Synthesis, Characterization and Application of Doped Carbon Nanotubes

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Abstract

Carbon nanotubes (CNTs) have been synthesized by pyrolysis of carbon tetrachloride in presence of organometallic catalyst ferrocene. The synthesis has been carried out at a temperature of 950^0C for three hours. A characterization of the samples has been done using optical microscopy, Raman Spectra, Scanning Electron Microscopy and Transmission Electron Microscopy. The synthesized doped CNTs were further explored for ethanol sensing. It was also found that the doped nanotubes were sensitive to ethanol and can act as an alcohol sensor.

KEYWORDS : Carbon nanotubes (CNTs), Hydrocarbon pyrolysis, Ethanol Sensing

1. INTRODUCTION

Carbon nanotubes (CNTs) have been an area of intense interest for many scientists and researchers since its discovery by Sumio Ijima(1991). In this era of cutting edge research, CNTs have been most interesting nanostructures due to their large application potential and unusual properties. Enormous scientific research has been carried out to explore the properties leading to the potential applications of CNTs. CNTs are the crystalline form of carbon, whose structures look like a rolled sheet of graphene capped in both ends by hemispherical fullerenes. There are two types of CNTs: single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). SWCNTs generally have a diameter of ~1 nm but the length can be hundreds of nanometers. MWCNTs have layers of graphene surrounding a central tubule of 1-10 nanometer diameters.

CNTs can be synthesized by various techniques such as,

- Arc discharge
- Laser vaporization
- Hydrocarbon pyrolysis
- High-pressure catalytic decomposition of carbon monoxide (HiPCO)
- Electrophoretic deposition (EPD)
- Flame synthesis
- Pyrolysis
- Chemical Vapour Deposition (CVD)
- Plasma enhanced CVD (PECVD), etc.

Every synthesis technique aims at economic, pure and large scale production of nanotubes. A carbon source and a catalyst are used as precursors and the synthesis takes place at high temperature. Gaseous hydrocarbons such as acetylene, methane, n-butane, propane and ethylene and liquid hydrocarbons such as benzene(C_6H_6, bp:79-

85^0C), methanol (CH_3OH bp: 64-65^0C), ethanol(C_2H_5OH, bp:78^0C), Xylene (C_8H_{10}, bp: 135-145^0C) etc. are used. Catalysts used for the synthesis of CNTs are mostly organometallic compounds such as Ferrocene, Nickelocene, cobaltocene etc. Many methods are applied to produce CNTs doped with elements such as nitrogen and boron to produce p-type or n-type semiconductors.

In the present work, synthesis of doped CNTs by one step co-pyrolysis has been accomplished. Precursors used are benzene, chloroform, carbon tetrachloride & catalyst ferrocene was used. Further, preliminary study on doped CNTs for ethanol sensing has been carried out.

- Carbon tetrachloride(CCl_4) was used in various amount as chlorine containing carbon precursor. It has a boiling point of 76.72^0C
- Ferrocene [$Fe(C_5H_5)_2$] was used in different proportions as catalyst for the growth of CNTs.

2. INSTRUMENTS AND APPARATUS

- **Quartz tube:** Thin and long tubes of length 60 cm and diameter 1 cm was used for the synthesis of chlorine containing carbon nanotubes.
- **Furnace:** Tubular furnace was used as shown in figure 1 along with calibrated temperature profile across it.

