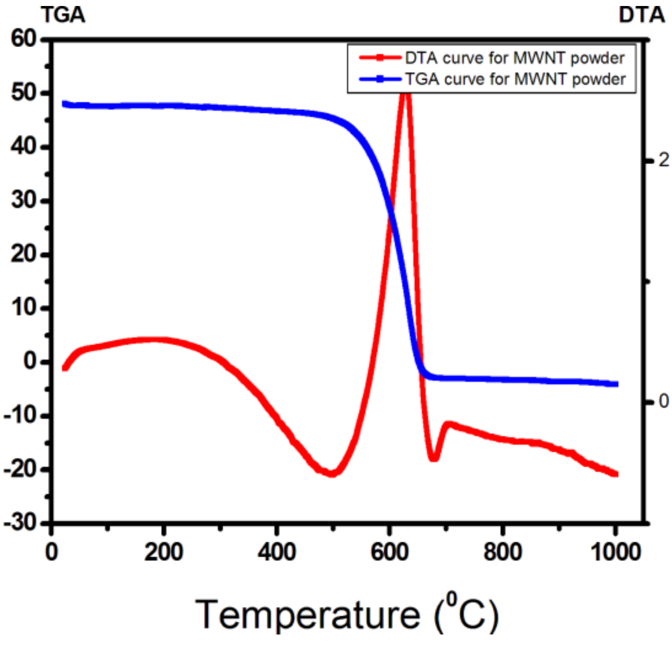
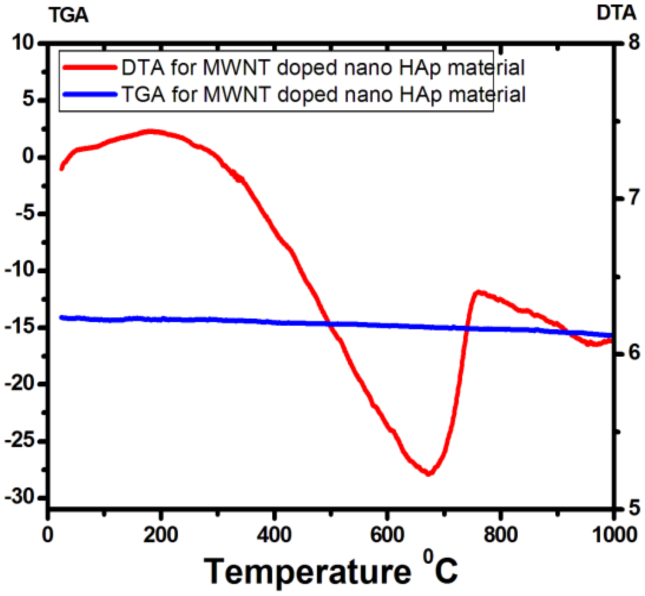


Fig. 3 XRD pattern for nano-HAp and MWNT doped nano-HAp composite material showing the intensity of diffracted X-ray from various planes as a function of 2θ value.

Fig. 4 shows typical thermo-gravimetry/ differential thermal analysis (TG/DTA) thermograms indicating the mass change as a function of temperature for MWNT and 0.2wt% MWNT doped nano-HAp composite. MWNT shows thermal stability up to 500^0C. The major mass reduction is observed after 550^0C up to 650^0C and is due to water dissolution and breakdown of CNT phase into graphite phase [22][26]. This result is well supported by corresponding DTA curve which shows a sharp endothermic peak in the range 550^0C to 650^0C as shown in Fig. 4 (a). From the thermogram displaying results for 0.2wt% MWNT doped nano-HAp composite (Fig. 4 (b)), it can be observed that, nano-HAp is highly thermally stable up to 1000^0C but it does not display changes occurs in MWNT because of its meager concentration (only 0.2wt %) in the composite nano-HAp material.



(a) MWNT Powder



(b) MWNT doped nano –HAp

Fig. 4 Thermo- Gravimetry / Differential Thermal Analysis showing mass reduction due to heating for (a) MWNT powder showing thermal stability up to 550^0C and (b) 0.2wt% MWNT doped nano-HAp composite showing high thermal stability (1000^0C) for nano-HAp.

