Electrophoretic deposition of multi-walled carbon nanotubes on stainless steel for ethanol sensor

Mangal Chaudhary*, Reema Chaudhary* and Sabita Shrestha*

*Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal.

Abstract: Ethanol sensors are attracting tremendous interest because of their wide spread application in industry, environmental monitoring, space exploration, biomedicine and pharmaceuticals. This paper describes the feasibility study and investigation of electrophoretic deposition of oxidized MWCNTs for the application in ethanol sensor. MWCNTs are used to obtain thin film by electrophoretic deposition. The oxidized MWCNTs were characterized by FTIR. The uniform electrophoretic deposition of MWCNTs are confirmed by SEM. Raman spectroscopy confirmed the MWCNTs as deposited material. The resistance of electrophoretic deposition material was measured in closed glass chamber. Then sensitivity percentage was calculated. It was observed that the rate of % sensitivity increases with time and became saturated after certain time.

Keywords: Carbon nanotubes; Ethanol sensor; Electrophoretic deposition; Sensitivity.

Introduction

Electrophoretic deposition (EPD) is a method having large number of applications for the processing of traditional and advanced ceramics that has been used in the field of academic as well as in the field of industrial areas. Electrophoretic deposition process was first discovered in 1808 by the Russian Scientist Ruess. But the first time was performed in 1993 for the deposition of thorium particles on a platinum cathode in the form of emitter for the electron tube application[1]. This process is very well-known because of its simplicity to manage, effectiveness and cost effective to produce deposit of controlled thickness and homogeneous microstructure having very high packing density. The process allows the application of coating, thin and thick films, shaping of bulk objects and the infiltration of porous materials, fibrous substances and textile structure with metallic, polymeric and ceramic materials[2].

Sensor is a device that transforms chemical data, ranging the strength of a particular sample to all analysis composition, into an analytically useful signal[3]. It measure physical input from its environment and convert it into data that can be interpreted by either a human or a machine. Gas sensors are one of the most important technologies required when producing or manufacturing such gases. Through this, it is possible to monitor productivity as well as the leakage of gases into the surrounding environment. Ethanol is a small organic molecule has attracted wide industrial applications such as in industry, environment, monitoring, biomedicine, pharmaceuticals, breathalyzer etc. Thus, its detection and quantification during every stage of industrial processes or in the final effluents resulting from these industrial activities in order to protect the soil and water from pollution cannot be exaggerated[4]. Ethanol sensor works on the principle that, the adsorption and desorption of reducing molecules on sensing materials. On increasing the contact interface between the analytes and sensing materials then the sensitivity can be remarkably increased. Carbon nanotubes, semiconductor metal oxides and polymers can be used as sensing element on the basis their variation on electrical properties, whereas other variation

Author for correspondence: Sabita Shrestha, Central Department of Chemistry, Tribhuvan Univeristy, Kathmandu , Nepal.
Email: sabita.shrestha@cdc.tu.edu.np; https://orcid.org/0009-0005-3025-3783
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A carbon nanotube is an effective material for the detection of various toxic gases such as NH_3, NO_2, H_2S and also for different types of volatile organic compounds. Utilization of CNTs for the gas sensing application provides affordable sensing performance[6] at room temperature with extremely low detection feature, and low power consumption.

Multi-walled carbon nanotubes are being explored for ethanol sensors due to their high surface area, electrical conductivity, and ability to interact with gas molecules, enabling the development of sensitive and selective sensors. The MWCNTs showed p-type semiconducting properties. It is a very good sensing material due to its non-toxicity, stability and low cost.

In this paper we have reported the ethanol sensor by electrophoretic deposited MWCNTs. Before electrophoretic deposition, purification and surface functionalization of MWCNTs is done by conc. nitric acid (HNO_3). The oxidized MWCNTs is characterize by FTIR. FTIR showed the presence of oxygenated functionalized groups on the surface of MWCNTs. The EPD experiments were carried out by using oxidized MWCNTs on stainless steel plate. The uniform electrophoretic deposition of MWCNTs are confirmed by SEM. Raman spectroscopy also confirmed the MWCNTs as deposited material. The resistance of electrophoretic deposition material was measured in closed glass chamber with digital multi-meter. Then sensitivity percentage was calculated. It was observed that the rate of % sensitivity increases with time and became saturated after certain time.