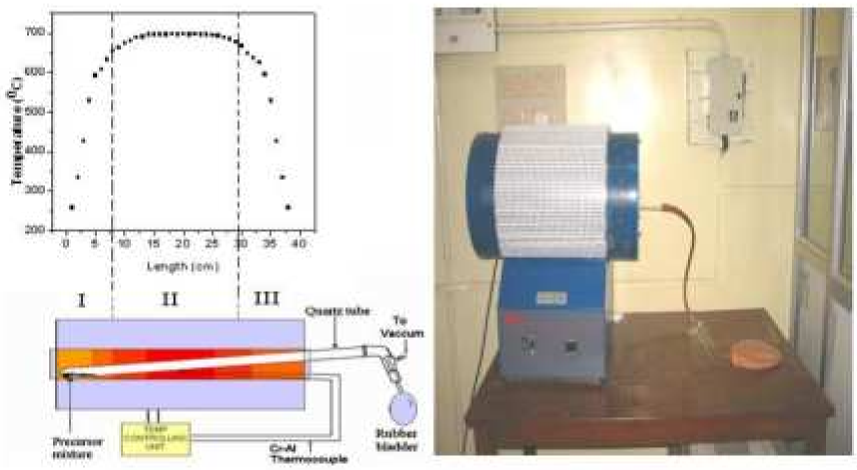

Figure 1: Images of the furnace used for synthesis of CNTs. (a) calibrated temperature profile across the furnace and (b) optical photograph outer view of the furnace.

3. SYNTHESIS OF CARBON NANOTUBES

CCl_4 has a boiling point of 76.72^0C. Doped CNTs are synthesized by taking 4 ml of carbon tetrachloride in a quartz tube of length 60 cm and diameter 1 cm. 40 mg ferrocene was added to it subsequently. Silicon wafer of length 10 mm and breadth 5 mm used as substrate was placed inside the tube. The open end of the tube was enclosed with a rubber bladder that collects unreacted gases. The experimental setup is clearly shown in figure-1. The tube was then kept in the furnace which was programmed such as the initial temperature was 25^0C ramped at 10^0C per minute and dwelled at a temperature of 950^0C for 3 hours. A black deposition inside the quartz tube as well as on the silicon substrates was observed. The depositions were then extracted out for further study.

4. Fabrication and Sensing Study of Alcohol

Doped CNTs films was prepared by drop cast technique. 2 mg of doped CNTs was sonicated with acetone for around 15 minutes for complete dispersion. Finally the dispersed sample was then drop casted on glass substrate (10mm x 5mm) by single drop casting method and dried in air. Electrodes were prepared using silver paste and are connected to Keitheley meter which are used for measuring the electrical properties of the sensing film. Doped CNTs grow on silicon substrate were also studied for sensing. The measurements were performed in a very simple home- made testing chamber as performed in GG/Ag nano composite for ammonia sensing. Schematic of sensing setup is provided in figure-2. The distance between ethanol solution and sensor film is kept 1 cm apart. In the sensing experiment, the concentrated absolute alcohol vapours were introduced into the testing chamber manually at room temperature. The detected ethanol vapors inside the testing chamber was determined by the change in current at constant voltage of 0.5 V.

The sensitivity is defined as $s = \Delta R / Ra$, $\Delta R = R_g - R_a$, where, R_a is the resistance in dried air and R_g is that in the dried air mixed with ethanol. The variation of current with time has been monitored for sensing study.

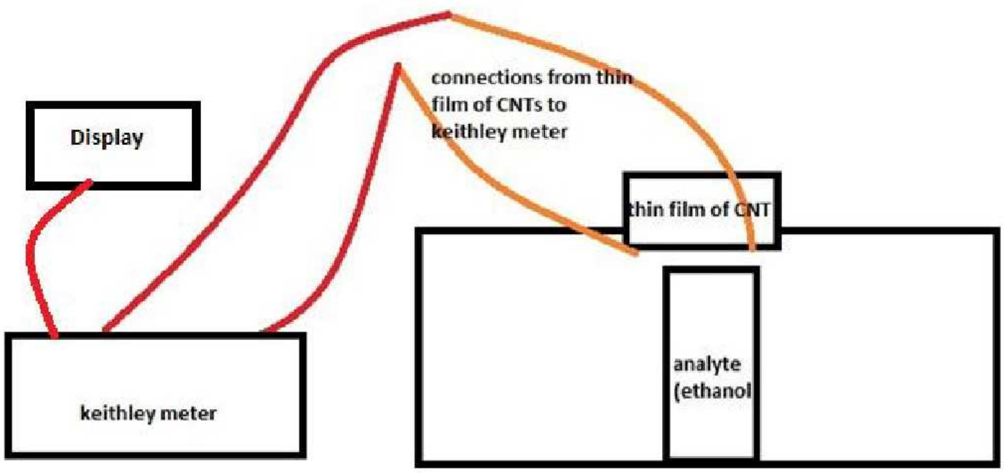

Figure 2: Schematic of the experimental set up for the ethanol sensing.