FTIR spectra of MWNT doped nano-HAp composite which gives chemical information about the material is represented in Fig5. This spectrum confirms the presence of characteristic bands of hydroxyl and phosphate group. The hydroxyl liberation mode is found to be present at 636 cm^{-1} . The phosphate band appears specifically in the range 1000 cm^{-1} to 1100 cm^{-1} showing asymmetric stretching mode (or ν_3 vibration mode). The band at 964 cm^{-1} is due to ν_1 fundamental mode of $(PO_4)_3$; whereas ν_2 mode of vibration is observed in the range 565 $cm^{-1}$to 605 cm^{-1} [3][4][7][10][13][22][25][27].

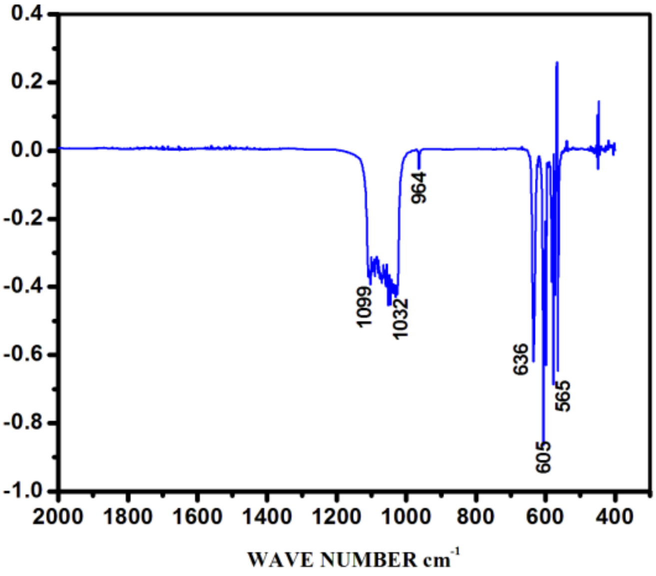


Fig. 5 FTIR spectra for MWNT doped nano-HAp composite material showing characteristics absorption peaks of the material as, hydroxyl liberation mode at 636 cm^{-1}, phosphate band present in the range 1000 cm^{-1} to 1100 cm^{-1}, ν_1

fundamental mode of $(PO_4)_3$ at 964 cm^{-1} and v_2 mode of vibration at 565 cm^{-1} to 605 cm^{-1}.

B) Gas sensing performance

Fig. 6 shows the sensor sensitivity evaluated as the ratio of $(R_g-R_a)/R_a$ v/s temperature of nano-HAp and various weight concentrations of MWNT doped nano-HAp composite sensor substrates. At low temperature, the sensor response to test gas (CO) is low which may be due to the fact that gas molecules do not have enough thermal energy to react with sensor substrate. Therefore there is negligible difference between R_{air} and R_{gas} values. At a particular temperature the difference between R_{air} and R_{gas} values is large, and hence at this particular temperature, the sensor shows response to test gas with maximum sensitivity. This temperature is called as active or operating temperature for the sensor. Nano-HAp substrate shows maximum response to CO gas at temperature of 175^{0}C .The maximum response of MWNT doped nano-HAp sensor material to 20 ppm CO gas varies inversely with variation in concentration of MWNT. As weight concentration of MWNT decreases relative operating temperature for the sensor substrate also decreases. For 0.05wt% MWNT doped nano-HAp the operating temperature is at 105^{0}C with sensitivity more than 100%, while for 0.1wt% and 0.2wt% MWNT doped nano-HAp the operating temperature is at 110^{0}C and 130^{0}C respectively. Further increase in temperature again decreases difference between R_{air} and R_{gas} values that is showing less sensitivity. Since the lower operating temperature is desirable for any sensor hence it is concluded that 0.05wt% MWNT doped nano-HAp composite is a better gas sensor matrix.

