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Carbon Dioxide Sensors Based on Carbon Nanotubes with and Without Catalyst

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Gas sensors have a wide range of applications in everyday life, whether in industry and medical. A good sensor should be selective, sensitive, responsive, reliable and cost effective. Currently available gas sensors are lacking in one or more of these criteria. In this work, carbon nanotubes (CNTs) with and without catalyst (Fe) are successfully prepared by chemical vapor deposition (CVD) and their structural, surface morphological and sensing properties are studied. The FESEM images clearly indicate that the samples have good CNT diameters of about 140 nm and 45-57 nm with and without catalyst, respectively. The sensing properties of CNTs are investigated as a function of time and operating temperature to find the sensitivity to CO_2 gas at different concentrations. High sensitivity (2.68 %) was achieved at 100 °C with a fast response and recovery times at a high concentration of 100 ppm.

Keywords: Carbon nanotubes, CVD, Carbon dioxide, Sensor.

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1. INTRODUCTION

Gas sensors, or chemical sensors, are attracting tremendous interest because of their widespread applications in industry, environmental monitoring, space exploration, biomedicine, and pharmaceutics. Gas sensors with high sensitivity and selectivity are required for leakage detections of explosive gases such as hydrogen, and for real-time detection of toxic or pathogenic gases in industries. They [1-3] have drawn the most research interest because of their unique geometry, morphology, and properties. Their preparation, properties (such as electronic, mechanical, thermal, and optical) and applications in various fields are all studied intensely. Theoretical and simulation works have also been conducted to understand this nanoscale material and related phenomenon [2-4]. In the present paper, we report the synthesis of carbon nanotubes (CNTs), which were prepared by chemical vapor deposition (CVD), and the study of structural, surface morphological, and CO_2 sensing properties of CNTs with catalyst (Fe) and without catalyst (purity).

2. EXPERIMENTAL PART

The production method employed in this study was CVD. Methanol and butanol were used as the source of hydrocarbons with nitrogen as carrier and purge gas. The reaction temperature was in the range of 650-700 °C, the reaction time was 30 min.

2.1 Synthesis of CNTs without Catalyst

In a typical experiment, we paced a quartz substrate (1 cm × 1 cm) in a ceramic boat, in a furnace. At first, the ceramic tube was flushed with nitrogen in order to eliminate oxygen from the reaction chamber during heating the reactor. Then, the furnace reached a temperature of 700 °C. After, N_2 carrier flow (150 ml/min) was bubbled into the mixture (50 ml) that was used as a source of hydrocarbons. The mixture was then decomposed in the furnace to form CNTs. The reaction was over after 30 min, and the furnace was cooled down with N_2 flow.

2.2 Synthesis of CNT with Catalyst

In a typical catalyst preparation, 0.5 g of ferrocene was dissolved within 30 ml of ethanol. The quartz bases were immersed in the solution and placed in an ultrasonic water bath at 40 °C for 30 min, until the mixing process and the release of volatile impurities behind the ferrocene material deposited on the quartz bases.

The source of carbon used in this study was a mixture of methanol/butanol in various ratios (1:1). In the CVD synthesis of CNTs, the first step was to dope the catalyst on the support surface. The as-prepared catalyst was placed in a quartz boat, evenly distributed and placed in the center of the CVD furnace, N_2 flow rate was 150 sccm, upon reaching 700 °C for 30 min.

To purify CNTs, the products were first removed from the quart boats with 200 ml of ethanol within an ultrasonic water bath. The second step involved immersing the black product in a 40 % H_2O_2 solution by ultrasonic water bath. The dispersed sample was then stirred in an H_2O_2 solution for 10 min, which left a black precipitation to dry at room temperature for 24 h, then we obtained the black powder (MWCNT).