Experimental Methods

Starting materials

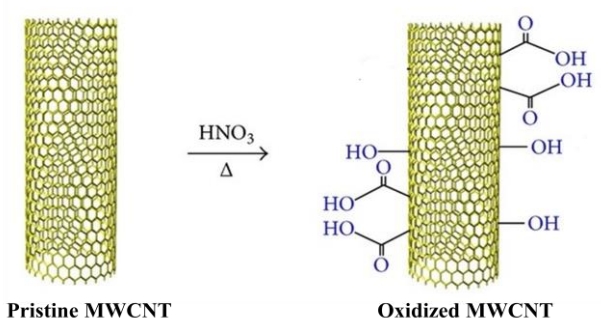
Multi-walled carbon nanotubes, which were synthesized by catalytic vapor deposition (CVD) process, were purchased from ILJIN Nanotechology Company Limited. South Korea (purity > 98%), used in work. Sodium Dodecyl Sulfate (SDS), sodium phosphate (Na_3PO_4) and sodium carbonate (Na_2CO_3) were purchased from HI-Media Laboratories Pvt. Ltd. And (Mumbai) India.

Oxidation and purification of multi-walled carbon nanotubes (MWCNTs)

For the oxidation of pristine multi-walled carbon nanotubes, basically produced powders contain not only MWCNTs but also contain some impurities like amorphous carbons, fullerenes, nano-crystalline graphite and transition metals that are used as catalyst during synthesis. These impurities sometimes enhance the accurate analysis of MWCNTs characteristics and limit the best performance of the MWCNTs applications to new functional device. Therefore, they should be purified before further treatment. There are different methods for the oxidation of MWCNTs, as air oxidation, acid refluxing method, ultra sonication, addition of surfactants, etc.

In this process, MWCNTs (0.2 g) were chemically oxidized in conc. nitric acid (40 mL) via sonication for about 15 minutes and then the solution was refluxed for about 4 hours. Then the solution was repetitively washed with distilled water until pH 7 and then filtered by using membrane filter paper having pore size 0.2 μm with the help of suction filter equipment. Then finally black residue was collected and dried in oven at 100 °C for 1 hour[7].

The principal purpose of this method was the removal of the metallic catalyst, amorphous carbon and chemical modification of MWCNTs by introducing different oxygenated functional groups such as –COOH, OH-, COO-, etc. on the surface of multi-walled carbon nanotubes as shown in Scheme 1. Moreover, the MWCNTs functionalized in this method are disperse in many solvents because the hydrophobic nature of MWCNTs was changed to hydrophilic due to attachments of polar group[8].



Scheme 1: Schematic representation of formation of oxidized MWCNTs.

Substrate preparation

For the preparation of substrate, first of all, the stainless steel plate was cleaved into 6 cm length and 5 cm breadth. Before deposition, the plates were mechanically and chemically cleaned to remove passive layers. For that the plates were abasing with silicon carbide paper having ranging number 1000, 1500 and 2000 respectively and then sonicated for 15 minutes and dipped into the solution of hydroxide, phosphate and sodium carbonate respectively at 60 °C to 80 °C for 15 minutes and finally dissolved in aqua-regia for 90 seconds and plates were rinsed with distilled water and then dried in oven for 10 minutes.

Electrophoretic deposition (EPD) process

For the EPD process, an oxidized multi-walled carbon nanotube was used. For this, first of all, oxidized MWCNTs (0.027 g) was dissolved in 30 mL of D.I. water and SDS (5 mL 1%) was added on it for well dispersion of MWCNTs and finally, sonicated for 6 hours.

The electrophoretic deposition process was carried out on an experimental set up consisting of a DC power supply, electrolytic baths and two electrodes, one of them was the substrate for MWCNTs coating. Out of two electrodes, one electrode was act as anode, while other as cathode. The inter-electrode distance was fixed at 1.5 cm. (Figure 1). The process was performed for the 10 minutes using voltage 10 V. Following the deposition process, the samples were carefully taken out of the solution and dried in oven for 24 hours. Figure 1(a) showed the EPD process and Figure (b) showed the deposited MWCNTs on stainless steel plate.

Measurements

Infrared Spectroscopy was carried out in Schimadzu IR tracer 100. The surface morphology of the sample was investigated by scanning electron microscope (QUANTA FEG 250). Raman spectra were obtained on a RM 1000-inVia, Renishaw.

