ELECTROPHORETIC DEPOSITION OF OXIDIZED MULTI-WALLED CARBON NANOTUBES ON STAINLESS STEEL FOR ETHANOL SENSOR

A DISSERTATION

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BOARD EXAMINER AND CERTIFICATE OF APPROVAL

This dissertation entitled **"ELECTROPHORETIC DEPOSITION OF OXIDIZED MULTI-WALLED CARBON NANOTUBES ON STAINLESS STEEL FOR ETHANOL SENSOR"**, by Mr. Mangal Chaudhary under the supervision of Assoc. Prof. Dr. Sabita Shrestha, Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal, is hereby submitted and has been approved for the partial fulfillment of the Master of Science (M.Sc.) Degree in Chemistry.

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This is to certify that the dissertation work entitled **"ELECTROPHORETIC DEPOSITION OF OXIDIZED MULTI-WALLED CARBON NANOTUBES ON STAINLESS STEEL FOR ETHANOL SENSOR"**, Submitted by Mr. Mangal Chaudhary for the Degree of M.Sc. in Chemistry of Tribhuvan University was carried out under my supervision in the academic year 2016-2023. During the research period, Mr. Mangal Chaudhary had performed the work sincerely and satisfactorily.

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DECLARATION

I, *Mr. Mangal Chaudhary,* hereby declare that the work presented herein is a genuine work and done originally by me and has not been published or submitted elsewhere for the requirement of a degree program. Any literature, data or works done by others and cited in this dissertation has given due acknowledgement and listed in the reference section. This dissertation work has not been submitted to any other degree in this institute.

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DEDICATION

(*Dedicated to my parents*)

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ABBREVIATIONS

EtOH	= Ethanol
EPD	= Electrophoretic Deposition
CNTS	= Carbon Nanotubes
SWCNT	= Single Walled Carbon Nanotube
MWCNTs	= Multi-Walled Carbon Nanotubes
EDL	= Electrical Double Layer
PTFE	= Promising Technique for Massive Fabrication Electrode
SEM	= Scanning Electron Microscopy
FTIR	= Fourier Transformation Infrared Spectroscopy
DC	= Direct Current
CVD	= Chemical Vapor Deposition
AC	= Alternative Current
°C	= Degree Celsius
SDS	= Sodium Dodecyl Sulphate
nm	= Nanometer
R_{EtOH}	= Resistance in presence of Ethanol
R_a	= Resistance in presence of Air
PANI	= Polyaniline
cm	= centimeter
min	= minute
%	= Percentage
mm	= Multi-meter
µm	= Micro-meter
IUPAC	= International Union of Pure and Applied Chemistry

ABSTRACT

This dissertation research describe the feasibility study and investigation of electrophoretic deposition of oxidized MWCNTs for the application in ethanol sensor. Ethanol sensors are attracting tremendous interest because of their wide spread application in industry, environmental monitoring, space exploration, biomedicine and pharmaceuticals. Ethanol sensors with high sensitivity and selectivity are required for leakage detection of explosive gases such as hydrogen and for real time detection of toxic and pathogenic gases in industries. There is also a storage demand for the ability to monitor and control our ordinary environment, especially with the increasing concern of the global warming. MWCNTs are used to obtain thin film by electrophoretic deposition. Before deposition, MWCNTs were purified and surface functionalized by concentrate nitric acid (HNO_3) under heating.

The oxidized MWCNTs were characterized by FTIR. FTIR shows the presence of oxygenated functionalized groups as carboxylic acid and hydroxyl group on the surface of MWCNTs. The uniform electrophoretic deposition of MWCNTs are confirmed by SEM. Raman spectroscopy confirmed the deposited material was nothing other than MWCNTs.

The EPD experiments were carried out by using oxidized MWCNTs on stainless steel plate at 10V at a constant time for 10 min and electrode were fixed at a distance of 1.5 cm. modification of carbon nanotubes with functional groups will greatly enhance the selectivity of the carbon nanotubes-based sensors. CNTs-based sensors have proved to work well at normal room temperature, which reduces power consumption of the device and enables the safer detection of flammable gases and alcohol. 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.

Key words:

Carbon nanotubes, Ethanol sensor, Electrophoretic deposition, Flammable, Global warming, Oxygenated, Uniform, Saturated.

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CHAPTER – I

INTRODUCTION

1 Electrophoretic deposition

1.1 General Introduction

It is a technique having large number of applications for the processing of traditional and advanced ceramics, which includes enamels and porcelain and different varieties of bulk materials and coating, 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 electron tube application [1].

1.2 Definition

Electrophoretic deposition (EPD) is a method which is too much promising, being developed for the manipulating carbon nanotubes and nano composite materials [2]. This process is very well-known because of it's 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 [3].

Earlier, electrophoretic deposition (EPD) has been used in the field of processing the functional and composite ceramics, rolled layers and functionally classified materials, thin layer film, high production ceramics and composite deposited and biomaterials as well as for the coating nano particles and carbon nanotubes to give modern nano structured materials [1].

EPD is accomplished by the motion of charged fragments scattered in the appropriate solvent, towards the respective electrode by the application of electric field [4]. Deposition process takes place through fragment clotting. Electrophoretic deposition consequence the curdling of particle via motion of charged fragments and the production of a uniform, fixed deposit at the appropriate electrode. EPD process is very much useful for particle having their sized <30 μm. The emulsion solution having low viscosity yield good processing and managing merits [2].

1.3 Fundamental concept of EPD

Electrophoretic deposition required a two steps. String fragments in a solution are forced to move in the direction of an electrode in the application of electric field to the solution, is the first step. On the other hand particles are deposited to the next other electrode, is the second step [5]. EPD is capable of to produce equivalent deposit with high crystal structural likeness, to give sufficient control of deposit thickness and to accumulate coating on a extensive range of shapes and 3D composite and permeable structures [1].

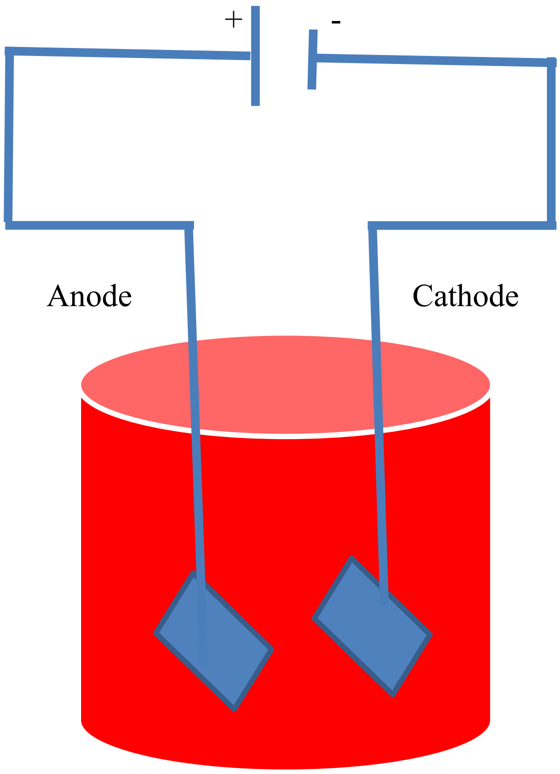


Fig. 1.3 Schematic diagram of electrophoretic deposition on stainless steel

1.4 Types of EPD

On the basis of polarity of electrodes, electrophoretic deposition (EPD) is of two types.

1.4.1 Anodic Electrophoretic Deposition

Electrophoretic deposition in which the negatively charged particles are deposited on the positive electrode is termed as an anodic electrophoretic deposition.

1.4.2 Cathodic Electrophoretic Deposition

The electrophoretic deposition, where the positively charged particles are deposited on the negative electrode is referred as cathodic electrophoretic deposition.

1.5 Factors Affecting on Electrophoretic Deposition

There are basically two parameters that can be used to determine characteristics of this process.

1.5.1 Parameters Related to the Suspension

Size of particles

To have a good deposition by this method, the size of particles must be <30 μm [6].

Zeta potential

It is the charge transfer between a solid and it's liquid and it is measured in millivolts. The magnitude of it confirmed the degree of electrostatic repulsion between abutting. If the magnitude is low then the attraction force may greater than this repulsion as a result dispersion may break and flocculate where as if potential is greater then superior dispersion takes place [7].

When the magnitude of zeta potential is lower than 25 mV, then the repulsive force is not strong enough to beat the Vander-walls force of attraction between the particles, and hence the particles start to collect, to remove this, high electrostatic repulsion causing high particle charge in necessary [8].

Dielectric Constant

The product of relative dielectric constant and dielectric constant in vacuum is termed as dielectric constant. When the dielectric constant is too low then the deposition can't tales place due to insufficient dissociative power, whereas with high value of dielectric constant, the high ionic strength in the liquid minimize the size of the double layer region which results in the decreases the electrophoretic mobility. Hence, low dielectric constant is more upgrade for EPD [9].