3. RESULTS AND DISCUSSION

3.1 FESEM Analysis

Fig. 1a shows the scanning electron microscopic (FESEM) images of CNTs with catalyst (Fe). As can be seen from the photos, the surface is completely covered by CNTs which shows a good quality of synthesis. CNT diameter is about of 140 nm. Some residuals of iron particles remained in this sample can be seen at the bottom

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images. In fact, these particles are surrounded and covered with CNTs as a result of the size and density of nucleation, which is in agreement with [5]. Fig. 2b shows the scanning electron microscopic (FESEM) images of CNTs without catalyst (purity). These CNTs have completely covered the surface, which indicates the synthesis quality, and in this sample, the CNT diameter is an order of magnitude smaller. It is seen that the diameter of the samples is smaller than 100 nm. In fact, the diameter is around 45-57 nm, as a result of the size and density of nucleation which is in agreement with [6, 7]. As can be seen from the images, the purity of this sample is better than that of the previous sample.

3.2 XRD Analysis

To study the purity and structure of samples, X-ray diffraction analysis was employed. As expected from the FESEM images, both samples show CNT peaks and some other peaks. In CNT with catalyst (Fe), as we have seen large Fe_2O_3 nanoparticles, there are several more peaks belonging to Fe_2O_3, as shown in Fig. 2a. At the same time, as can be seen from the FESEM images, CNT without catalyst (purity) is more purified, and the XRD pattern shows fewer peaks for Fe_2O_3 and other residues, as shown in Fig. 2b.

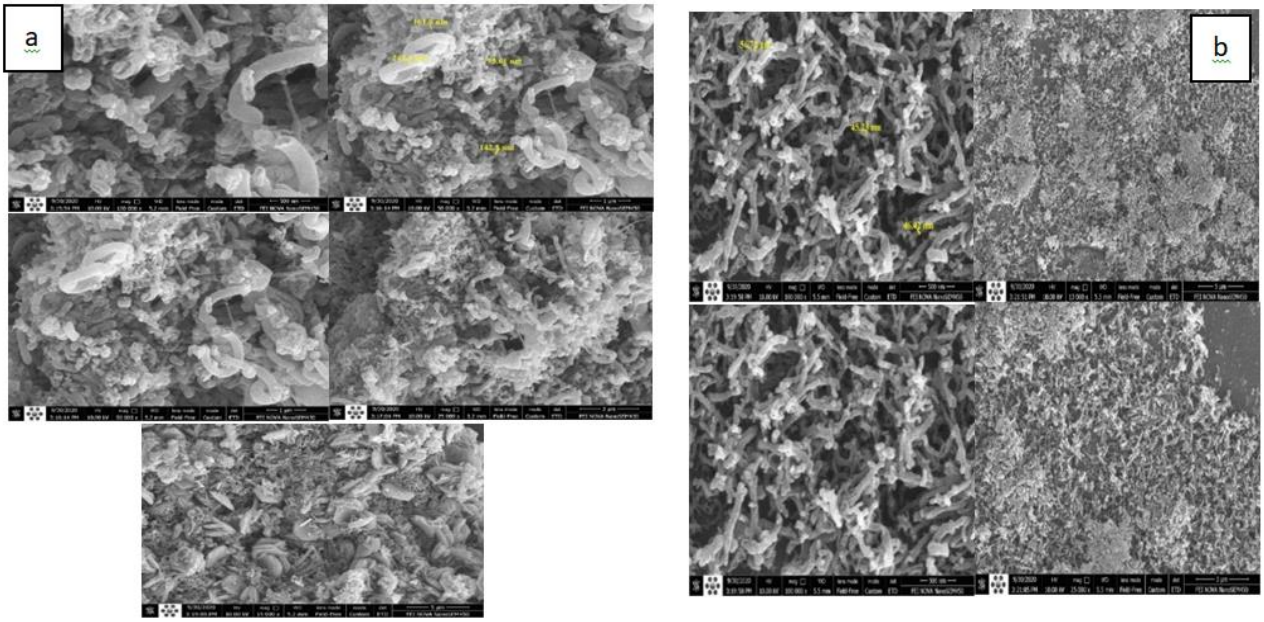

Fig. 1 – FESEM images of CNT a) with catalyst (Fe) and b) without catalyst (purity)

