

# Carbon nanosphere black, soot synthesis by chemical vapor deposition for multi gas sensor

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## Abstract

Carbon Nanosphere synthesized by chemical vapor deposition from acetylene at 750°C. Fe particles of diameter ranging from 30 to 90 nm were used as the catalyst particles. The catalyst was prepared from an Iron chloride FeCl<sub>3</sub> precursor solution that was spin–coated on *P*-SiO<sub>2</sub>/ (100) substrate. The growth produced were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Scanning electron microscopy (SEM), X-ray diffraction (XRD), Transmittance electron microscopy (TEM) and Raman spectroscopy in order to investigate the behavior of the growth process. The carbon nanosphere sensor show the working temperature influences the sensitivity and the response time, and the best results are obtained when the sensor is at a working temperature of 200 degrees or so. The CNS displayed a specific sensitized for NO<sub>2</sub> and H<sub>2</sub> gases. In the same experimental conditions, the recovery of the sensors was different for NO<sub>2</sub> and H<sub>2</sub>.

## **Keywords**

Carbon Nanosphere, Characterize, CVD, Gas Sensor

## 1. Introduction

Since their discovery in 1991 by Iijima [1]. Carbon nanotubes (CNTs) continue to attract increasing attention and extensive studies, owing to their unique structure and extraordinary properties which render wide potential applications in many fields [2-4]. Various synthetic methods such as arc discharge [5], laser vaporization [6], pyrolysis [7, 8], plasma- enhanced [9,10] or thermal chemical vapor deposition (CVD) [9,10] have been developed for the production of CNTs. The synthesis of CNTs using CVD method has attracted many attentions because of many advantages such as high purity, high yield, controlled growth, and vertical alignment [12]. Hollow spherical carbon exhibits unique properties with low weight, thermal insulation, and high compressive strength. However, reports about hollow carbon structure are very limited. In this paper, we describe a new route for synthesizing fluffy hollow carbon spheres by FeCl<sub>3</sub> catalyzed solvent-thermal reaction with CaC<sub>2</sub> and CCl<sub>4</sub> as carbon sources. This is the first report where CaC<sub>2</sub> was used as a carbon precursor to get hollow spherical carbon.

The reaction can be represented as [13]:

$$2\text{CaC}_2 + \text{CCl}_4 \xrightarrow{\text{FeCl}_3} 2\text{CaCl}_2 + 5\text{C}$$

However the involved growth mechanism is rather different and an adsorption-diffusion-precipitation model has been widely accepted [14].

## **2. Experimental Method**

Silicon *p*-Si/100 ( $1 \times 1 \times 0.05$ ) cm<sup>3</sup> with resistivity of 15( $\Omega$ .cm) and quartz glass ( $1 \times 1$ ) cm<sup>2</sup> substrate was used. The substrate was cleaned in acetone 99.99 purity 100 ml inside and put in the digital ultrasonic at 40 <sup>o</sup>C for 10 min with deionised water, ultrasonic with alcohol 99.99 purity for 5min, rinsing with deionised water, last step substrate were then dried with dry nitrogen. After cleaning substrate put the Silicon into a reactor, we have allowed the temperature increase to about 900 °C, for removing again the remaining dirtiness. In this stage we inject 100cm<sup>3</sup>/min pure oxygen in reactor for about 20 min, Later we turn off furnace and cooling the substrate. The thickness of the SiO<sub>2</sub>