Application in ethanol sensor

Sealed glass chamber was taken to measure the electrical resistance. The glass chamber was tightly attached with rubber socket to stop in and out of the air. In glass

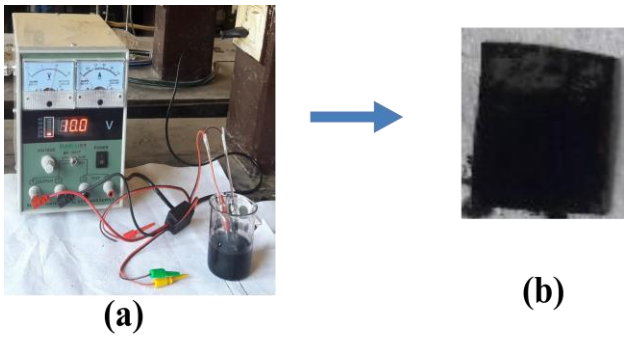


Figure 1: (a) Electrophoretic deposition (EPD) process (b) deposited oxidized MWCNTs on the stainless steel plate (black portion indicates the deposition of oxidized MWCNTs).

Application in ethanol sensor

Sealed glass chamber was taken to measure the electrical resistance. The glass chamber was tightly attached with rubber socket to stop in and out of the air. In glass chamber, a small 4/4 cm of plywood board were also taken with two screws in which deposited oxidized MWCNTs on stainless steel was placed in fixed position. Both right and left side of sealed glass chamber 1/1 holes were created and fitted with cork for inlet and outlet of target gas. One stainless plate (6/6 cm) was placed inside the chamber, which was heated at temperature (~ 60 ^{o}C) by heating coil and temperature was controlled by temperature controller. Then from top hole of chamber ethanol was poured drop by drop in that stainless steel plate. The resistance was measured by digital multi-meter. The whole set up for measuring sensitivity of the target substance i.e., ethanol is shown in the Figure 2 below.

Results and Discussion

FTIR analysis

Multi-walled carbon nanotubes was successfully purified and oxidized by acid reflux method. The oxidation of MWCNTs was ensured by Fourier transform infrared spectroscopy. Figure 3 (a) shows the FTIR spectrum of pristine MWCNTs. The spectrum does not show any sharp infrared peaks, which indicates, it does not contain anyother hand, the peak located around 1600 cm^{-1} assigned as carbonyl (C=O) stretching vibration of carboxyl group[9]. This confirms the presence of oxygenated functional groups.carboxyl group[9]..Figure 3

(b) shows the FTIR spectrum of oxidized MWCNTs. If we compared the FTIR of pristine MWCNTs with that of oxidized MWCNTs, many changes can be seen. The peaks around 3600 cm^{-1} may be due to hydroxyl (OH) group, because the oxidized MWCNTs is hydrophilic in nature.

On the other hand, the peak located around 1600 cm^{-1} assigned as carbonyl (C=O) stretching vibration of carboxyl group[9]. This confirms the presence of

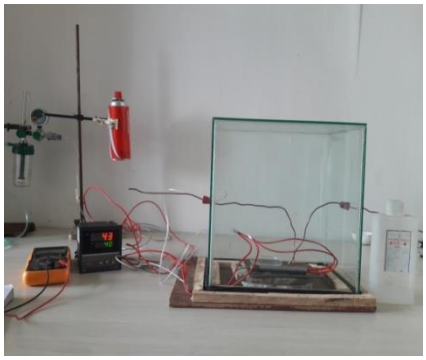


Figure 2: Experimental set up for ethanol sensor.

oxygenated functional group after treatment with acid.

SEM analysis

Oxidized MWCNTs was successfully deposited on stainless steel by electrophoretic deposition (EPD) process. The deposited oxidized MWCNTs on stainless steel substrate was confirmed by SEM. Figure 4 showed the SEM image of electrophoretic deposited oxidized MWCNTs on stainless steel substrate. The image showed that the oxidized MWCNTs deposited with appreciable homogeneity and excellent packing density without any porosity in the film morphology as well as uniform and evenly distributed oxidized MWCNTs were exhibited. This observation is in accordance with the deposition characteristics reported by Thomas et. al.[7] who performed CNT film deposition by EPD on stainless steel substrates.

Raman analysis

Oxidized MWCNTs was successfully deposited on stainless steel by EPD technique and was analyzed by Raman spectroscopy. Figure 5 depicted the Ramanspectrum of electrophoretic deposited oxidized MWCNTs on stainless steel substrate. The spectrum shows two characteristic peaks of oxidized MWCNTs. The peak at 1570 cm^{-1} is G-band and the peak at 1343 cm^{-1} is D-band. The G-band is indicative of well-ordered structure associated with sp^2 carbon atoms or it corresponding to the crystalline graphitic structure in the CNT. The D-band was due to the induction of significant defects or dis-order in the CNT[10].