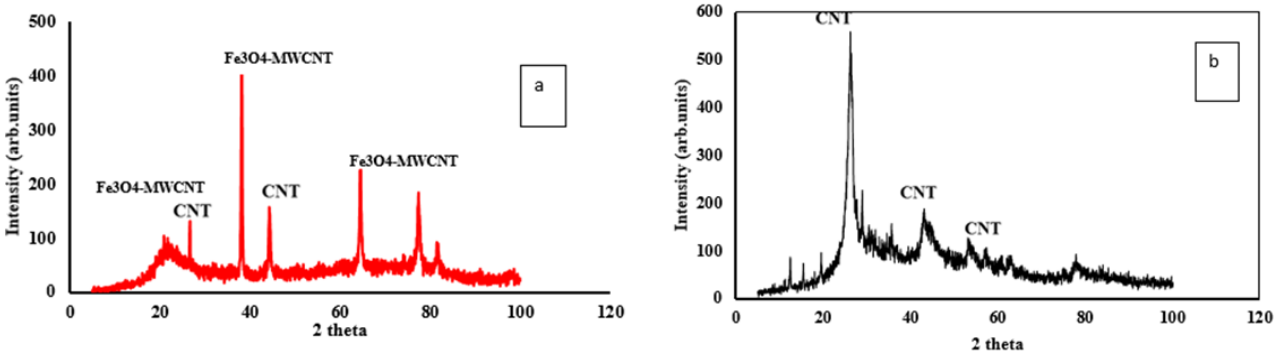

Fig. 2 – XRD of CNT a) with catalyst (Fe) and b) without catalyst (purity)

4. GAS SENSING RESULTS

The sensing properties of CNTs are investigated as a function of time and concentration of CO_2 to find the sensitivity of this gas.

4.1 Measurement of CO_2 Gas

Fig. 3 and Fig. 4 show the sensing properties for CNTs without catalyst (purity) and with catalyst (Fe), respectively, at different concentrations of 10, 25, 500 and 100 ppm. CO_2 is an oxidant gas, and it accepts electrons. In fact, when CO_2 interacts with the *p*-type material, it absorbs electrons from the *p*-type material, so the concentration of holes in the *p*-type material increases, which means that the majority carriers in the *p*-type material increases and the resistivity decreases. When the material resistivity decreases, the current through the *p*-type material increases. At the same time, if CO_2 is absorbed on the surface of the *n*-type material, the molecular gas accepts electrons from the material, the carrier concentration decreases, the resistivity of the material increases and the current through the *n*-type material decreases [8].

