

## Fabrication of Polyaniline–Carbonnanofibers for Hydrochloric Acid and Ammonia Sensing at Room Temperature

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### ABSTRACT

The multiwall Carbon nanotubes (CNTs) of 0.25wt %, 0.5wt % and 1wt% was added to 0.1 M distilled aniline under reflux procedure with 0.3 H<sub>2</sub>SO<sub>4</sub> for fabricating PANI/CNTs nanofibers. A cyclic potential ranged from -100 mV to 1500 mV was applied with six repetition on working electrodes stainless steel (SUS 304) which were dipped in these solutions at scan rate of 30mV s<sup>-1</sup> at room temperature. Scanning Electron Microscope (SEM) images showed that the PANI-CNTs nanofibers structure with diameters range (50nm-70 nm). In the liquid type sensing, it was found that with the increase of HCl concentrations, the value of current density (J) could be raised and found pronounced at 3000 ppm and 4000ppm concentration along with PANI/0.5 wt % CNTs and PANI/1 wt% CNTs sensors out of the four corresponding four solutions and for sensors. The reason behind that may be the enhancement of more efficient transfer of charges. On the other hand a reduction in current density (J) was obtained with increasing concentration of NH<sub>3</sub> and clearly observed at 1000 ppm and 2000 ppm for PANI/0.5 wt % CNTs and PANI/1 wt% CNTs sensors.

**Keyword:** Electropolymerization, Redox, Charge Transfer

تصنيع الياف البوليمر انيلين-كاربون النانوية لمتحسسات حامض الهيدروكلوريك  
والامونيا بدرجة حرارة الغرفة

### الخلاصة

اضافة متعدد جدران انابيب الكربون النانوية وبنسب وزنية 0.25 %، 0.5 %، 1 % الى 0.1 % انيلين مقطر واجراء عمليات الانعكاس الكيميائية وبوجود 0.3 مولارتي من حامض الكبريتيك. تم تسليط جهد دوري من -100 الى 1500 ملي فولت وبسنة تكرارات على قطب الفولاذ المقاوم للصدأ (SUS304) مغمور في المحلول بسرعة مسح 30 ملي فولت /ثانية. اظهرت فحوصات المجهر الالكتروني الماسح الى تكون الياف بولي انيلين-كاربون ذات اقطار (50-70) نانومتر وواضهت نتائج التحسس لحامض الهيدروكلوريك عند زيادة تركيزه تزداد كثافة التيار المولد وخاصة عند

تراكيز 3000، 4000 جزء بالمليون خلال المتحسسات المكونة من البولي انيلين /0.5 %نسبة وزنية من انابيب الكربون النانوية والبولي انيلين /1 % نسبة وزنية من انابيب الكربون النانوية الامر الذي يعزز انتقال الشحنات ،في حين اظهرت نتائج التحسس لسائل الامونيا زيادة كثافة التيار المتولد عند انخفاض تركيز الامونيا ويكون ذلك واضحا عند تراكيز 1000 و2000 جزء بالمليون ولمتحسسات من البولي انيلين /0.5 %نسبة وزنية من انابيب الكربون النانوية والبولي انيلين /1 % نسبة وزنية من انابيب الكربون النانوية.

## INTRODUCTION

**P**olyaniline (PANI) is one of the most widely studied conducting polymers because of its good conductivity that can be influenced both by the charging level and degree of protonation, its well defined electrochemical (redox) response, easy preparation and possible applications in rechargeable batteries, corrosion protection, light emitting diodes, molecular sensors, electrochromic devices and microwave screening [1]. Carbon nanotubes are unique nanostructured materials with remarkable physical and mechanical properties [2]. These properties have inspired interest in using CNTs as the nano-fillers in polymer composite systems to obtain composite structural materials with enhanced electrical, mechanical and optical characteristics [3]. Recent studies have shown that carbon Nanotubes can be dissolved in aniline via formation of donor–acceptor complex [4]. In this work, we have prepared Polyaniline/multi-walled carbon nanotubes (PANI/MWNT) composite by electro-polymerization of aniline containing well-dissolved MWNTs.