Conductivity of Suspension

The movement of charge particle is very low, if the suspension is too conductive, where as if the suspension is too resistive then the particles are electronically charged and the stability is lost [10]. Appropriate conductivity is different for different substance and systems [11].

Viscosity of Suspension

A good electrophoretic deposition is takes place when the suspension have a low viscosity.

Stability of Suspension

If suspension is stable and well-dispersed then deposition is better in comparison to that of unstable suspension.

1.5.2 Parameters Related to the Process

Deposition Time

In EPD, the time is directly proportional to thickness of deposition [12].

Applied Voltage

The applied voltage in EPD is directly proportional to the amount of deposition. It is reported that, at 25-100V/cm, homogeneous and uniform are deposited, on the other hand, at >100V/cm, deposition quality is decreases [13].

Concentration of solid in Suspension

Normally, rate of deposition is directly proportional to the concentration of solid in suspension.

Conductivity of Substrate

It has been reported found that low deposition and non-uniform occurred with low conductivity with respect to higher conductivity [14].

Electrode Separation

It has been reported that higher thickness film is deposited with closer distance between the electrodes [14].

1.6 Ethanol Sensor

International Union of Pure and Applied Chemistry (IUPAC) sensor is a device that transforms chemical data, ranging the strength of a particular sample to all analysis composition, into an analytically useful signal [15].

Sensor is a device that measures physical input from it's environment and convert it into data that can be interpreted by either a human or a machine. Sensor can be classified in different ways on the basis of

a) Power source (active and passive sensor)
b) Detection (electrical sensor, biological sensor, chemical sensor etc.)
c) Conversion phenomenon (photoelectric sensor, electromagnetic sensor etc.)
d) Output (analog and digital sensor)

Ethanol sensor have charming huge interest due to their widespread application in

I. Industry
II. Environmental monitoring
III. Biomedicine
IV. Pharmaceuticals
V. As Breathalyzer

On the basis of sensing methods, it is divided into two categories.

a) Variation on electrical properties
b) Variation of other properties

Carbon nanotubes can be used as sensing element on the basis their variation on electrical properties, whereas other variation are optic, acoustic, chromatographic and calorimetric [16].

Ethanol sensor works on the principle that, "the adsorption and desorption of reducing molecules on sensing materials.

The operating principle of the receptor, the sensor is differentiate into three groups.

a) Physical sensor
b) Chemical sensor
c) Biochemical sensor

In physical sensor, there is no chemical reaction occur at the receptor and the signal is a result of a physical process like mass, absorbance, refractive index, temperature or conductivity change. Chemical sensor are based on chemical reaction between analyze molecule and the receptor. Biochemical sensor are a sub-class of chemical sensors where the reaction is biochemical.

The MWCNTs showed p-type semiconducting properties. It is a very good sensing materials due to its non-toxicity, stability and low cost.

1.6.1 Ethanol Sensing Parameters

Sensitivity

The degree of influence of certain gas on the change in resistance, conductance or conductivity is referred as sensitivity. Sensitivity can also be defined in terms of conductance, resistance or conductivity. For p-type semiconductor, the resistance increases whereas, for n-type semiconductor, the resistance decreases when it is expose to the reducing substances. For p-type semiconductor, the sensitivity percentage is calculated by using formula,

Sensitivity percentage S (%)] = $\left[\frac{R_{EtOH-R_{air}}}{R_{air}}\right]$×100 %

Where,

R_{EtOH} = the resistance in presence of ethanol at a given temperature

R_{air} = the resistance in air

The sensor having higher sensitivity percentage is taken as very good sensor [17].

Selectivity

The ability of the sensor which determine how well it selects the response from the adjacent inputs. For example, if the gas sensor is designed for ethanol and how well it responds to ethanol in presence of other reducing substances is its selectivity. The response is generally like a Gaussian curve [18].

Stability

The ability of a sensor to provide reproducible results for a certain period of time which includes retaining the sensitivity, selectivity and recovery time [15].

Response Time

The time required for the sensor to responds to a step concentration change from zero to certain concentration value [17].

Recovery Time

The time required for the sensor signal to return to it's initial value after a step concentration changes from a certain value to zero is termed as recovery time [17].

Operating temperature

The temperature corresponds to the maximum sensitivity is known as operating temperature [17].

1.7 Application of Ethanol Sensor

The effects of environment pollution by toxic and greenhouse gases, methane from industries, have been increment day by day. Recognition of toxic and injurious gases is extreme to help human health and to make better life standard. Ethanol sensor are very useful device to do such a task.

The measurement of methane concentration in coal mining by the optical interference method, detection of concentration of ethanol in air by alcohol sensor, detection of automobile exhaust by catalytic combustion type sensor, determining the rate of ethanol production during fermentation, cobalt detection with the help of potential electrolysis cell, detection of alcohol drunk or not by Breathalyzer, oxygen detector by galvanic cell, ethanol gas leakage alarm by using SnO_2 semiconductor sensor, practically applied on ZrO_2 oxygen sensor corresponding to automobile exhaust gas regulator, city gas alarm using SnO_2 semiconductor sensor, city gas alarm by using catalytic combustion sensor, hydrogen sulphide detector with the help of tin oxide semiconductor gas sensor are the best example of sensor [18]. In overall, ethanol sensor are used as domestic ethanol detector, air purifier, alcohol checker etc.

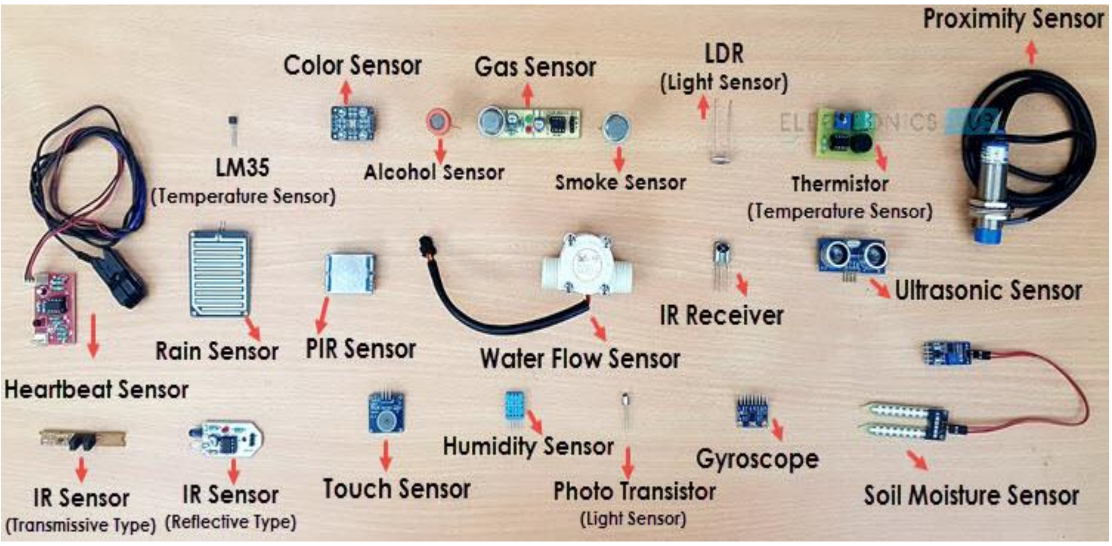


Fig. 1.7 Different kinds of sensor

1.8 Thin Film Technology

A thin film includes layers of materials ranging from fraction of nanometer scale to large micro structure scales in thickening and are synthesized by the process termed as deposition. Deposition is a process of thin film coating, that can be gained by modifying the four states of matter.

On the basis of nature of deposition method, thin film deposition process can be divided into chemical or physical technique.

A. Chemical Vapor Deposition

a) Plasma chemical vapor deposition

b) Plasma polymerization

c) Atomic layer deposition

B. Physical Vapor Deposition

a) Evaporation

b) Sputtering deposition

c) Plasma immersion ion implantation and deposition

C. Electrophoretic Deposition

D. Sol-gel method

E. Spraying process

Out of them, electrophoretic deposition(EPD) is the very good process for the deposition of thin film because, technique like CVD, evaporation and sputtering have little bit limitation like requirement of strict instruments, high cost, as well as the strict treatment [12-14].

1.9 Nanotechnology

The study of very small materials in the size of about 0.1 to 100 nm and can be employed in wide range of applications and the formation of numerous kinds of nano materials and nano devices. The term "nano" is a Greek word means "dwarf" and development was started in 1958 A.D.

Moreover, it is the treatment of single atom, molecule or compound into structures to yield materials and device with special properties. There are two approaches to get nanotechnology.