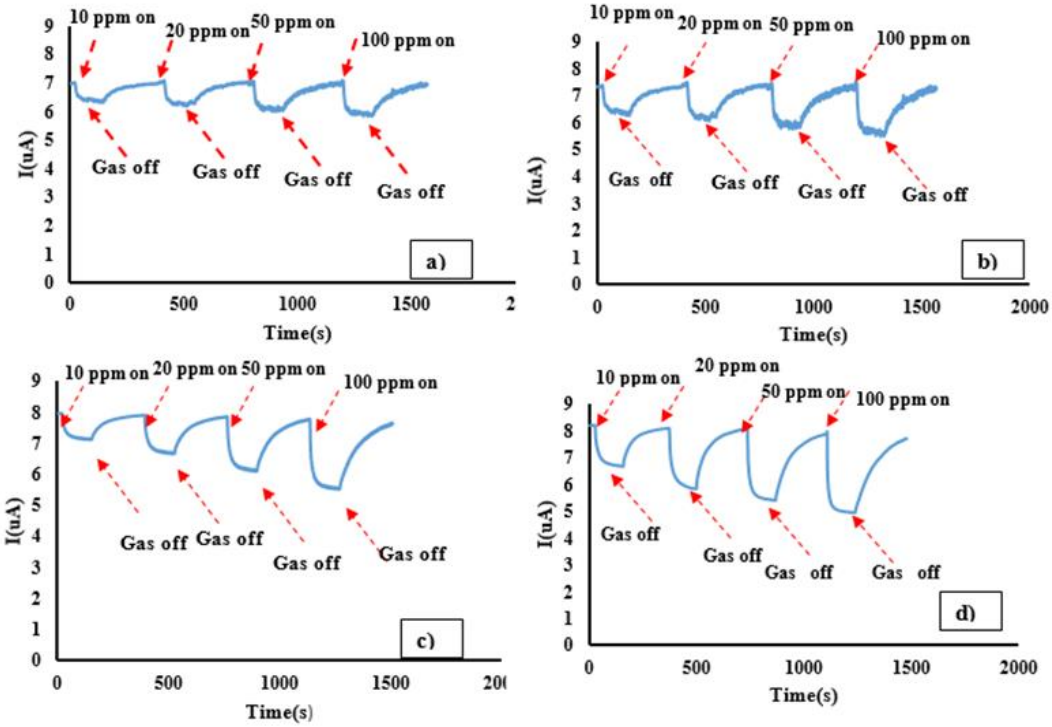

Fig. 3 – Variation of current with time for CNT without catalyst (purity) for CO_2 with different concentrations and temperatures

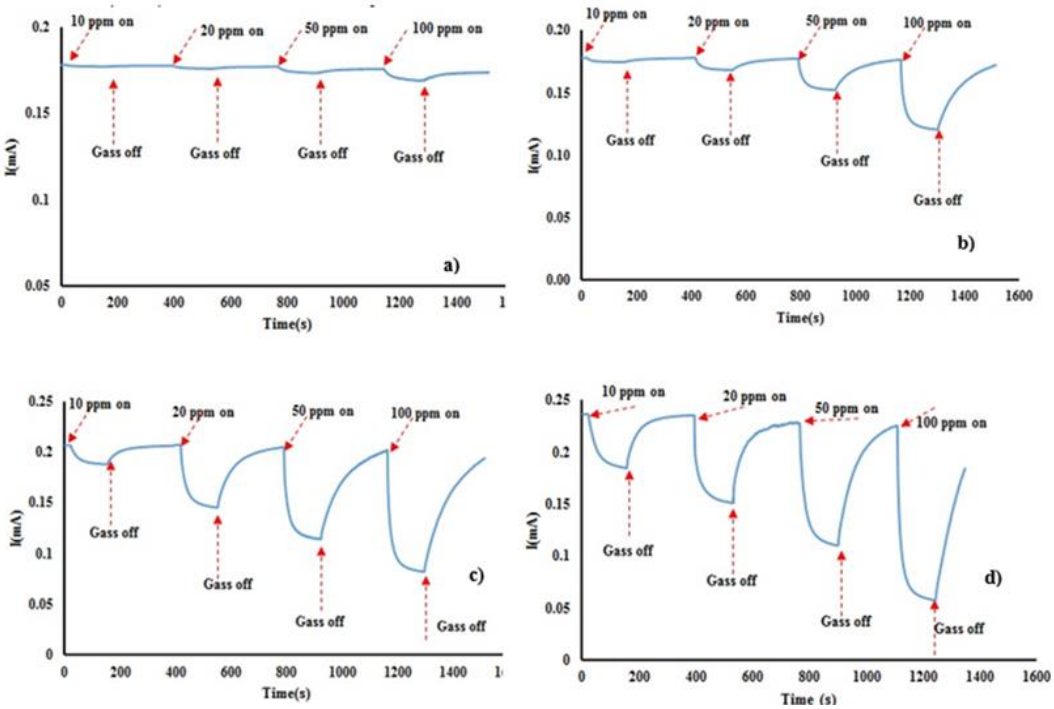

Fig. 4 – Variation of current with time for CNT with catalyst (Fe) for CO_2 with different concentrations and temperatures