Hydrochloric acid is corrosive to the eyes, skin, and mucous membranes. Acute inhalation exposure may cause coughing, hoarseness, inflammation and ulceration of the respiratory tract, chest pain, and pulmonary edema in humans [5]. Acute oral exposure may cause corrosion of the mucous membranes, esophagus, and stomach, with nausea, vomiting, and diarrhea reported in humans. Dermal contact may produce severe burns, ulceration, and scarring [5]. Ammonia is a toxic in liquid as a gas that is naturally present in the atmosphere in sub part per million (ppm) levels. However, much large concentrations can be detected near farms with domestic animals.

A large amount of ammonia is produced by the chemical industry for production of fertilizers or for used in refrigeration system. Increase of amount of ammonia contained in exhaled air can be connected with certain disease, including kidney disorders [6]. In this work, we have prepared Polyaniline/multi-walled carbon nanotubes (PANI/MWNT) composite by electro-polymerization of aniline containing well-dissolved MWNTs for Hydrochloric acid and ammonia.

## EXPERIMENTAL

Aniline (Sigma Aldrich purity 90%) was purified by distilled under reduced pressure of 0.05 MPa and stored in darkness before use. CNTs purity 95% were produced via the chemical vapor deposition method (CVD), average outer diameter 20-30nm and the length 10-30  $\mu\text{m}$  purchased from Cheap Tubes Inc. USA. CNTs of 0.25wt%, 0.5wt% and 1wt% were added to aniline and the mixture was heated at reflux for 3 h in dark. Dissolution of CNTs in aniline can be observed by color change of the solution with continuous heating. The original colorless aniline solution first become brownish and then turned dark red. After has been cooled to room temperature and settled 24 h, a small quantity of undissolved CNTs were precipitated from CNTs- aniline solution. Electrochemical experiments were performed on

Wenking M Lab Bank Elektronik-Intelligent controls GmbH. A stainless steel (SUS 304) sheet geomatric surface area  $1\text{cm}^2$  was used as substrate -working electrode. A platinum rod and sturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The two electrode (SUS 304 and platinum rod )cleaned by potential cycling between  $-100\text{mV}$  and  $1500\text{mV}$  at  $30\text{mV/s}$  in  $0.3\text{M H}_2\text{SO}_4$  (GCC) U.K until astable cyclic voltammogram was obtained. The potential was varied between  $-100\text{mV}$  and  $1500\text{mV}$  for depositing PANI and PANI/CNTs with scan rate  $30\text{mV/s}$  with six repetitions. The Fourier Transformation Infrared (FT-IR) spectra measurements of PANI /CNTs composite were used Shimadzu spectrophotometer model 8300, Japan. The scanning electron microscopy (SEM) examinations were carried out for PANI/MWNTs composite thin films were analyzed for structure morphology and nanostructure using Hitachi FE-SEM model S-4160. The cyclic potential mode from  $-1000\text{mV}$  to  $1000\text{mV}$  at scan rate  $20\text{mV/s}$  was applied on the electrode surface of PANI and PANI/CNTs composite films (thickness about  $204\text{nm}$ ). These films had been deposited on SUS304 stainless steel and dipped in to an aqueous of two types' hydrochloric acid (HCl) and ammonia (NH<sub>3</sub>).

## RESULT AND DISCUSSION

### Fabrication of PANI and PANI-CNTs nanofibers

Figures (1) shows the cyclic voltammograms of PANI films recorded at  $0.1\text{M}$  distilled aniline in concentration  $0.3\text{M H}_2\text{SO}_4$  at scan rate  $30\text{mV/s}$  with six repetitions The polymerization takes place by oxidation at  $(700-1300)\text{mV}$  while potential is increasing followed by a de-protonation at  $(200-100)\text{mV}$  in the reverse direction of potential . Figures (2 , 3 , and 4) show cyclic voltammogram with potential range  $-100\text{mV}$  to  $1500\text{mV}$  and scan rate  $30\text{mV/s}$  for six repetition of PANI( $0.1\text{aniline}+0.3\text{M H}_2\text{SO}_4$ )/ $0.25\text{wt\% CNTs}$  ,PANI/ $0.5\text{wt\% CNTs}$  and PANI/ $1\text{wt\% CNTs}$  composite respectively on SUS(304).