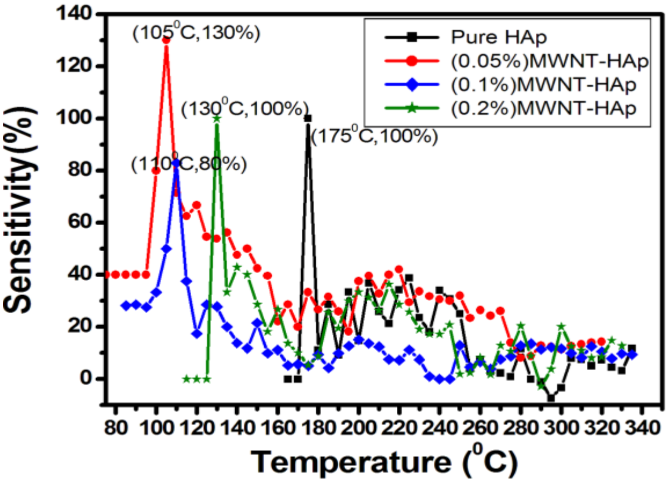
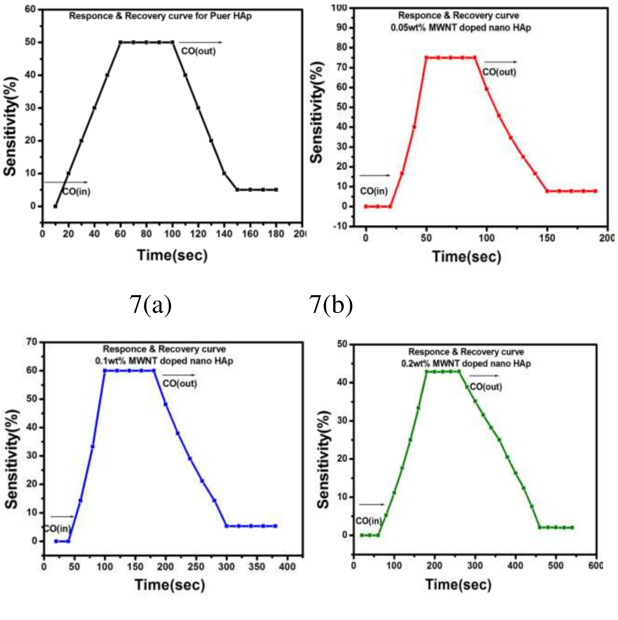


Fig. 6 Sensor sensitivity evaluated as the ratio of (Rg-Ra)/Ra v/s temperature for nano-HAp and MWNT doped nano-HAp composites sensor substrate to determine functional temperature in presence of 20 ppm CO gas.

Fig. 7 represents the variation in resistance value with time of the sensor material upon exposure to test gas and air alternately. After injection of test gas (20 ppm of CO) there is a slow variation in resistance value with time because there is a slower interaction between sensor substrate and the test gas molecules, and after some time the sensor shows no further variation in resistance value with time. This gives the response time of the sensing material. Later on the sensor is exposed to atmospheric air so that the sensor resistance reverted to its initial value. When the sensor is exposed to atmospheric air, again there is variation in resistance value with time, achieving an earlier constant value of resistance. Nano-HAp gives response within 58 sec and recovers after 48 sec, showing a quick regenerative capacity as sensor substrate (Fig.7 (a)). The doped sensor shows longer recovery time than response probably due to larger volume of gas being occupied in randomly placed nanotubes which takes more time to be released. This can be confirmed by the more recovery time taken by the substrate having higher doping concentration of MWNT in nano-HAp. The lower concentration of doping material 0.05wt% MWNT doped nano-HAp shows quick response within 48 sec to test gas with rapid regenerative capacity, after 62 sec (Fig. 7(b)). 0.1wt% concentration of MWNT gives response after 100 sec and recovers after 120 sec (Fig.7(c)) where as 0.2wt% concentration MWNT shows response within 180 sec and recovery after 200 sec (Fig 7(d)). Thus lower concentration of doping material shows better response and regenerative capacity compared to higher one it means that 0.05wt% MWNT doped nano-HAp material behaves like better gas sensor substrate for the detection of CO gas.



7(a) 7(b)

7(c) 7(d)

Fig. 7 Variation in sensitivity with time of the sensor material upon exposure to 20 ppm CO gas and air alternately for the determination of response and recovery time for sensor held at their operating temperature respectively.

(a) Nano-HAp showing response within 58sec and recovery after 48 sec

(b) 0.05 wt% MWNT doped nano-HAp showing response within 48 sec and recovery after 62 sec

(c) 0.1wt% MWNT doped nano-HAp showing response within 100 sec and recovery after 120 sec

(d) 0.2wt% MWNT doped nano-HAp showing response within 180 sec and recovery after 200 sec.