5. RESULTS AND DISCUSSIONS

(i) The synthesis of doped CNTs was performed at two different temperatures i.e. at 950 and 1100^{0}C keeping the other parameters such as 40 mg ferrocene, 4 ml carbon tetrachloride and ramped time of 10^{0}C every minute constant. It was observed that best results were found at 950^{0}C.

(ii) For the synthesis of doped CNTs the carbon as well as chlorine containing precursors used was carbon tetrachloride. The catalyst meant for the growth of CNTs was ferrocene. Experiments were also carried out with chlorine containing precursor chlorobenzene but not much satisfactory results were obtained. The catalyst and carbon precursor ratio was varied to different amount but the best formation was for 40 mg ferrocene and 4 ml carbon tetrachloride.

(iii) All the four synthesis samples were observed under optical microscope. Grass like structures were observed. The images under optical microscope of all the four samples are shown in figure 3(a-d). Figure 3(a) depicts the image of sample present in the first part of the inner wall of quartz tube. Figure 3(b) shows the image of the deposits in the inner part of the inner wall of quartz tube. Figure 3(c) and 3(d) are the images of the thin film of doped CNTs on silicon and glass substrates respectively. It can be concluded from the figures that some hair-like structures do exist in the prepared sample that may be doped CNTs.

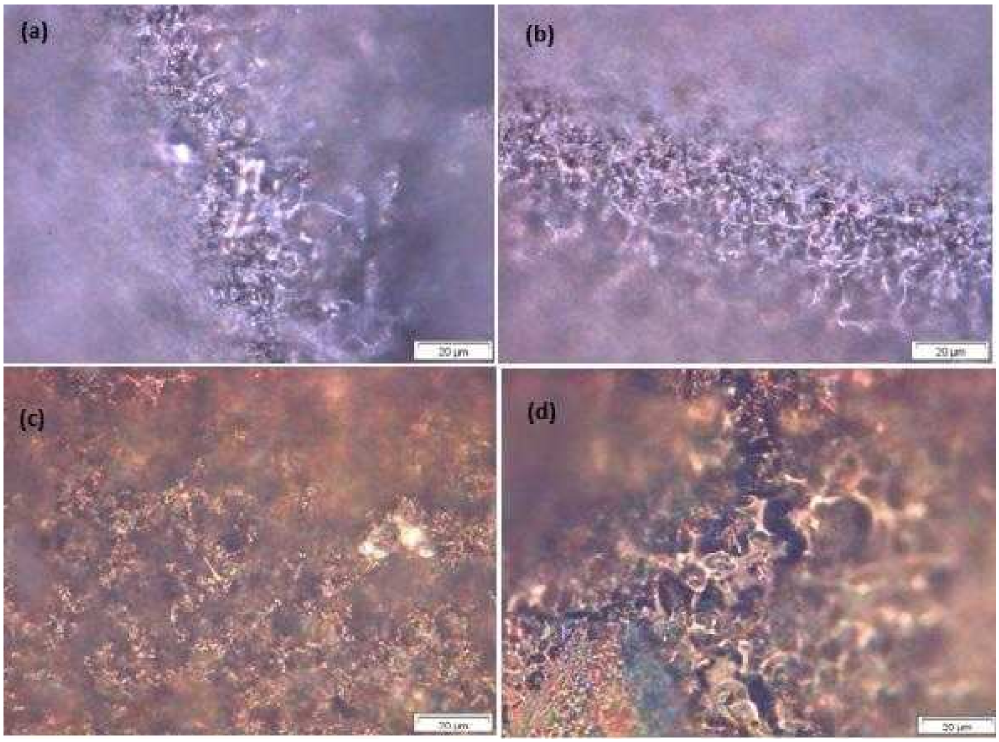

Figure 3: Images under optical microscope. (a) deposits in the first part of the inner wall of the quartz tube, (b) deposits in the innermost part of the wall of the tube, (c) doped CNTs grown on glass substrate, (d) doped CNTs made into thin film upon glass substrate.