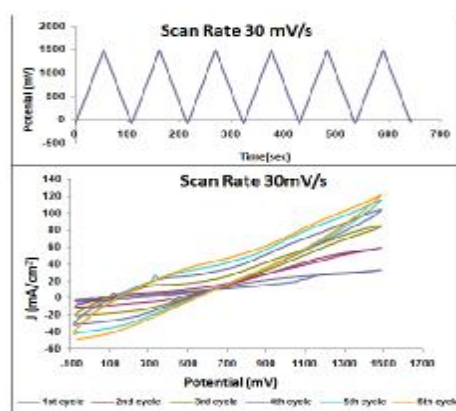


Figure (1) Cyclic voltammograms of SUS (304) electrode in PANI electrolyte ( $0.1\text{M aniline} + 0.3\text{M H}_2\text{SO}_4$ )( $\text{PH}=4.0$ ) (From  $-100$  to  $1500\text{mV}$ ) scan Rate  $30\text{mV/s}$  at room temperature.

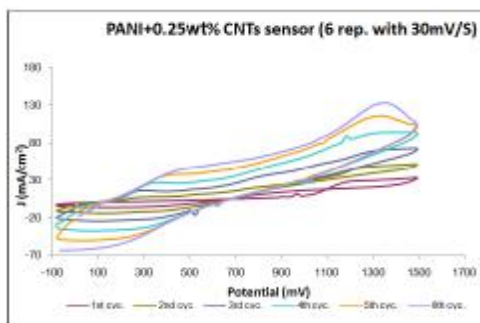


Figure (2) PANI+0.25 wt% CNTs composite Fabricated at scan rate 30mV/s with six.

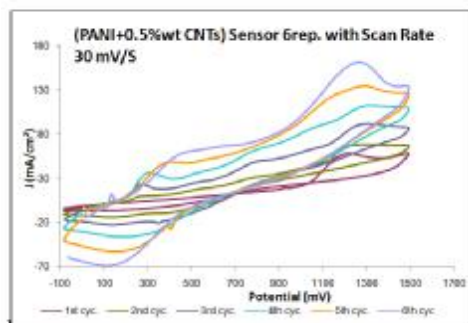


Figure (3) PANI+0. 5 wt% CNTs composite Fabricated at scan rate 30mV/s with six.

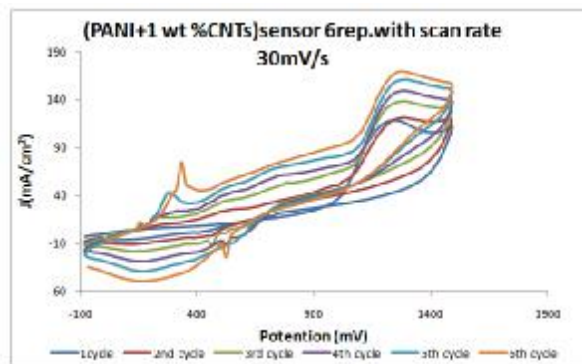


Figure (4) PANI+1 wt% CNTs composite fabricated at scan rate 30mV/s with six repetition.