1. **Top-down approaches** i.e., reducing the size large to smallest structures.
2. **Bottom-up approaches** i.e., changing individual atom and molecules into nano structures.

1.10 Applications

a) Health and medicine

b) Electronics

c) Transportation

d) Energy and environment

e) Space exploration

1.11 Carbon Nanotubes (CNTs)

In the fullerene sheet, carbon is arranged in tubular form on a nano scopic level. The first observation, Sumia made were of multi-walled carbon nanotubes, and after two year later when single walled carbon nanotubes were seen. SWCNT are generally a single fullerene molecule which has been stretched out their length is a million time its diameter.at same time, Donald Bethune and Colleagues also seen the SWCNT. In 1996, Smalley prepared bundles of SWCNT for the first time [19].

1.11.1 Synthesis of Carbon Nanotubes (CNTs)

There are various process for the preparation of carbon nanotubes like arc growth, condensation vaporization densation (CVD), catalytic decomposition of hydrocarbons, heat treatment of polymer, low temperature pyrolysis, catalytic vapor deposition etc.

Out of them, more attractive commercially used technique is CVD. The characteristics of thus formed CNTs by CVD method depend on the working condition like pressure, temperature, volume and concentration of methane, the size and the pre-treatment of metallic catalyst and the time of reaction [19].

1.11.2 Types of Carbon Nanotubes (CNTs)

On the basis of grapheme sheet layer present in carbon nanotube, they are,

a) Single Walled Carbon Nanotubes (SWCNT)

b) Multi-walled carbon nanotubes (MWCNTs) [19].

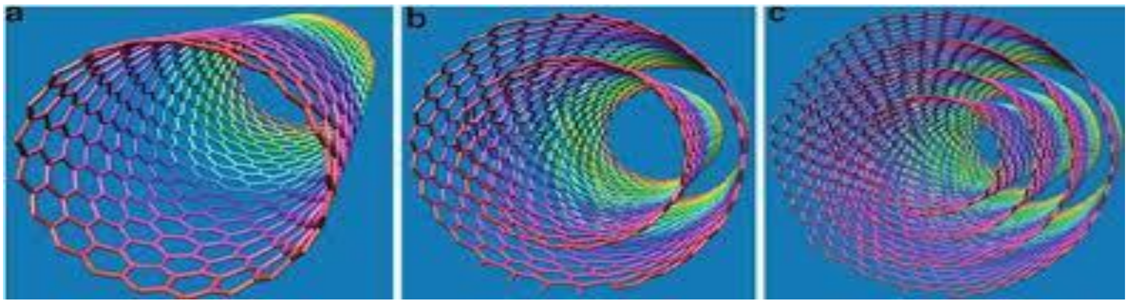


Fig. 1.11.2 Images of single, double and multi-walled carbon nanotubes

1.11.3 Applications Of Carbon Nanotubes (CNTs)

Carbon nanotubes are excellent nano structures that have been broadly range over and researched over a years. Due to their extraordinary electronic and mechanical properties, a large number of applications in various areas were investigated and includes microelectronic devices, flat panel displays, high power electrochemical capacitors etc [19].

Some of the important applications are as follows.

a) Thermal conductivity

b) Field emission

c) Conductive properties

d) Energy storage

e) Conductive adhesive

f) Molecular electronics

g) Thermal materials

h) Structural applications

i) Fibers and fabrics

j) Catalyst support

k) Biomedical application

l) Air and water filtration

1.12 Mechanism of Electrophoretic Deposition (EPD)

1.12.1 Flocculation by Particle Accumulation

The process of electrophoretic deposition was made by Hamaker and Verwey. They suggested that the production of deposit by EPD is similar to the yield of sediment due to gravitation. The main cause to applied an electric field in electrophoretic deposition is to force the particles in the direction of the target electrode and gather near it [20].

1.12.2 Particle Charge Neutralization Mechanism

The particle which undergo charge neutralization on contact with the deposited electrode. This tool is only available for single layer deposit and it includes the deposition of powders which are charged because of addition of salt to the solution [21]. However, this mechanism is not applicable under the following conditions.

a) Electrophoretic deposition for long time (thickness deposit).

b) In case of particle-electrode processes are stopped.

c) When P^H changing electrochemical reaction near or at the electrodes.

1.12.3 Electrochemical Particle Coagulation Mechanism

This technique involve decrease of the repulsive force between particles that in the end leads to coagulation due to increase of electrolyte concentration as discussed by Koelmans [22]. This process is true if the electrode produce OH^-, eg. Solution containing water. Moreever, this method is not applicable if there is no increase of electrode concentration close to electrode.

1.12.4 Electrical Double Layer (EDL) Distortion and Thinning Mechanism

Sarkar and Nicholson provide the description for particles deposition mechanism when there is no increment of concentration of electrolyte close to the electrode by supposing the motion of positively charged particle in the direction of the cathode in an electrophoretic deposition cell [23], they have proposed the following model as shown in figure.

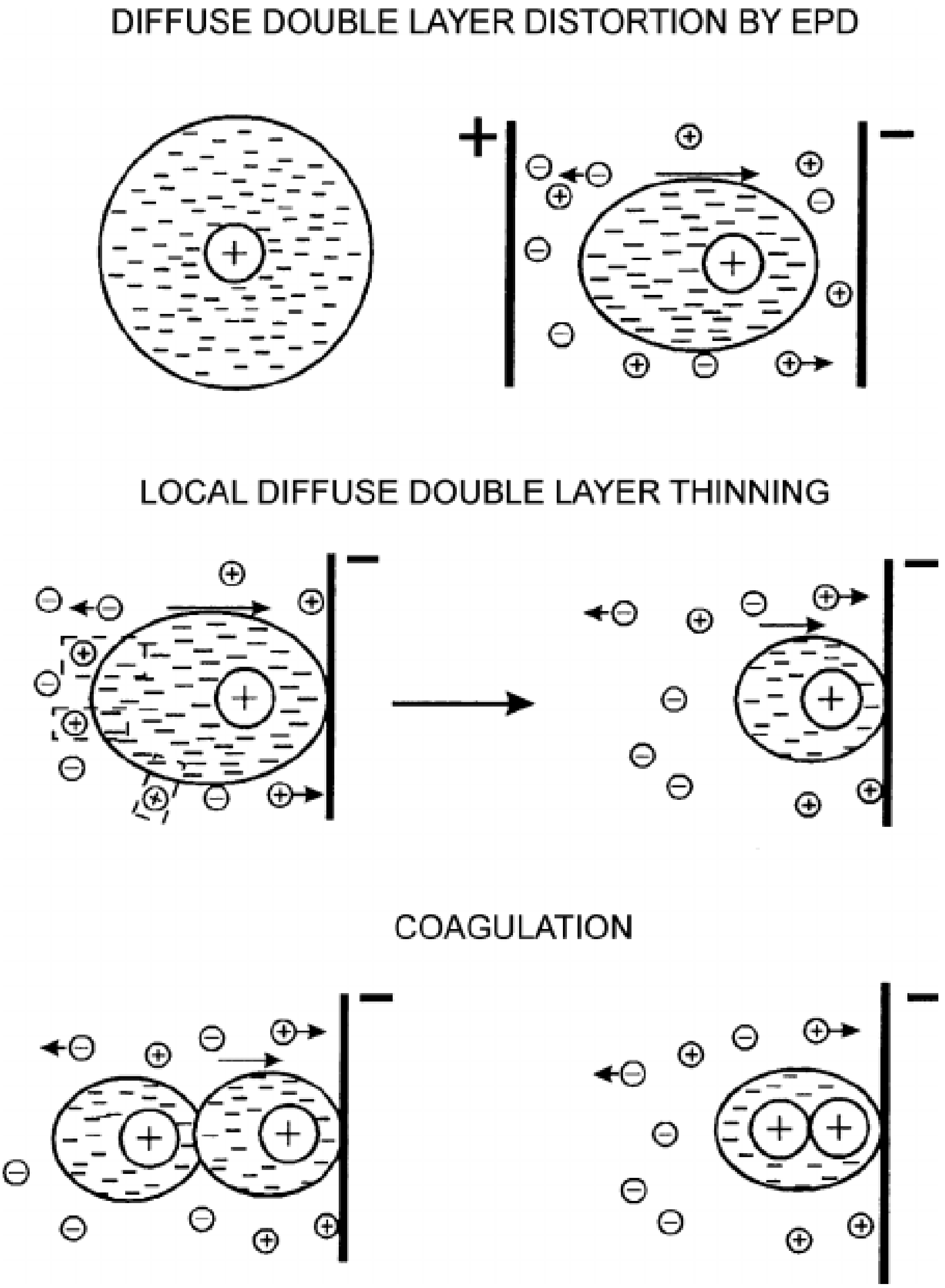


Fig. 1.12.4 Electrical Double Layer (EDL) Distortion and Thinning for EPD Process

CHAPTER-II

OBJECTIVES OF THIS STUDY

General Objectives

The major objectives of this study is electrophoretic deposition of oxidized MWCNTs on stainless steel substrate for ethanol sensor.