(iv) When observed under Scanning electron microscope, tube like structures were confirmed. The images of the samples are shown in figure 4(a) and (b). A bunch of tube like structures were seen which were somewhat bamboo like structures that may give some hint about doping.

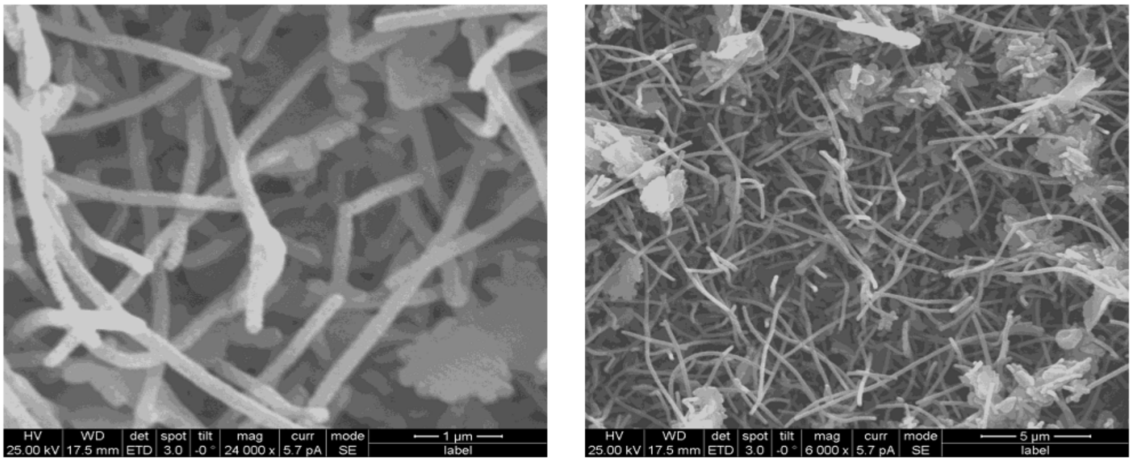

Figure 4:(a) & (b) SEM images of the CNTs.

(v) The TEM characterization of doped CNTs was performed. Figure 5 (a) & (b) depicts the TEM images of the prepared sample. 5(a) clearly shows the tubular structure of the nanotubes. In figure 5(b), there are some twisting and bulging along the length of the tubes that may give evidence of some kind of impurities.

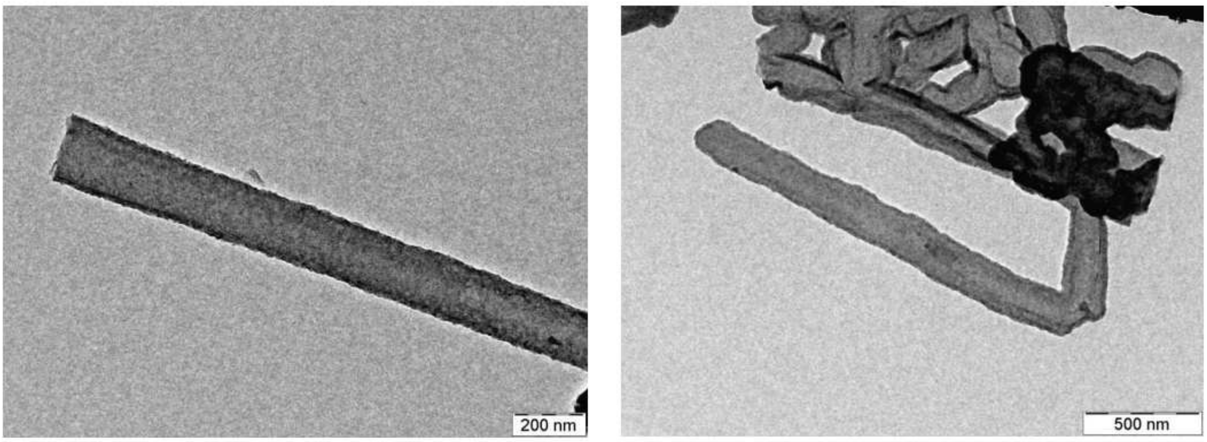

Figure 5: (a) & (b) TEM images of the CNTs.