### Fourier Transformation Infrared (FT-IR) spectra of PANI/CNTs Composite synthesis

Figure (5) gives a typical Infrared spectra of the PANI/1wt%CNTs composite product where the main absorption peaks shows  $3448\text{ cm}^{-1}$  it is possible assign asymmetric stretching vibration of  $\text{NH}_2$ . The N-H stretching in benzoid-NH-benzoid (B-NH-B), the broad band at  $3232\text{ cm}^{-1}$  to hydrogen stretching bonded NH and  $3163\text{ cm}^{-1}$  to terminal quinoid  $=\text{NH}$  (Q= $\text{NH}$ ). The  $2954\text{ cm}^{-1}$  represented C-H stretching region. The absorption peak observed at  $1643.35\text{ cm}^{-1}$  were attributed to C=C stretching in aromatic nuclei Absorption bands. the bonds situated  $1482.04\text{ cm}^{-1}$  and  $1585.49\text{ cm}^{-1}$  are attributed to benzoid and quinoid ring vibration respectively<sup>[7]</sup>. its commonly observed for PANI that the quinoid band at  $1585\text{ cm}^{-1}$  is less intense than that benzenoid band at  $1482\text{ cm}^{-1}$ . As shown in spectrum of PANI/CNTs composite, an inverse  $1585/1482\text{ cm}^{-1}$  intensity ratios was exhibited. These data reveal that PANI in composite is richer in quinoid units than the pure PANI. This fact may suggest that PANI-CNTS. The polymer shows a interaction promote and stabilize the quinoid ring structure. this interaction between PANI and CNTs may result in "charge transfer"<sup>[165]</sup>. The  $\pi$ - bonded surface of carbon Nanotubes might interact strongly with conjugated structure of poly aniline, especially through the quinoid ring[8]. The strong band at  $1149\text{ cm}^{-1}$  is considered to be a measure of the degree of delocalization of electrons and thus it is characteristics peak of PANI conductivity [7]. The increase of the signal at  $1149\text{ cm}^{-1}$  is in good agreement with conductivity measurements result given by S. Quillard et al. [7]. It appears that the interaction between PANI and CNTs increase the effective degree of electron delocalization, and thus enhances the conductivity of polymer chains.

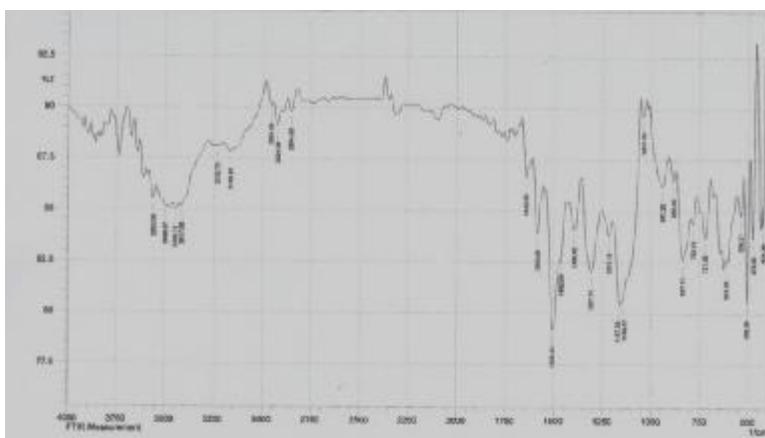


Figure (5) FT-IR spectra for PANI/ 1wt% CNTs.

### Morphology of PANI/CNTs composite

Figures (6,7,8) showed SEM images of PANI (0.1 M aniline+0.3 M  $\text{H}_2\text{SO}_4$ )/0.25wt% CNTs, PANI/0.5 wt % CNTs, and PANI/1wt% CNTs respectively. This all images appear that the well –formed CNT inside PANI. This result can be considering that agreement with the schematic of Chuizhou Meng et al [9] Figure (9). SEM revealed a uniform deposition of PANI onto the CNTs, whereby the diameter of the PANI-coated CNTs was estimated to be in the range (55-80) nm.

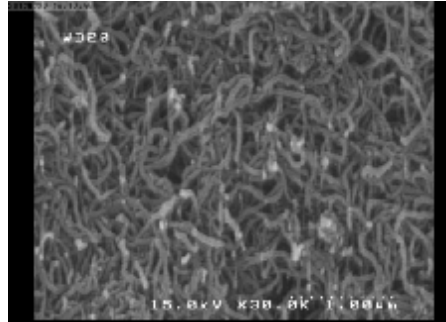


Figure (6) SEM image of PANI/0.25 wt% CNT Composite magnified 30000 times.