Specific Objectives

I. Oxidation and purification of MWCNTs.

II. Electrophoretic deposition of oxidized MWCNTs on stainless steel substrate.

III. It's application in ethanol sensor.

CHAPTER-III

LITERATURE REVIEW

Hieu *et al.,* well ordered conducted an inquired and differentiate the performance of metal oxide and MWCNTs-coated tin oxide thin film sensor to LPG and ethyl alcohol. Thus coated films were examined by XRD, FE-SEM and TEM and found that the SnO_2 coated with the 1 weight% PtO_2 sensor exhibited the maximum response to ethyl alcohol and LPG as compared to that of SnO_2 coated with the other dopants. From that, the sensor coated with 0.1 weight% MWCNTs with a diameter ranging from 20 to 40 nm showed the greater response to ethanol and LPG. The interesting outcome is that the PtO_2 doped SnO_2 sensor appeared good selectivity towards ethanol and LPG, on the other hand the MWCNTs coated with SnO_2 sensor exhibited good selectivity to LPG over ethyl alcohol at the same experiment conditions. Ethanol sensor are widely used for the control of drunken driving and observing of fermentation and other process in the field of chemical factories, whereas LPG sensor are regularly used in the detection of the leakage to avoid accidental blow-up [24].

Arautiounian *et al.,* studied with the preparing and conducted an inquires of ceramic and thick film species sensors prepared nano composite MWCNTs/SnO_2/ Pd form and were examined by SEM, EDX, and SRD. Thus, prepared sensors were sensitive towards 200 ppm concentration of isobutene and greater response achieved at 500 ppm. Isobutene gas is widely used in the domestic purpose for cooling plant as well as a fuel, being a part of LPG [25].

Sonker *et al.,* made ZnO-MWCNTs nano composite as a LPG sensor and were examined by XRD, UV-Visible spectroscopy, SEM, and TEM. They were concluded that the highest sensing response as 61.57 and sensitivity as 41.95 for 1500 ppm concentration of LPG. Thus, prepared sensor is too sensitive below the permissible exposure limit (PEL) and an applied in the field of commercial yield [26].

Esfandyarpour *et al.,* manufactured SnO_2 thin film as an ethanol sensor on Silicon substrate by the application of sol-gel process. The highest sensitivity of 175 was found in the presence of 50 ppm (parts per million) ethanol for the sample heated at 550s°C whereas, lowest sensitivity for both ethanol and CO for the sample which is heated at 850°C. The pure SnO_2 exhibited acceptable response and recovery time at the favorable operating temperature of 270°C [27].

Shinde *et al.,* prepared ZnO thin film as a LPG sensor composed and showed highest response deposited at 80 min for LPG than other samples as well as maximum response of 28% at the experimental temperature of 673K was exhibited at 10% of lower explosive level (LEL) sample [28].

Van *et al.,* deals about the sensing features of Nb-Pt co-doped TiO_2 thin film in presence and in absence of SWCNT including prepared by sol-gel spin coating method and it was found that the responses to ethanol of Nb-Pt co-coated TiO_2 sensors in presence of SWCNT increases by a factor of 2-5 with respect to in absence of SWCNT and were characterized by FC-SEM, TEM, and XRD as well as are very useful as portable breath alcohol sensors. 0.1% SWCNT coated sensor was the good choice for ethyl alcohol sensing [29].

Paraguay *et al.,* discovered the sensing properties of ZnO:X, thin film coated with various elements, where, X= Al, Cu, Fe, and Sn with the application of spray pyrolysis method. The results showed that the Sn-coated with a dopant Zn in the ratio of 0.4 at % have maximum sensitivity towards ethyl alcohol vapor and were examined by XRD, TEM and SEM [30].

Ramli *et al.,* describe about the hydrogen sensing characteristics of good MWCNTs/Pd thin film on paper prepared by Langmuir-Blodgett process and were examined by SEM, Raman Spectroscopy as well as found that the MWCNTs/PD film showed very high hydrogen sensing response on that substrate paper [31].

Ferroni *et al.,* deals and examined the nano sized TiO_2 sensor by SEM and TEM. It was confirmed that thin film TiO_2 showed improved sensing ability to detect NO_2 and therefore used in the sensor for environmental purpose [10].

Promsong *et al.,* successfully deposited tin-oxide thin film by electron beam evaporator to sense alcohol. Besides coating the sensor with aluminum or calcium oxide then the selectivity is decreased to 200°C. Thus, prepared sensor can be very useful to measure alcohol concentration in commercial wines, which correlate very well with the value of labeled on the wine bottles [32].

Bokobza *et al.,* deals about the Raman Spectroscopic properties of MWCNTs and MWCNTs/rubber composites and were examined by TEM and Raman Spectroscopy, as well as MWCNTs composites showed very good Raman Spectroscopic properties having band shift to higher wavenumber upon de-bundling [33].

Thomas *et al.,* coated and examined MWCNTs films onto stainless steel substrate in the application of electrophoretic deposition from solution of an acid. The homogeneous microstructure with10 µm thickness MWCNTs was coated under the 5-50V of electric field at 0.5-10 min were achieved. So, EPD process is fast, effective can be applied in heat extraction devices, active coating for tissue engineering platform [34].

Szczypta *et al.,* deals with the spectroscopic study of MWCNTs coated on metal substrate by the application of electrophoretic deposition method under two model deposition systems which includes, types of suspension of CNTs used during EPD process and types of and number of functional groups and manner of distribution on the electrode's surface. Both type of coated were characterized by Raman as well as X-ray photoelectron Spectroscopy [8].

Kasim *et al.,* describe about the effect of oxidation on the structure of MWCNTs through HNO_3 under reflux conditions. Higher the concentration of charger salt in carbon nanotubes solution, greater is the Mg and O content on thin films and were characterized by Raman Spectroscopy, SEM and EDX [4].

Dangi *et al.,* studied about the electrophoretic deposition of nickel decorated MWCNTs for the yield of H_2 gas. Nickel decorated oxidized MWCNTs carried out with the help of electrophoretic deposition and examined by FTIR, SEM and EDX technique as well as hydrogen gas was produced from nickel decorated multi-walled carbon nanotubes (MWCNTs) via basic electrolysis, sodium hydroxide (NaOH) as electrolyte [3].

Rastogi *et al.,* describe about the comparative study of scattering parameters of MWCNTs and used different surfactants, like Triton X-100, Tween 20, SDS, which were characterized with help of characterization technique such as Ultra Violet-visible Spectroscopy and Transmission electron microscopy (TEM). From them, Triton X-

100 as well as sodium dodecyl sulfate (SDS) gives highest and lowest scattering respectively [35].

CHAPTER-IV

MATERIALS AND METHOD

The experimental procedure is divided into 6 sections

a) Starting materials
b) Oxidation and purification of MWCNTs
c) Substrate preparation
d) Electrophoretic deposition process
e) Application in ethanol sensor
f) Characterization techniques

4.1 Starting Materials

Multi-walled carbon nanotubes (MWCNTs), which were synthesized by catalytic vapor deposition (CVD) process were purchased from ILJIN Nanotech. Company Ltd. South Korea (purity > 98%), used in thesis work. Sodium Dodecyl Sulfate (SDS) from HI-Media Laboratories Pvt. Ltd. (Mumbai) India. Concentrated Nitric acid (HNO_3), sodium hydroxide (NaOH), sodium phosphate (Na_3PO_4) and sodium carbonate (Na_2CO_3) were used that are available in laboratory.

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

For the synthesis of pristine multi-walled carbon nanotubes, basically produce powders contains not only multi-walled carbon nanotubes but also contains some impurities like amorphous carbons, fullerenes, nano-crystalline graphite and transition metals that are used as catalyst during oxidation, etc. These impurities sometimes enhances the accurate analysis of MWCNTs characteristics and limits 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 work, acid reflux method was done for the oxidation of MWCNTs. 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. Moreover, the functionalized MWCNTs are dissolve in huge solvent due to the hydrophobic characteristics of MWCNTs was alter to hydrophilic because of attachments of polar groups [36].