The figures show a decrease in the current value when their CNTs are exposed to CO_2 gas (gas ON), then the current value goes to the top at the closure of the gas (gas OFF) for all samples. Electron transfer can cause changes in the resistance and work function of the sensing material. This process occurs when CNTs are exposed to CO_2. Electron acceptors can remove electrons from CNT. An opposite process will occur when detecting an electron donating gas. The gas sensing property of the sensor is measured by recording a change in the resistance over two sensing electrodes under CO_2 gas. The change in the sensor resistance is attributed to ion adsorption of gas molecules, the surface reaction of the target gas with adsorbed oxygen on the surface of the metal oxide [8, 9].

The sensitivity factor (S, %) is calculated using the following equation [10-17]:

$$S = \left| \frac{R_g - R_a}{R_a} \right| \times 100\%, \quad (1)$$

where S is the sensitivity, R_a and R_g are the electrical resistances of the film in air and in the presence of gas, respectively. The maximum sensitivity to CO_2 gas was observed for CNT with catalyst (Fe) at a high concentration of 100 ppm, was found to be 2.68 % at T_0 = 100 °C and exhibited a fast response speed and a short recovery time less than 14. The quick response sensor for CO_2 gas may be due to faster oxidation of gas [7, 14], as shown in Table 1.

Table 1 – Sensitivity (%), recovery time and response time of CNTs with and without catalyst (Fe) for CO_2 with different concentrations and temperatures

CO_2	Sensitivity %								Response time (s)		Recover time (s)	
Sample	10 ppm		20 ppm		50 ppm		100 ppm					
	purity	With (Fe)	purity	With (Fe)	purity	With (Fe)	purity	With (Fe)	purity	With (Fe)	purity	With (Fe)
25 °C	0.38	0.01	0.12	0.2	0.14	0.03	0.15	0.05	90	88	64	60
50 °C	0.125	0.02	0.19	0.07	0.25	0.16	0.28	0.47	104	50	40	46
75 °C	0122	0.08	0.16	0.43	0.26	0.69	0.36	0.75	75	40	105	14
100 °C	0.18	0.26	0.36	0.52	0.45	1.06	0.62	2.68	93	35	43	10

5. CONCLUSIONS

In this study, CNTs were prepared by CVD method, and the study of the structural, surface morphological, and CO_2 sensing properties of CNTs with catalyst (Fe) and without catalyst (purity) was performed. The sensing properties of CNTs are investigated as a function of time and operating temperature to find the sensitivity to CO_2 gas at different concentrations. High sensitivity (2.68 %) was achieved at an operating temperature of 100 °C with a fast response and recovery time at a high concentration of 100 ppm.

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Сенсори вуглекислого газу на основі вуглецевих нанотрубок з каталізатором і без нього

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Сенсори газу мають широкий спектр застосувань у повсякденному житті як у промисловості, так і в медицині. Ефективний сенсор повинен бути вибірковим, чутливим, надійним і економічно вигідним. На даний момент доступні газові сенсори не відповідають одному або кільком з цих критеріїв. У роботі успішно виготовлені методом хімічного осадження вуглецеві нанотрубки (CNTs) з каталізатором (Fe) і без нього з пари (CVD) та досліджено їх структурні, морфологічні та сенсорні властивості. Зображення FESEM чітко вказують, що зразки мають діаметри приблизно 140 нм і 45-57 нм для CNTs з каталізатором і без нього відповідно. Сенсорні властивості CNTs досліджуються як функція часу та робочої температури, щоб знайти чутливість до CO_2 при різних концентраціях. Висока чутливість (2,68 %) була досягнута при 100 °C із швидким відгуком та часом відновлення при високій концентрації 100 ppm.

Ключові слова: Вуглецеві нанотрубки, CVD, Діоксид вуглецю, Датчик.