layer was estimated at approximately 300 nm. The preparation of catalyst, iron chloride (FeCl<sub>3</sub>) was dissolved in ethanol purity 99.99 to obtain variety molarities (90) mM. The solution was spin coating at 1000 r.p.m for 60 sec.The catalyst deposited substrate were loaded on a quartz boat, nitrogen (N<sub>2</sub>) purity 99.99 was flow rate 90sccm at 750 °C into a quartz reactor in order to prevent the oxidation of the catalyst films. After formation of nanometer size catalyst particle, the CNTs were sequently growth using C<sub>2</sub>H<sub>2</sub> purity 99.99 with a flow rate of 100sccm for 1min at the same temperature. After finishing the CNTs growth the reactor was cooled down to room temperature under N<sub>2</sub> ambient. The CNTs grown on catalyst practical were examined by scanning electron microscopy (SEM) (TEM) to measure the diameter, and the uniformity. The CVD apparatus used in experiments is basically composed of a quartz glass tube with diameter 3.5cm, and tube furnace with diameter 4.5cm and bulbar show in figure (1). The coated substrate was carried out into quartz tube and introduces N2 high purity 99.99 with flow rate 90 sccm in tube after this heating the tube with heat rate 20°C/min until to reach the final temperature at 750°C. Stay in this temperature 30min to forming Iron oxide clusters. The synthesis of CNS was performed by adding a constant flow rate of acetylene (20 sccm) to the nitrogen carrier gas during 15 min. After this step the acetylene switch off and the N<sub>2</sub> continuously in flow until to cooling in room temperature.



Fig. 1. Photograph of setup CVD.

#### 2.1. Experimental Setup of Gas Sensor

Figure (2) shows the gas sensor is placed inside a sealed stainless steel test chamber and the variation of its electrical signal is monitored by an instrument. The electrical instruments have been used for sensor testing Brymen (BM850) digital multimeter for resistance measurement. Alcatel vacuum system was used to evacuate the chamber. The target gases are pure (NO<sub>2</sub> and H<sub>2</sub>). A needle valve controller is used for mixing current response the carrier and target gases and feed them into the test chamber at the desired concentrations and flow rates. The gas flow rates and concentrations are varied, which is controlled by pump the known volume of NO<sub>2</sub> in volume chamber that already calculate. A computer was used for analyzing and processing the measurements. The sensors were tested at room temperature or at moderate temperatures 30 °C. The sensor testing system is schematically depicted in figure (2).



Fig. 2. Schematic description of the gas sensor testing system.

The sensor sensitivity (S) is calculated using (1):

$$S(\%) = ((R_g - R_0)/R_0)*100$$
 (1)

where,  $R_g$  and  $R_0$  are the resistance values of the sensor with and without gas exposure, respectively.

#### 2.2. NO<sub>2</sub> Gas Preparation

NO<sub>2</sub> gas was prepared in laboratory by adding three gm of potassium nitrate to (100 ml) of dilute sulfuric acid.

$$H_2SO_4 + 2KNO_3 \rightarrow 2NO_2 + K_2SO_4 + H_2O_2$$
 (2)

### **2.3. Sensor Testing Protocol for NO<sub>2</sub>**

The following is the protocol used in the operation of the test setup,

- The test chamber is opened and the sensor placed inside it. and necessary electrical connections between the pin feed through and the sensor spring loaded pins and Digital multi meter are made. The test chamber is closed.
- Then, the rotary pump is switched on to evacuate the test chamber to approximately 50 mbar .
- By use Hetmental for boiling NO<sub>2</sub> at room temperature.
- After that, using the needle valves the flow rate of the carrier and vapor of ethanol is adjusted.
- Next, the vapor of NO<sub>2</sub> known concentration in mixing chamber is allowed to flow to the test chamber by opening the two-way valve.
- Measurement of the current variation of the sensor for the known concentration of test gas mixing ratio is observed by the PC –inter-faced digital multi meter DMM.
- After the measurement, the needle valve of the vapor of ethanolis closed to allow the sensor to recover to the base line current value I<sub>0</sub>.
- The above measurements are repeated for the other required tem peratures and/or concentrations of the

vapor. to calculate the concentration of vapor use equation:

$$\frac{\text{valume of NO}_2(\text{mel})}{\text{valume of test chamber(mel)}} = \frac{\text{valume(ppm)}}{10^6} \quad (3)$$

## **3. Results and Discussion**

The catalyst was examined by AFM model (AA3000) to calculate the roughness and that arrangement of nanoparticles on the surface of SiO<sub>2</sub> and quartz substrates. The solution was dropped on P/100/SiO<sub>2</sub> substrate in number of circular 1000 r/min for each once with spin coater at room temperature. The samples were allowed to dry in air. The average grain size and average roughness of nanoparticles is a direct function to concentration and homogeneity. This means that there are some other parameters that are important in the dispersion. The distribution of clusters is strongly dependent on the type of salt, support and the distance from the center of the support to the edge. The most obvious is the quantity of liquid dropped on surface which will affect the quantity of iron molecules per unit area.