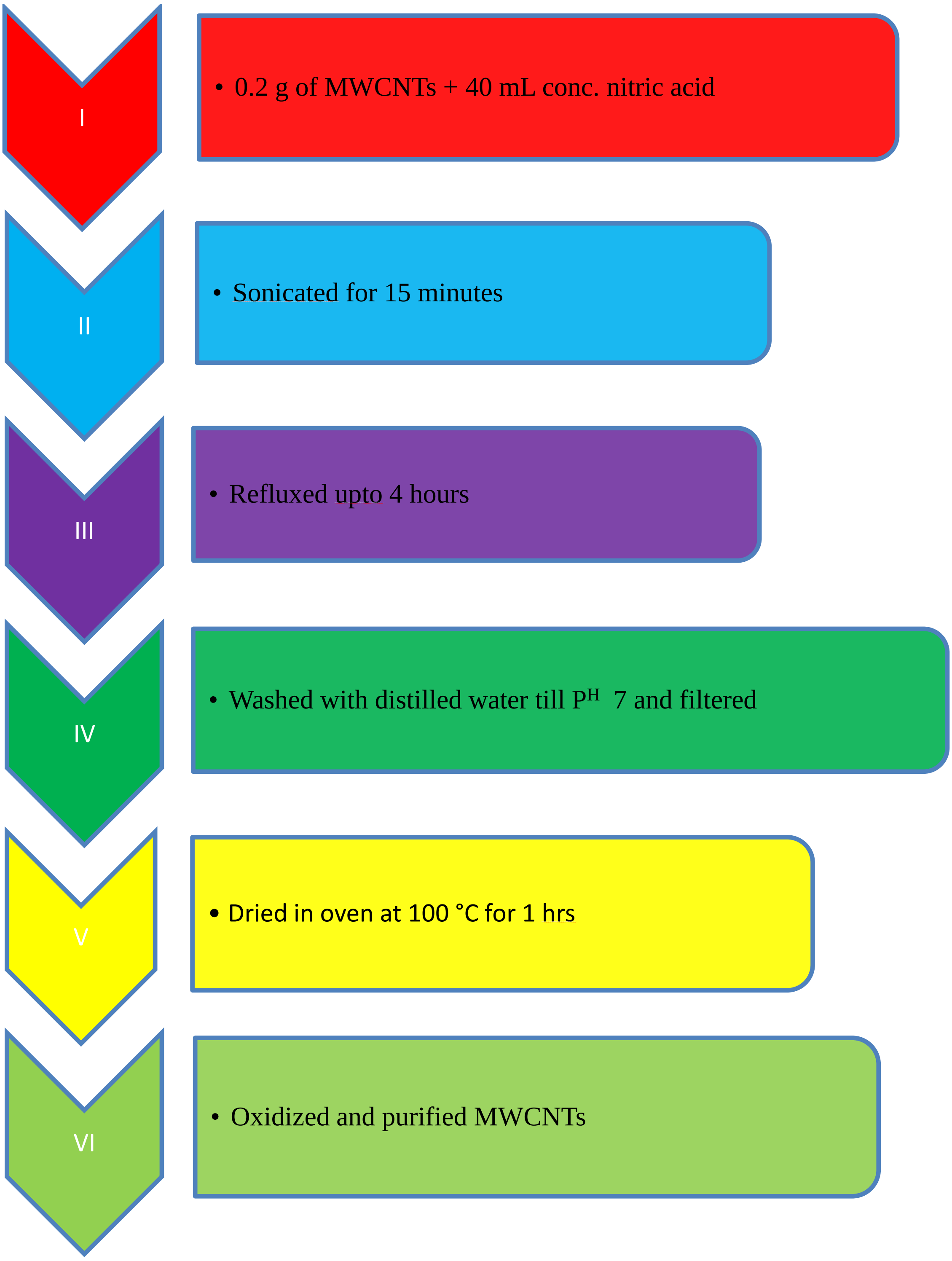

I
• 0.2 g of MWCNTs + 40 mL conc. nitric acid
II
• Sonicated for 15 minutes
III
• Refluxed upto 4 hours
IV
• Washed with distilled water till P^{H} 7 and filtered
V
• Dried in oven at 100 °C for 1 hrs
VI
• Oxidized and purified MWCNTs

Fig. 4.2 (a) Oxidation of MWCNTs by acid reflux method

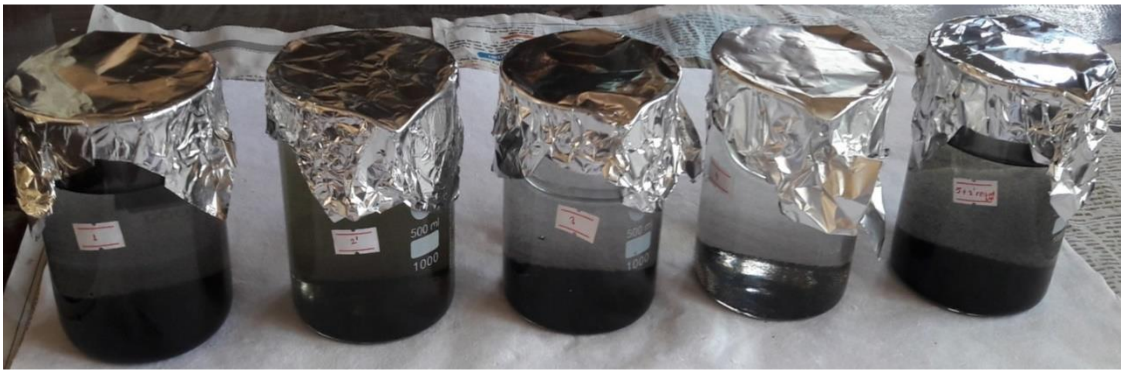


Fig. 4.2 (b) Purification of oxidized MWCNTs by decantation process

Fig. 4.2 (c) Purification of oxidized MWCNTs by Suction pump

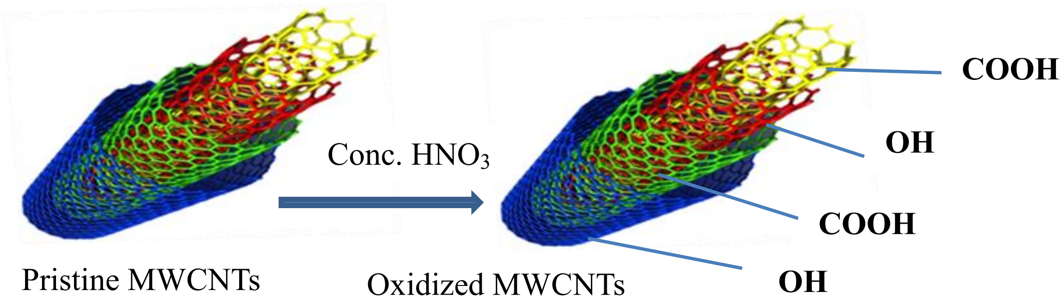
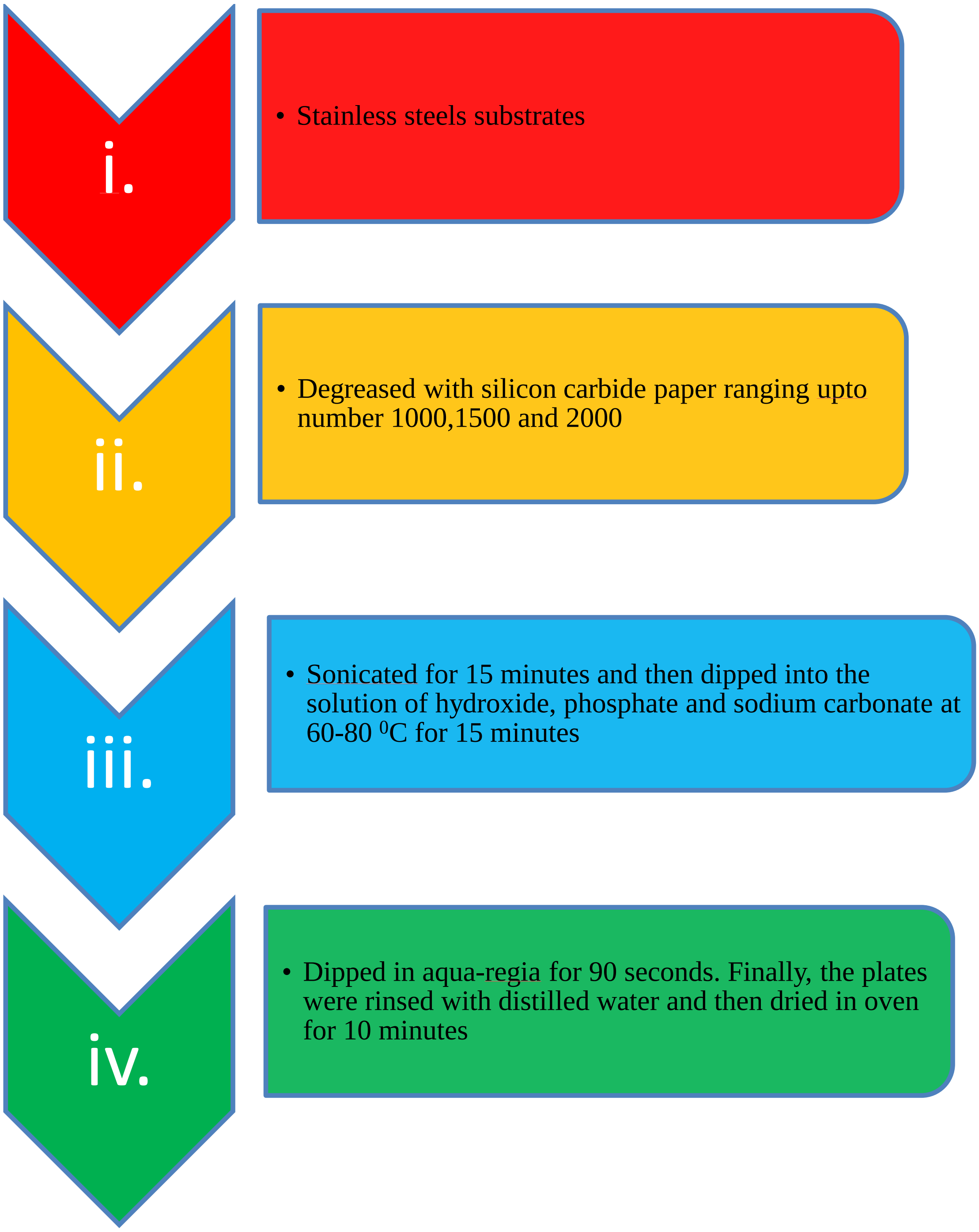