Sensing response of oxidized MWCNTs on ethanol

When the ethanol molecule adsorbed on the sidewalls, edges or tube ends, then the electrical conductivity of the oxidized MWCNTs is changed. The sensing mechanism of

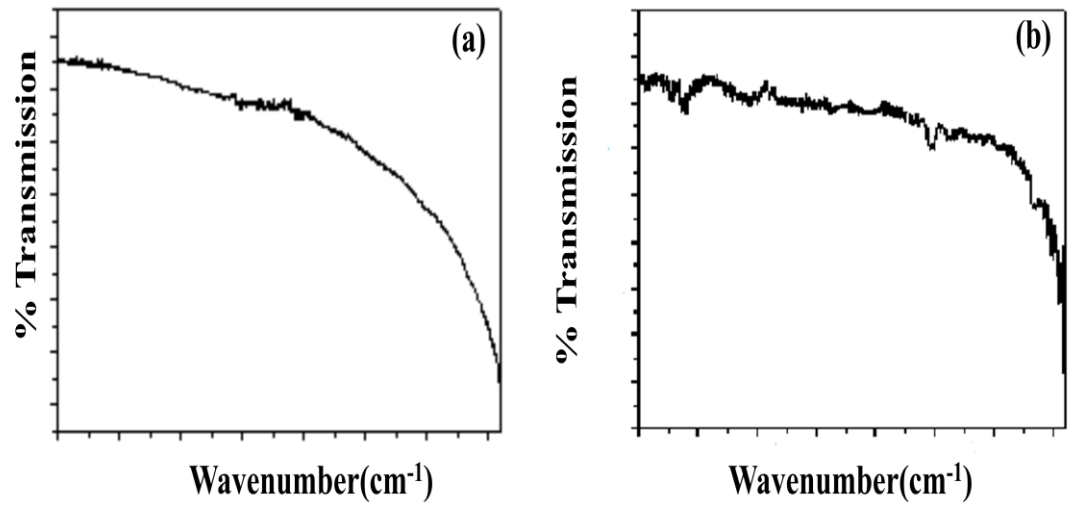


Figure 3: (a) FTIR spectrum of pristine MWCNTs (b) FTIR spectrum of oxidized MWCNTs.

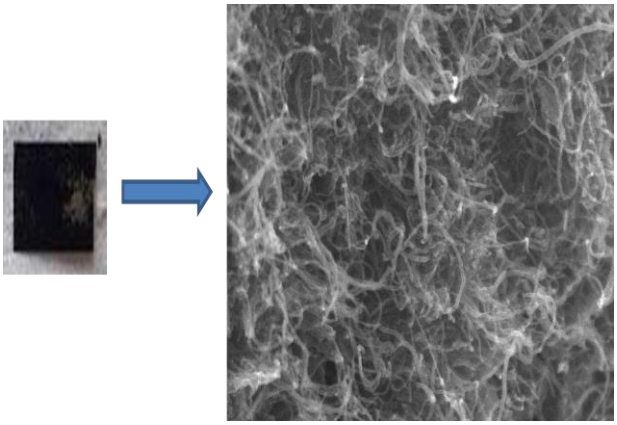


Figure 4: SEM image of oxidized MWCNTs on stainless steel substrate.

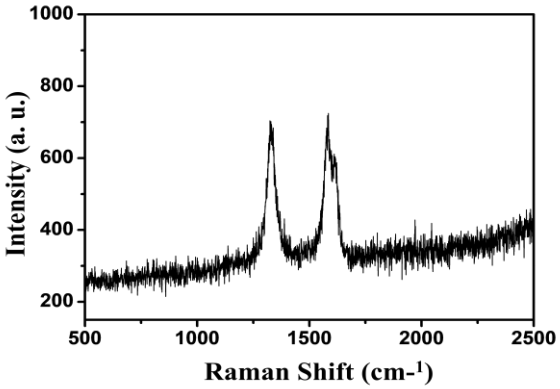


Figure 5: Raman spectrum of electrophoretic deposited MWCNTs.

CNT-based ethanol sensor involves charge transfer, which takes place during the interaction of ethanol molecules with the CNT surface. This interaction modifies the conductivity of CNTs. The resistance of the MWCNTs is changed, when exposed to ethanol molecules. Therefore, electrons are transferred from ethanol molecules to CNTs and hence form a space charge region (depletion region) on the CNT surface. This depletion region decreases the holes transport, thereby changing the electrical resistances of CNTs. The ethanol sensing properties were studied by keeping test sample in a sealed glass chamber. The electrical resistivity of electrophoretic deposited sample in absence of ethanol (air) was measured (i. e., R_{air}). Then ethanol was introduced into the chamber and electrical resistivity of the sample film was measured by using multi-meter (i. e., R_{EtOH}).