(vi) Raman spectroscopy is very important for analysing carbon containing compounds. Any impurity can be depicted by observing the D peak of the spectra that accounts for the presence of any impuriy.The Raman spectra for pure CNTs and prepared doped CNTs has been compared in the following figure.The graphs of Raman spectroscopy of the prepared sample is shown in figure 6 (b). In figure 6 (a) the Raman spectra of pure CNTs has been shown. The sharp peak obtained at

1584cm^{-1} and 1598cm^{-1} as shown in the figures 6(a) and (b) can be identified as graphitic peak for doped and undoped CNTs respectively, which is also called the G peak. Whereas the peak obtained in the region of 1357cm^{-1} (undoped CNTs) and 1336cm^{-1} (doped CNTs) as shown in the figures corresponds to D peak, which can be attributed to the lattice distortion of the graphite crystals. This observed disorder or distortion has given an hint about presence of chlorine that may be confirmed by further characterization using energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

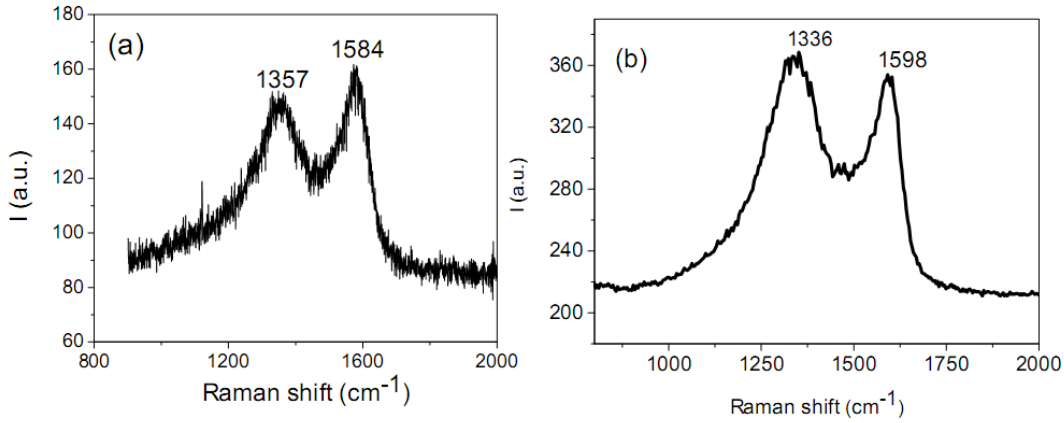

Figure 6 : Raman spectra of (a) pristine CNTs and (b) CNTs prepared using CCl_4 as precursor at 950°C.

6. Ethanol sensing of doped CNTs

Figure 7a and 7b shows the I-V characteristics of doped CNTs grown on silicon wafer and on glass substrate respectively at room temperature. Temporal response for concentrated ethanol on glass substrate and silica are shown in Figure 7c and 7d. It was observed that exposure of concentrated ethanol vapour to sensing film result in decrease in current (increase in resistance). The response time of 93 and 23 s and recovery time of 238 and 317 s was observed in glass substrate and silicon substrate respectively (figure 7c,d). The sensitivity was estimated to be 8.75 and 0.08 for glass and silicon substrate, respectively (table 1). This depicts that for the better sensitivity the doped CNTs deposited on glass substrate is useful for ethanol sensing. Thus our preliminary study on ethanol sensing give the indication that after varying some parameter the synthesis doped CNTs can be used for ethanol sensing application.