Fig. 4.2 (d) Schematic representation of formation of oxidized MWCNTs

In this process, first of all 0.2 g of MWCNTs (fabricated by CVD method) were chemically oxidized in a 40 mL concentrated nitric acid (HNO_3) via sonication for about 15 minute and then the solution was refluxed for about 4 hours. It was repetitively washed with distilled water until p^H 7 after that 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 [37].

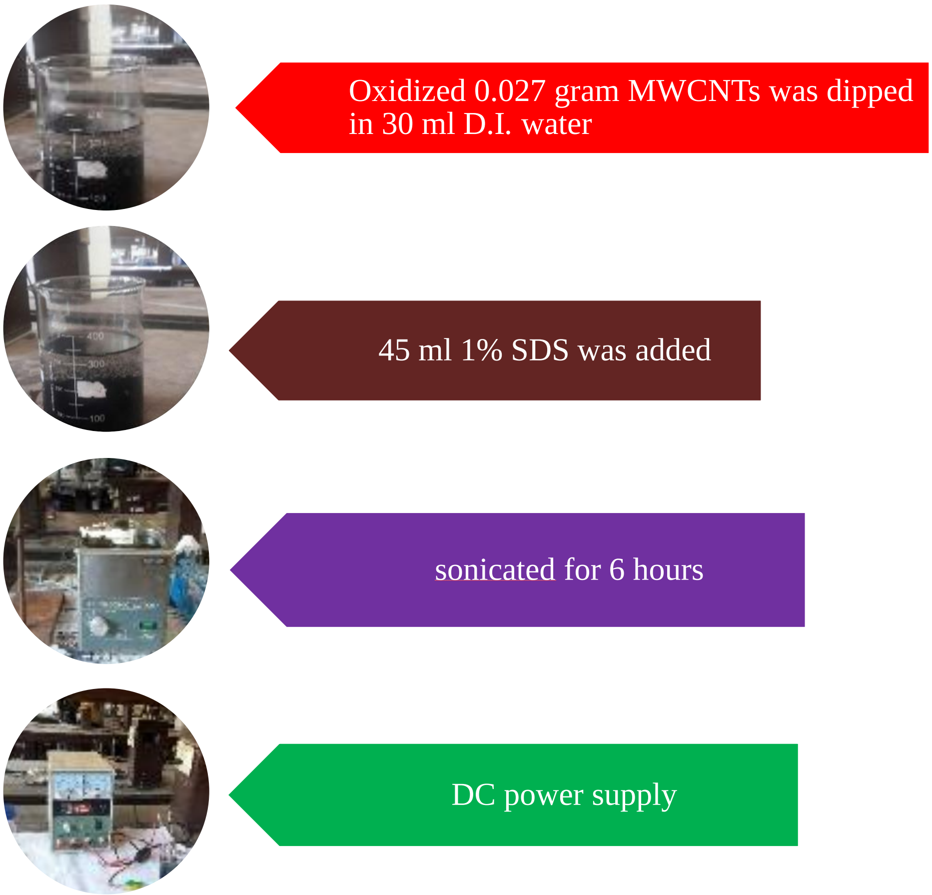
Fig. 4.2 (e) The process of stirring the solution by sonication

4.3 Substrate Preparation



For the preparation of substrate, first of all, the stainless steel plate were 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 sonication for 15 minute and dipped into the solution of hydroxide, phosphate and sodium carbonate respectively at 60°C to 80°C for 15 minute and finally dissolved in aqua-regia for 90 second and plates were rinsed with distilled water and then dried in oven for 10 minute.

4.4 Electrophoretic Deposition (EPD) Process



For the electrophoretic deposition process, oxidized multi-walled carbon nanotubes was used. For this, first of all, 0.027 g oxidized MWCNTs was dissolved in 30 mL of D.I. water. Then the solution was kept in bottles and then 5 mL of 1% SDS was added on it for well dispersion of MWCNTs and finally, sonication for 6 hours.

Fig. 4.4 (a) Well dispersed oxidized MWCNTs solution

The electrophoretic deposition process was carried out on an experimental set up consisting of a DC power supply, electrolytic baths and two electrode, one of them was the substrate for MWCNTs coating. Out of two electrode, one electrode was act as anode while other as cathode. The inter- electrode distance was fixed at 1.5 cm for all experiments. The process was performed for the 10 min using voltage s 10V.

Fig. 4.4 (b) Represents the deposition of oxidized MWCNTs on stainless steel plate at 10 min for 10V.

(where, black portion indicates the deposition of oxidized MWCNTs)

Following the deposition process, the samples were carefully taken out of the solution and dried in oven for 24 hours.

Fig. 4.4 (c) Electrophoretic deposition (EPD) process

4.5 Application in Ethanol Sensor

To measure the electrical resistance, I took a sealed glass chamber. 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 which maintained the entering and outing of target reducing substance, ethanol in my case study. 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 below.

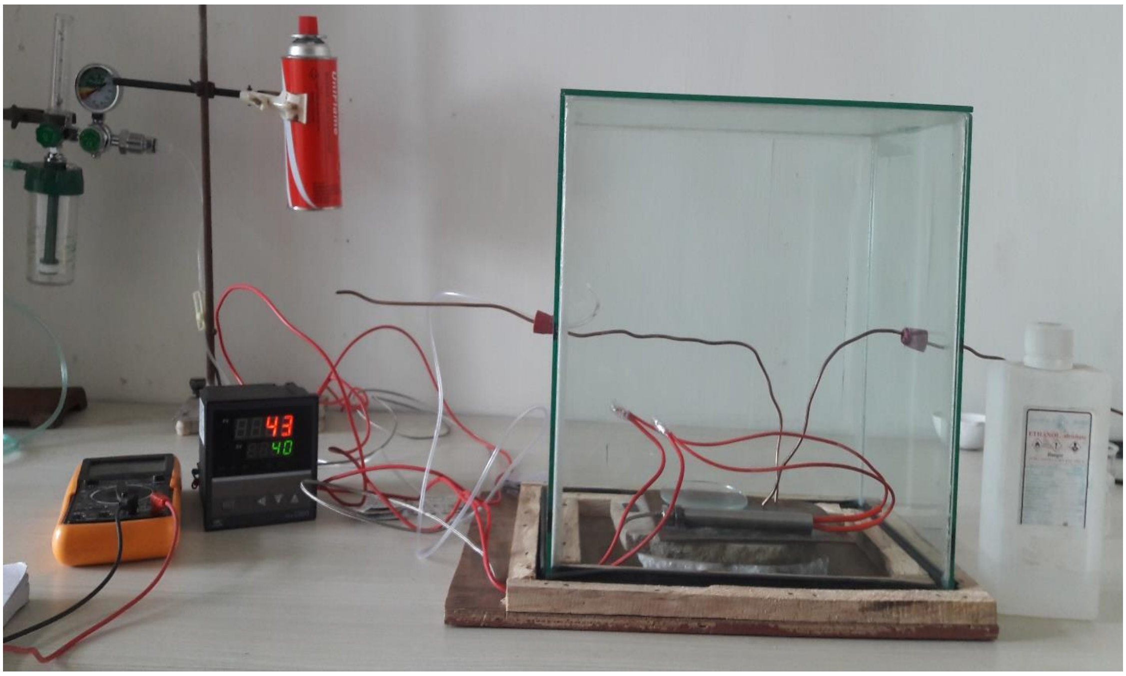


Fig. 4.5 Experimental set up for ethanol sensor

4.6 Characterization Techniques

4.6.1 Infrared Spectroscopy

Infrared radiation lies between the visible and microwave portion of the electromagnetic spectrum. Infrared waves have wave length longer than that of visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves. This technique is used to identify functional group by analysis of their constituent band position. It is divided into three.

a) Near-infrared (overtone region) 0.7-2.5 μm (14000-4000 cm^{-1})

b) Middle-infrared (vibration-rotation region) 2.5-25 μm (4000-400 cm^{-1})

c) Far-infrared (rotation region) 25-1000 μm (400-10 cm^{-1})

4.6.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a type of electron microscope that produces images of sample by scanning the surface with a focused beam of electrons. The electron interact with atoms in the sample, yielding various signals that contain information about the surface topography and composition of the sample.