Figure (3) illustrates the average roughness about 4.11nm and average grain equal 8.28 nm.



Fig. 3. AFM image for the catalyst prepared by Spin Coater 90 mM of FeCl<sub>3</sub>.

The AFM technique uses a laterally moving tip, while the cantilever reflects the sample's topography, or the Z measurements. Even though the tip is very sharp, it is impossible to gather the information from the underside of

specimen. The spherical particle will be viewed as a bump by the Atomic Force Microscope. To correct the AFM image for this effect some deconvolution techniques are used. In conclusion, the AFM and SEM images are complementing each other. Surface morphologies obtained through Scanning Electron Microscope (HR-SEM) study carried out by (Hitachi FE-SEM model S-4160, Japan) in University of Tehran at 24 kV of carbon Nanosphere formed by the Thermal Decomposition of Acetylene and TEM (Using an instrument called (TEM Philips EM208). This system is available in Day Petronic Company in Iran Tehran) is presented in figure (4) (a, b). The surface morphology of the soot deposited appears to be nonuniform nanospheres. TEM image of CNTs with few catalytic particles inside is shown. Carbon nanospheres depend on the gas flow rates. We have introduced N<sub>2</sub> at 90 sccm into the reaction systems. Carbon spheres with nonuniform sizes. However, the carbon spheres could not be separated from the other spheres even at 20 sccm of N<sub>2</sub> flow. The flow rate of C<sub>2</sub>H<sub>2</sub> has less effect on the separation of the carbon spheres. Few nanotubes with amorphous carbon and more of catalyst particles were seen in the carbon soot deposited at 750°C. The amount and the nature of the deposited carbon were found to depend strongly on the quartz tube diameter at constant gas flow rates. The variation of quartz tube dimension (inner diameter) also influence the nature and yield of carbon nanostructures deposited. We reminded avoiding higher flow rates of  $C_2H_2$ to avoid experimental hazards. Fig. 4.a shows the SEM image of the particles is spherical and adheres to each other. Fig. 4.b shows the average particle size was estimated based on the TEM image is less then 30nm in diameter. As shown in HRTEM image, light and dark concentric contrast areas are visible on an individual sphere, clearly revealing the core/shell geometry of the carbon sphere.



Fig. 4. (a) SEM image and (b) TEM of carbon Nanosphere with catalyst prepared by Spin Coater 90 mM of FeCl3.

To characterize the samples of CNS, it has been employed XRD system (Lab X, XRD 6000). The comparative study of the XRD profiles of sample is presented in figure (5) at different point on sample. The samples show two distinct peaks at  $\sim 25^{\circ}$  of higher intensity and a slightly broadened peak around 42°. The prominent (002) peak at  $\sim 25^{\circ}$  is assigned to the graphitic carbon in the sample. The presence of strong and broadened  $\pi$  band in all the samples suggests that the carbon nanospheres (CNSs) formed is composed more of crystalline graphitic carbon. The  $\gamma$ -band at  $\sim 20^{\circ}$  originates from the disorder in the sp<sup>2</sup> hybridized carbon and indicates lattice disorder in the curved graphene sheets, spheres, tube ends etc. A comparatively low intensity of the  $\gamma$ -band in the XRD profile of the samples indicates that all the nanomaterials synthesized have a very low percentage of disordered amorphous carbon while the appearance of the high intensity  $\pi$  band in all of them shows that the samples have a high degree of crystallinity or graphitization. The disordered carbon are composed of both  $sp^3$  and  $sp^2$  sites. The sp<sup>3</sup> sites have only  $\sigma$  states whereas the sp<sup>2</sup> sites also possess  $\pi$  states.  $\pi$  states are different, because a  $\pi$  orbital usually interacts with  $\pi$  states of more than one atom to

form a conjugated system such as in benzene. The mediumrange order due to  $\pi$ -bonding distinguishes disordered carbons from the  $\sigma$ -bonded amorphous carbon.  $\pi$ -bonding is maximized if the  $\pi$  states form pairs of aligned  $\pi$ -states, or six fold aromatic rings or graphitic clusters of aromatic rings. This usually occurs in graphitic carbon with microcrystalline structure [15-18].