For 'p' type semiconductor materials, sensitivity percentage (%) is calculated by using following formula[11].

$$S\ (\%) = \frac{R_{EtOH} - R_{air}}{R_{air}} \times 100$$

Where, R_{air} = resistance in air

R_{EtOH} = resistance in presence of ethanol

The graph (b) in the Figure 6 shows that increment of the response (S %) takes place with the time with ethanol in the chamber but after 10 minutes it was stable. Response achieves the saturation value after 10 minutes of the target gas. Then the nature of the graph was observed to be linear.

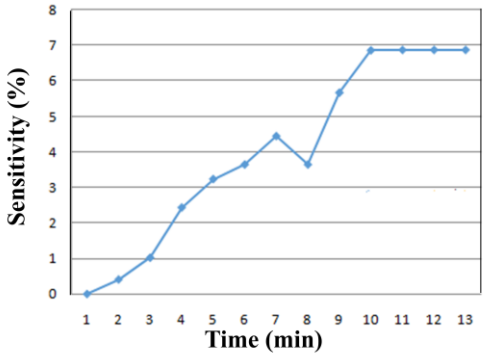


Figure 6: Sensitivity percentage (%) vs time (min).

The CNTs can be functionalized to improve their sensitivity. Functionalization of the CNTs exhibit with new properties that were different from those of their individual parts. Study showed that the CNTs decorated with Pd, Pt, Rh, and Au demonstrated improved sensitivity towards the gases[12]. In this work, oxidized MWCNTs was used and inquired the effect of interaction of oxidized MWCNTs on ethanol sensor. The increase of sensitivity can be caused by the oxidized MWCNTs interaction. The ethanol molecule donate electrons to the CNT sidewall, thereby expanding the empty region that decreases the carrier (holes) transport on the CNT wall and change the carrier mobility as well as the conductivity of the device.

Ethanol sensing mechanism

Before exposure ethanol to the sensing materials, the chamber was allowed to stabilize at normal room temperature for 30 minutes. Multi-walled carbon nanotubes are widely used as gas sensors due to their high surface area, electrical conductivity, and ability to interact with gas molecules. The sensing mechanism for ethanol (C_2H_5OH) involves changes in the electrical resistance of MWCNTs when ethanol molecules adsorb onto their surface.

When MWCNTs are exposed to air, oxygen molecules (O_2) adsorb onto their surface and capture free electrons from the conduction band. This results in negatively charged oxygen species (O_2^-, O^-) accumulating on the surface. Because MWCNTs are typically p-type semiconductors, this electron capture increases the hole concentration in the valence band, causing a decrease in resistance.

O_2 (gas) + $e^- \rightarrow O_2^-$(ads)

$O_2^- + e^- \rightarrow 2O^-$(ads)

The adsorption of O^- was the most interesting technique in sensors, because these oxygen ions were more reactive and thus made the material more sensitive in the presence of reducing substance ethanol. When ethanol (C_2H_5OH) is introduced, it reacts with these adsorbed oxygen species, donating electrons back to the MWCNT surface:

$C_2H_5OH + O^- \rightarrow CO_2 + H_2O + e-$

This reaction releases electrons, which neutralize some of the trapped charges, thereby reducing hole concentration and leading to an increase in resistance of the MWCNTs[13].

Conclusions

Carbon nanotubes have several advantages as active sensing materials due to high surface-area-to-volume ratio, high carrier mobility, and the ability to operate at room temperature. This paper reported the ethanol sensor by electrophoretic deposited multi-walled carbon nanotubes on stainless steel substrate. The gas sensing mechanism of direct interaction between the gas molecules and nanotube surface was studied. Before deposition oxidation and purification of MWCNTs was successfully conducted by concentrated nitric acid.Presence of oxygenated acidic surface group was characterized by FTIR. It is found that major functional group is carboxylic acid and hydroxyl group generated by strong acid treatment which is absent in pristine multi-walled carbon nanotubes.The uniform electrophoretic deposition of oxidized multi-walled carbon nanotubes on stainless steel was performed for 10 min at 10 volt and fixed inter-electrode distance of 1.5 cm. The deposition of MWCNTs on steel substrate was confirmed by SEM and Raman. Electrical resistance was measured via sealed glass chamber using ethanol as reducing substance. The sensitivity was calculated by using change in resistance. The results obtained in this study showed the applicability of the MWCNTs film for ethanol sensing.

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