4.6.3 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to detect vibrational, rotational and other states in a molecular system, capable of probing the chemical composition of materials. Raman spectroscopy measures relative frequencies at which a sample scatters radiation, unlike IR spectroscopy which measures absolute frequencies at which a sample absorbs radiation.

CHAPTER-V

RESULTS AND CONCLUSION

5.1 Fourier Transform Infra-red Spectroscopy

Multi-walled carbon nanotubes was successfully purified and oxidized by acid reflux method. The oxidation of multi-walled carbon nanotubes was ensured by Fourier transform infrared spectroscopy.

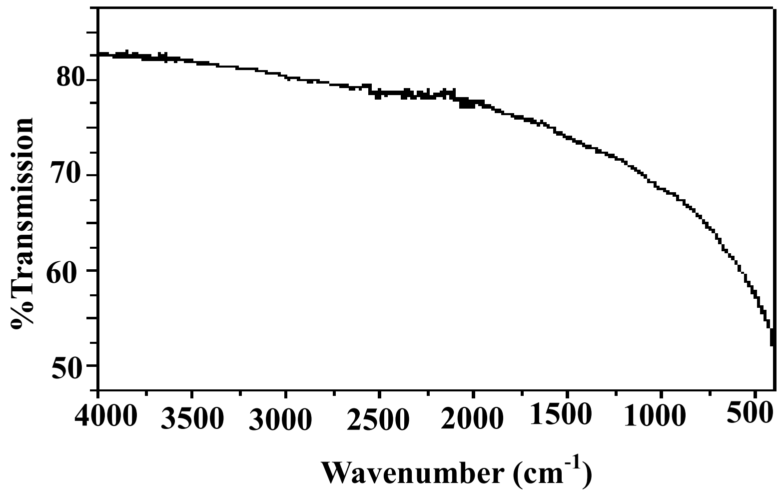


Fig. 5.1 (a) FTIR spectrum of pristine MWCNTs sample

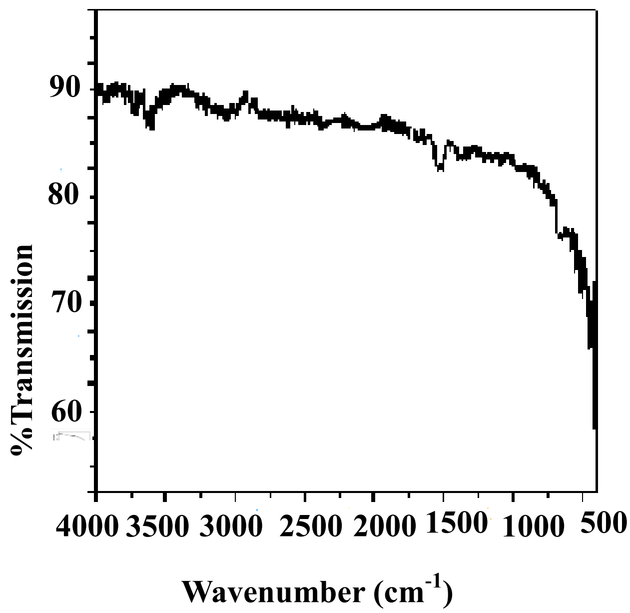


Fig. 5.1 (b) FTIR spectrum of oxidized MWCNTs sample

Fig. 5.1 (a) shows the FTIR spectrum of pristine MWCNTs. The spectrum does not show any sharp infrared peaks, which indicates, it does not contain any functional groups whereas fig. 5.1 (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. This confirms the presence of oxygenated functional group after treatment with acid.

5.2 Scanning Electron Microscopy (SEM)

Oxidized MWCNTs was successfully deposited on stainless steel by electrophoretic deposition (EPD) process. The deposited oxidized MWCNTs on stainless steel substrate was ensured by SEM technique.

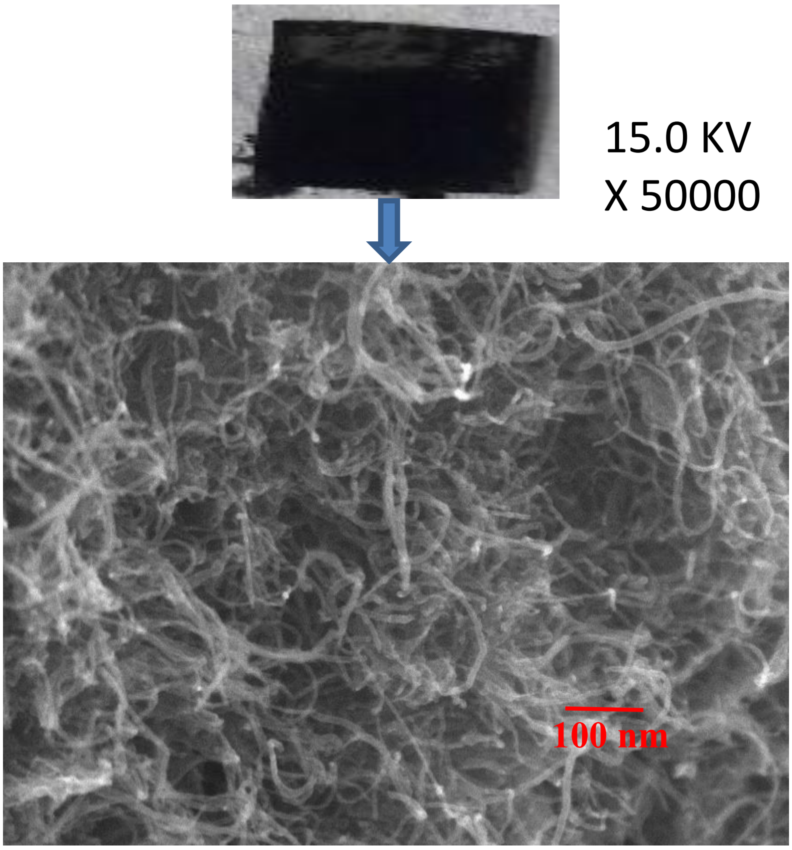


Fig. 5.2 SEM images of oxidized MWCNTs on stainless steel substrate

Fig. 5.2 showed the SEM image of electrophoretic deposition of oxidized MWCNTs on stainless steel substrate. The image shows 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 accordance with the deposition characteristics characterized, who performed CNT film deposition by EPD on stainless steel substrate [38].

5.3 Raman Spectroscopy

Oxidized MWCNTs was successfully deposited on stainless steel by EPD technique and was analyzed by Raman spectroscopy.

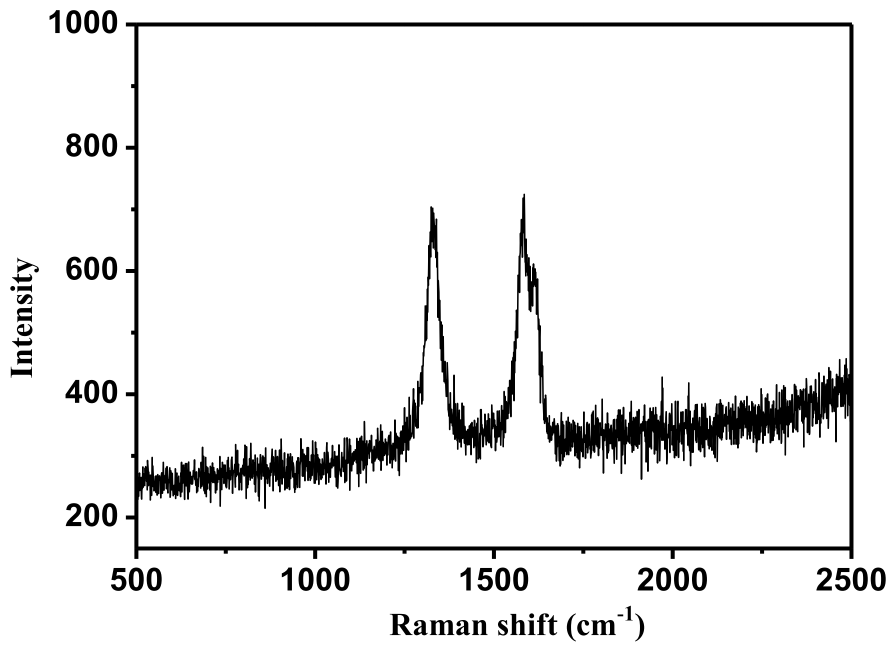


Fig.5.3 Raman spectrum of electrophoretic deposited multi-walled carbon nanotubes on stainless steel substrate

Fig. 5.3 shows the Raman spectrum of electrophoretic deposited oxidized MWCNTs on stainless steel substrate. The spectrum shows two characteristic peaks of oxidized MWCNTs. The peak at 1570 and 1343cm^{-1} are G and D-band respectively. The G-band is indicative if 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.