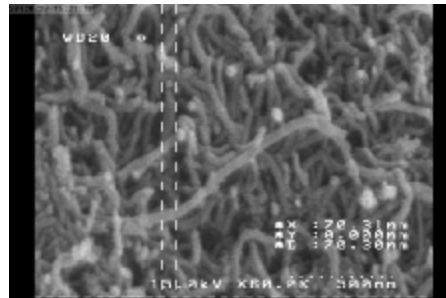


Figure (7) SEM image of PANI/0.5 wt% CNT Composite magnified 60000 times.

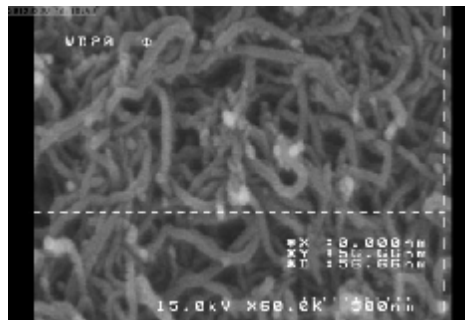


Figure (8) SEM image of PANI/1 wt% CNT Composite magnified 60000 times.

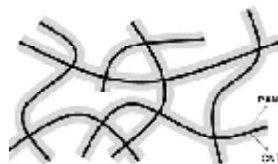
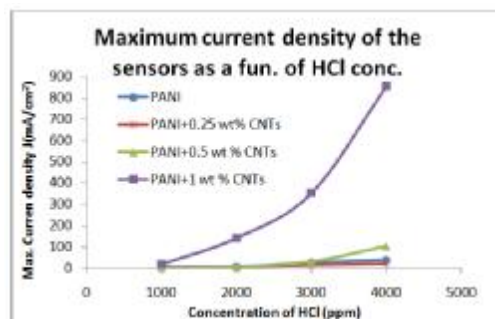


Figure (9) Schematic illustration the well-formed CNTs network inside PANI [9].

**Sensors in aqueous solution of HCl**

The surface electrode of PANI and PANI/(0.25, 0.5, and 1)wt %CNTs composite electrochemically deposited on SUS 304 stainless steel in aqueous solution of 1000, 2000, 3000, and 4000ppm concentrations of HCl acid . Figure (10) shows the maximum current density of the sensors obtained at varying HCl concentrations. Table (1) lists all different values of maximum current densities for the all fabricated sensors.



**Figure (10) Maximum current density of the Sensors obtained at the varying HCl concentrations.**

**Table (1) Maximum current density of the sensors obtained at the varying HCl concentrations.**

Sensor	J <sub>1</sub>	J <sub>2</sub>	J <sub>3</sub>	J <sub>4</sub>
PANI	6.67	5.65	25.9	38.1
PANI/0.25wt% CNTs	4.18	4.54	13.95	20
PANI/0.5 wt% CNTs	2.04	3.83	31.22	104
PANI/1 wt% CNTs	18.5	142.6	353.8	855

J<sub>1</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 1000 ppm HCl conc. J<sub>2</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 2000 ppm HCl conc. J<sub>3</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 3000 ppm HCl conc. J<sub>4</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 4000 ppm HCl conc.

A highest increase in the current density is recorded of PANI/1wt% CNTs sensor in aqueous of 1000, 2000, 3000, and 4000 ppm concentration of HCl when compared with all other conditions specially at 3000 and 4000ppm conc. Often, the desired redox reaction at the bare electrode involves slow electron transfer kinetics and therefore occurs at an appreciable rate only at potentials substantially higher than thermodynamic redox potential. such reaction can be catalyzed by attaching to the surface a suitable electron transfer mediator [10].Since this does not respond to the required reaction , a modifying material was added to the bare electrode (mediator) .the function of the mediator(PANI and PANI/CNTs composite) is to facilitate charge transfer between analyte HCl and electrode. In most cases the mediated reaction sequence (e.g., for an oxidation process) is described in equations (1) and (2) [11].