Fig. 5. XRD partten of carbon Nanosphere with catalyst prepared by Spin Coater 90 mM of FeCl<sub>3</sub>.

Figure (6) shows the Raman spectra of grown carbon nanomaterials excited by a 1064 nm laser. The spectrum consists of mainly two peaks at 1360 and 1595 cm<sup>-1</sup>, which are designated as the tangential modes of carbon nanotubes. The peak at 1595 cm<sup>-1</sup> is due to the Raman-active  $E_{2g}$ mode analogous to that of graphite. A slight red shift was observed for the D-band of our sample, which was located at 1360 cm<sup>-1</sup>, as the D-band frequency shows a strong linear dependence on the excitation laser energy (E<sub>laser</sub>), which is further attributed to the electronic transition between bands, which is in resonance with the incident photon. This is mainly derived from the disordered carbon and defects of graphite's, which is a feature common to all sp<sup>2</sup> hybridized disordered carbon materials. In the Ramanshift range 1200-1800 cm<sup>-1</sup>, two peaks are observed at ~1360 and 1595 cm<sup>-1</sup> corresponding to graphite's D-and Gbands respectively. The G band corresponds to the firstorder scattering of the E<sub>2g</sub> mode observed for sp<sup>2</sup> domains and the D band is ascribed to edge planes and disordered structures. The D band is a breathing mode associated with defects as it is forbidden in perfect single layers of graphene. The high intensity G band, assigned to the graphite phonon mode often associated with single-layer

graphene, appearing in all the samples suggests the CNS is composed of crystalline graphitic carbon. The D-band, originating from the disorder in  $sp^2$ -hybridized carbon and thereby indicating the lattice distortions in curved graphene sheets and spheres etc., is very weak in the present study and is attributed to the absence of structural defects and less  $sp^3$ -hybridized carbon.



Fig. 6. Raman spectra of carbon Nanosphere with catalyst prepared by Spin Coater 90 mM of FeCl<sub>3</sub>.



Fig. 7. FTIR spectra of carbon Nanosphere with catalyst prepared by Spin Coater 90 mM of FeCl<sub>3</sub>.

Infrared spectral data are used to study the functional group of CNSs formed (figure 7). The assignments of frequencies to their functional groups are carried out by comparison with the published work reported by various authors [15]. A broadened peak centered at 3441.12 cm<sup>-1</sup> is present in all the samples, which is assigned to the (O-H) stretching vibration of the carboxylic acid group or adsorbed water. The peaks at 2925 and 2850 cm<sup>-1</sup> are assigned as CH<sub>2</sub> asymmetric stretching vibration and CH<sub>3</sub> symmetric stretching in aliphatic groups comes mainly

from methyl, methylene and methane groups bonded to aromatic rings. The peak observed at ~ 1630 and 1650 cm<sup>-1</sup> is due to the C=C stretching vibrations of graphite band (Gband) in the sample and also corresponds to the E2g mode of highly oriented pyrolytic graphite. This suggests that the CNSs are composed more of crystalline graphitic carbon and the higher intensity of G-band is due to the higher degree of crystallinity/graphitization. The FTIR study reveals the presence of strong G-band with less disorder in all the samples. These results corroborate the SEM-TEM and XRD analysis [16].