5.4 Sensing Response of Oxidized MWCNTs on Ethanol Sensor

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 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, being electron donating molecule like ammonia. Therefore, electrons are transferred from ethanol molecules to CNTs and hence form a space charge region (depletion region) on the semiconducting 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_a). Then ethanol was introduced into the chamber and electrical resistivity of the sample film was measured by using multi-meter (i. e., R_{EtOH}). MWCNTs is ‘p’ type semiconductor materials and resistance decreases when expose to ethanol, the reducing substance [38].

For ‘p’ type semiconductor materials, sensitivity percentage (%) is calculated by using following formula [17].

Sensitivity percentage (%) = $\left[\frac{R_{EtOH-R_{air}}}{R_{air}}\right]\times 100$

Where, R_{air} = resistance in air

R_{EtOH} = resistance in presence of test ethanol reducing substance at a room temperature

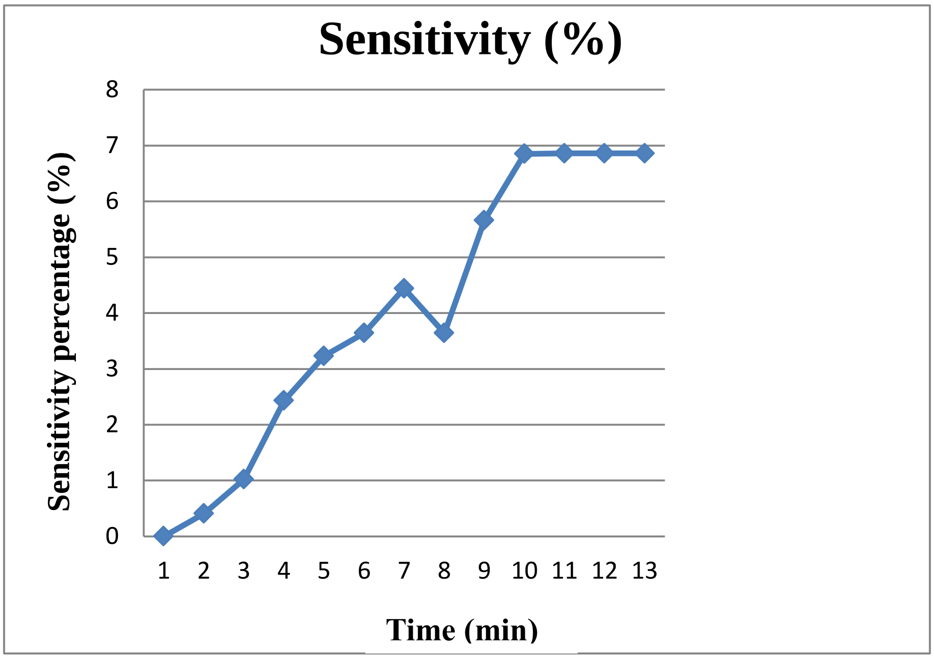


Fig. 5.4 Sensitivity percentage (%) Vs time (min) at 10 min for 10 volt

The CNTs can be functionalized to improve their sensitivity. On the other hand, the functionalization of the CNTs involves the combination of the properties of the CNTs, CNT formed, which can exhibit with new properties that were different from those of their individual parts. Various studies have illustrated that the CNTs can be decorated with Pd to increase the sensitivity, nano composite coated with Pt, Pd, Rh, and Au for the selectivity of a gas sensor arrangement or deposited with Ti for gas sensing at low temperature [39].

In this work, I used oxidized MWCNTs 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.

5.5 Ethanol Sensing Mechanism

Before the exposure the ethanol to the sensing materials, the ethanol chamber was allowed to stabilize at normal room temperature for 30 min.

For this, first of all, reactive oxygen species were formed by the following reaction as,

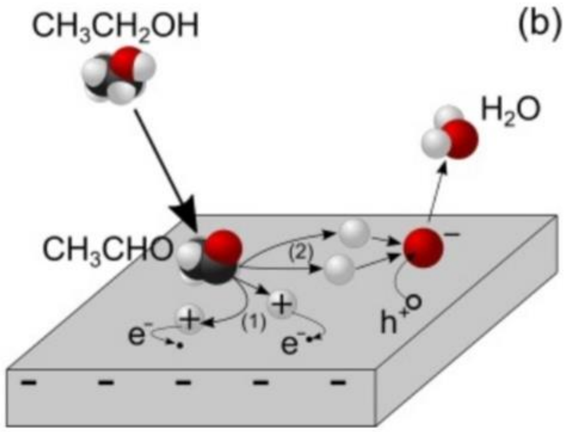
½ O_2 (gas) + e^- → O^- (ads)

½ O_2 (gas) + $2e^-$ → $2O^-$ (ads)

Then the surface between the reducing substance ethanol and the reactive oxygen species can be described as follow.

EtOH (ads) + O^- (ads) → CH_3CHO + H_2O + e^-

EtOH (ads) + O^{2-} (ads) → CH_3CHO H_2O + $2e^-$



Or

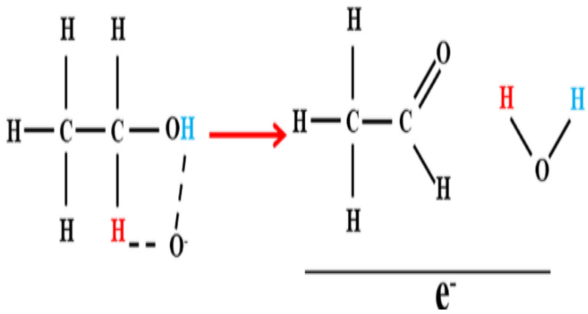


Fig. 5.5 Ethanol sensing mechanism

Carbon nanotubes basically show p-type semiconductor properties under ordinary conditions. When a sensor is exposed to air, oxygen molecules are adsorbed on the surface of MWCNTs. It traps electrons from the conduction band and produce negatively charged adsorbed oxygen species such as O^-, and O^{2-}. Hence, the concentration of holes in valence band increases and the resistance of the materials decreases. 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.

CHAPTER-VI

CONCLUSIONS

The dissertation was undertaken in the purpose of electrophoretic deposition of oxidized MWCNTs on stainless steel substrate in order to observe the sensor response of deposited oxidized MWCNTs. Oxidation and purification of MWCNTs was successfully conducted by using concentrated nitric acid (HNO_3) solution through acid refluxing method. Oxygenated acidic surface group functionalized MWNTs. Characterization of oxygenated acidic surface group was examined by FTIR techniques for evaluation of the chemical structure of MWCNTs. 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 deposition of oxidized MWCNTs on substrate was performed at 10 min for 10 volt and fixed inter-electrode distance of 1.5 cm which were analyzed by SEM. Measurement of electrical resistance and sensitivity via sealed glass chamber using ethanol as reducing substance. Multi-walled carbon nanotubes were successfully grown on the stainless steel substrate with CNTs to fabricate ethanol sensor. The sensor was sensitive to ethanol at a wide range. It was observed that the rate of sensitivity increases with decrease of resistance by EPD with oxidized MWCNTs on stainless steel plate at 10 min for 10 volt.

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APPENDIX

The sample which deposited on stainless steel plate at 10 minute for 10V are taken as follows.

Time (min)	Sensitivity percent (%)
0	0
1 (on) 1 (of)	0.408
2 (on) 2 (of)	1.02
3 (on) 3 (of)	2.43
4 (on) 4 (of)	3.23
5 (on) 5 (of)	3.64
6 (on) 6 (of)	4.44
7 (on) 7 (of)	
8 (on) 8 (of)	3.64
9 (on) 9)of)	5.66
10 (on) 10 (0f)	6.85
11(on) 11 (of)	6.86
12 (on) 12 (of)	6.86