The sensor is exposed to various concentration of test gas to study the gas uptake capacity of the sensor substrate. Fig. 8 is a typical gas sensor response curve showing the response of

CO gas for various concentrations at functional temperature 175^{0}C for nano-HAp, 105^{0}C for 0.05wt% MWNT doped nano-HAp composite, 110^{0}C, and 130^{0}C for 0.1wt% and 0.2wt% MWNT doped nano-HAp composites respectively. Initially the sensor response increases with increase in concentration of test gas (Carbon monoxide). This is because increase in concentration of gas results in the interaction of a large number of molecules of test gas with the material surface causing a rapid increase in electric resistance. After that further increase in gas concentration does not cause any noticeable change as the curve becomes straight line (saturation region), this is because the surface of substrate is fully covered with residual gas molecules. The gas uptake capacity of nano-HAp is more .The gas uptake capacity of MWNT doped nano-HAp sensor substrate reveals better linearity at lower weight concentration of dopant (MWNT) than at higher one. That means the gas uptake capacity of nano composite material is more (700ppm) when concentration of MWNT as dopant is low 0.05wt% and decreases with increase in weight concentration. It is 200 ppm for 0.1 and 0.2wt% MWNT doped nano-HAp composites.

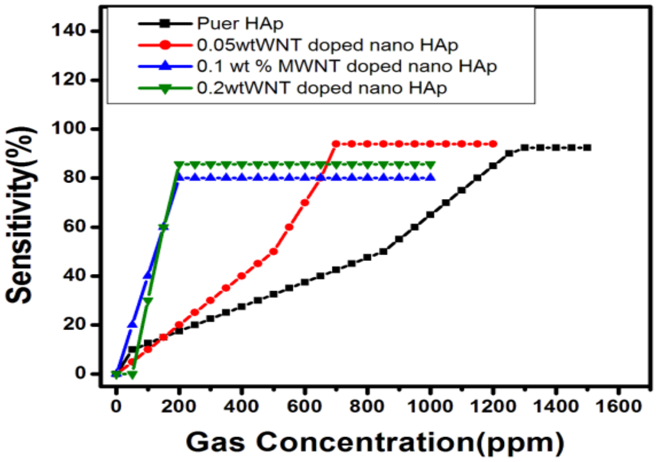


Fig.8 Gas uptake capacities of nano-HAp and MWNT doped nano-HAp composite sensor material at their respective operating temperature for various concentrations of CO

IV. CONCLUSION

The utilization of multiwall carbon nanotube doped nano-hydroxyapatite sensor matrix for gas sensing application is an experimental approach towards the development of an effective gas sensor which works at low operating temperature with better sensitivity even at low ppm level. From the outcomes it is concluded that, minimal weight concentration of doping material (0.05wt% MWNT) gives a useful sensing material for the detection of 20 ppm CO gas. The films with 0.05wt% MWNT doped nano-HAp composite gives prompt response within 48 sec at low operating temperature 105^{0}C with regenerative capacity after 62 sec which is very low as compared to virgin nano-HAp whose operating temperature is 175^{0}C giving response after 58 sec and recovery after 48 sec. Also MWNT doped nano-HAp sensor substrate reveals better gas uptake capacity at lower weight concentration of dopant (0.05wt% MWNT) than at higher weight concentration. These above mentioned favorable parameters are attributed to small grain size, large surface area with many sites available to absorb gas molecules, hollow geometry that helpful to enhance sensitivity, their high surface to volume ratio to increase gas uptake capacity of MWNT. Thus we conclude that 0.05wt% MWNT doped nano-HAp material is potential candidate as a CO gas sensor device.

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R.S. khairnar ,is professor in physics at SRTMU Nanded, India, since 2004. He has initiated new courses in fiber optic and laser and material science at master's level. He has varied research interest particularly in the area of nano bio-ceramics gas sensors, optical fiber sensor, zeolite blended material synthesis for soil and water purification and soil waste management.

Shaikh Reshma Anjum has received her post-graduate degree from SRTMU Nanded in the year 2009. Presenstly she is doing her reseach work on nano ceramic gas sensor under the guidence of Prof. R. S. Khairnar, School of Physical Science, SRTMU Nanded.

Dr. Vanje Kokal is Associate Professor at Institute of engineering material and design. She is actively engaged in the research area of bioactive materials and bio-polimeric blended matrix for various device application.

Institute of Engineering Materials and Design Faculty of Mechanicla Engineering S Smetanova ulica 17 Si-2000 Maribor University of Slovenia

Megha P. Mahabole has received her Ph.D. in 2005 from SRTM University, Nanded, India. Currently she is an Associate Professor at School of Physical Sciences, SRTM University, Nanded. She has more than 12 years of experience in teaching and research field. Her research areas are synthesis and characterization of hydroxyapatite biomaterial, gas sensor, natural and synthetic zeolites.