## 4. Discussion on the Mechanism of CNSs Sensor Array Gas-Sensitive Response

The performance of Carbon Nanosphere gas-sensitive materials is greatly influenced by the working temperature. The present study tested the NO<sub>2</sub> and H<sub>2</sub> gas sensor response curve of the CNS sensor at 200 °C working temperature. According to procedures of the experiment described in method section, under the condition that the sensor is under a 200 °C working temperature, the gas sensitivity (response curve) of the CNS sensor is measured at NO<sub>2</sub> and H<sub>2</sub> gas concentrations of 3, 5, 7 and 9 ppm, and the result is shown in figure (8). The figure illustrates that the bigger the concentration of NO<sub>2</sub> and H<sub>2</sub> gas, the higher the sensor response (sensitivity). The sensors were employed to detect NO<sub>2</sub> and  $H_2$  gases. Figure (8) shows the electrical current variations of CNS-based sensor to H<sub>2</sub> gas. We obtained our sensor are highly sensitive with a fast response time of 50 seconds. It also indicates that the recovery of the sensors is relatively fast and complete. This can be due to the fact that hydrogen is a saturated hydrocarbon, resulting in the weak interaction between tested gas and CNS molecules. The recovery of the NO<sub>2</sub> sensors is slow compared to that of the H<sub>2</sub> gas within the same time frame. This can be ascribed to the higher adsorption energy and rather strong interaction between NO<sub>2</sub> molecules and CNS molecules resulting in the incomplete NO<sub>2</sub> desorption in the short time. CNS as a sensitive material that detects gases through changes in physical properties, such as electric conductivity, when the gas comes in contact with a CNS molecule surface. Oxygen has a very strong adsorption. Oxygen in the air at room temperature adsorbs physically on the CNS surface. When a certain energy is gained, oxygen adsorbs on the CNS sensor surface in the form of chemical adsorption. The common forms of chemical absorption oxygen are O2ads,  $O_{ads}$ , and  $O_{ads}^{2-}$ , which relate to the environmental temperature. The experimental results indicate that under low temperatures, the CNS surface exists in the form of a "molecular ion"  $\mathrm{O}_{2ads}$  , and changes into aform of an "atomic ion"  $O_{ads}^{-}$  and  $O_{ads}^{-2}^{-}$  with the rise in temperature. At more than 450 K,  $O_{ads}^{-}$  dominates the surface oxygen adsorption. In the current study, the working temperature of the sensor is 200 °C (473.15 K); hence, in the process, the oxygen in the air captures the surface electron of CNS, changing into chemical adsorption. The chemical reaction equation is:

$$0_2 + 2e' \rightarrow 2 0_{ads} - \tag{4}$$

when the sensor surface has reduced the  $NO_2$  gas, the response between the adsorption of oxygen and the  $NO_2$  gas sensor is as follows:

$$NO_2 + O_{ads} \rightarrow NO_2 O_{ads} + e' \qquad (5)$$

NO<sub>2</sub> gas undergoes an ionic reaction with the surface

adsorption oxygen, removes an electron, releases back into the conduction band, and causes the conductivity of the CNS materials to increase, thus causing the resistance to decrease. In this manner, the CNSs sensor plays a sensing function [20].

The vapor NO<sub>2</sub>,  $H_2$  gas sensor sensitivity of a CNS is usually measured as the percentage change in CNS current on gas exposure, or may be defined as the ratio of its current in air to its steady state value in the presence of a gas, or vice versa. Irrespective of the definition one uses, it is important to monitor the (change in) electrical current of a sensor film. For measurement of change in current on exposure to gas, the sensor head was put in an air-tight chamber, a pre-defined concentration of gas taken from calibrated cannister of (3-9) ppm gas was introduced in this chamber by syringe (Fig. 2).



**Figure 8.** Relation between current and time of CNSs with different vapor  $NO_2$  and  $H_2$  gas concentration.

## 5. Conclusion

Fe particles of diameter ranging from 30 to 90 nm were used as the catalyst particles. The catalyst was prepared from an Iron chloride FeCl<sub>3</sub> precursor solution that was spin –coated on P-SiO<sub>2</sub>/ (100) substrate. CNS synthesized by chemical vapor deposition from acetylene (20 sccm) and nitrogen (90sccm) during 15 min at 750 °C. Diameter from the CNS about 30nm or less then. The sensor response of 3–9 ppm NO<sub>2</sub> and H<sub>2</sub> gas is tested, and the sensitive response mechanism is discussed. The test results show that the CNS sensor has high response for H<sub>2</sub> gas and less then about NO<sub>2</sub> gas.

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