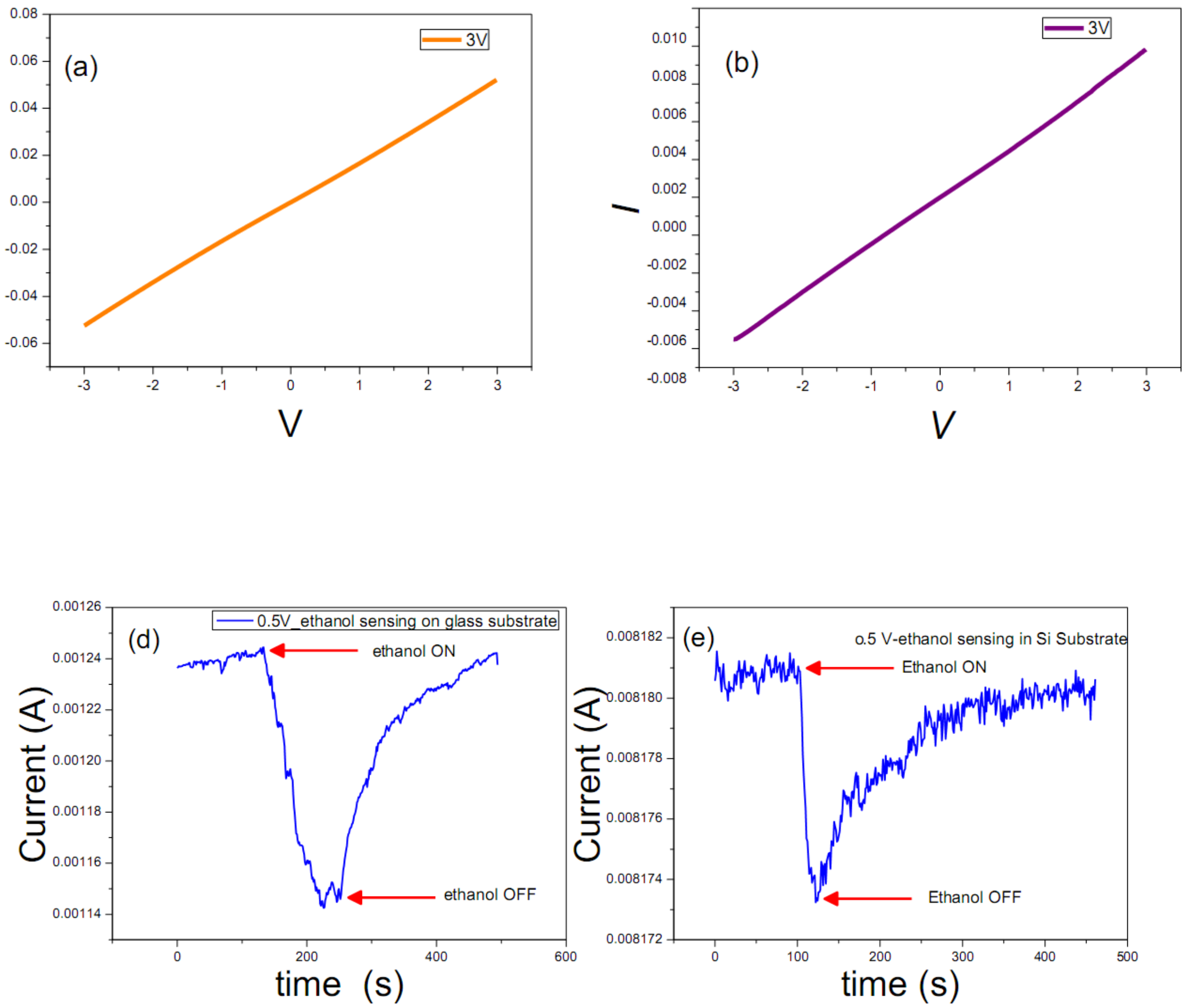

Figure 7. (a, b): I-V characteristics of a doped CNTs grown on silicon wafer and on glasssubstrate respectively at room temperature. (c,d), Temporal response for concentrate ethanol on glass substrate and silica.

Table 1

(Comparative study of response, recovery and sensitivity of ethanol sensing on different substrates)

Sample	Response (s)	Recovery (s)	Sensitivity (%)
Glass substrate	93	238	8.75
Silicon wafer	23	317	0.08

7. CONCLUSION

It can be concluded that doped CNTs can be obtained by pyrolysis using carbon tetrachloride as precursor. It is a simple process which does not need much optimisation. It was also found that the doped nanotubes were sensitive to ethanol and can act as an alcohol sensor.

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