Where M represents the mediator (or modifier) on the electrode surface and A is analyte[11]. Hence, the electron transfer takes place between the electrode and mediator and not directly between the electrode and analyte .the active process produced by a catalyst is being electrochemically regenerated .The net results of the electron shutting are a lowering of the overvoltage of analyte oxidation to be the formal of the mediator and increase in current density [see figure (10)] . The PANI/1 wt %CNTs have a high electron transfer rate constant because this modifier in the absence of HCl analyte exhibit a well-behaved redox reaction in cyclic voltammery technique. But in the presence of analyte the anodic peak current in cyclic voltammogram increased drastically and cathodic peak eliminated at suitable potential scan rate[10].

**Sensors in aqueous solution of NH<sub>3</sub>**

In order to detecting ammonia ,the surface electrode of PANI and PANI/(0.25, 0.5, and 1)wt %CNTs composite films(sensors) deposition electrochemically on SUS 304 stainless steel in aqueous of (1000, 2000, 3000, and 4000)ppm concentration of ammonia (NH<sub>3</sub>) .Figure (11) and table (2) demonstrates the maximum current density of the PANI, PANI/(0.25, 0.5, and 1)wt% CNTs sensors at varying NH<sub>3</sub> concentrations .

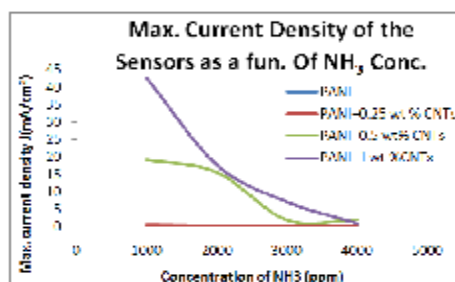


Figure (11) Maximum current density of the sensors obtained at the varying NH<sub>3</sub> concentrations.

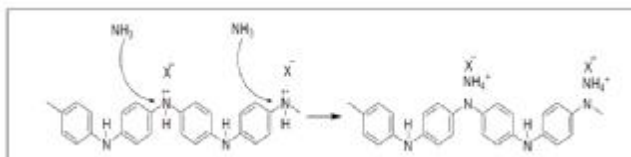
**Table (2) Maximum current density of the sensor obtained at the varying NH<sub>3</sub> concentrations.**

Sensor	J <sub>a</sub>	J <sub>b</sub>	J <sub>c</sub>	J <sub>d</sub>
PANI	0.357	0.275	0.195	0.168
PANI/0.25wt% CNTs	0.555	0.257	0.132	0.1006
PANI/0.5 wt% CNTs	19.26	15.61	1.9	2.04
PANI/1 wt% CNTs	42.8	17.74	7.13	0.927

J<sub>a</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 1000 ppm NH<sub>3</sub> conc. J<sub>b</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 2000 ppm NH<sub>3</sub> conc. J<sub>c</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 3000 ppm NH<sub>3</sub> conc. J<sub>d</sub>: Max. Current Density J (mA/cm<sup>2</sup>) 4000 ppm NH<sub>3</sub> conc.



In general, it is concluded that as the concentrations of  $\text{NH}_3$  is reduced there is a corresponding reduction in the resistance of the sensors. When exposed in ammonia, PANI undergoes dedoping by deprotonation<sup>[12]</sup> Figure (3.12).



**Figure (12) Shown the protons on –NH– groups transferred to  $\text{NH}_3$  molecules to form ammonium ions [13].**

The protons on –NH– groups were transferred to  $\text{NH}_3$  molecules to form ammonium ions while PANI itself turned into its base form. This process is reversible, and in fact, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and proton<sup>[13]</sup>.

The existence of CNTs contributes to the enhancement of electrons transfer. This may justify the reduction of the resistance at a concentration of 1000 ppm with increasing proportions of carbon nano tubes. Addition of CNTs in the process provides a subsequent explanation for the reasons behind the improvement of the response of PANI sensors. All above characteristic behaviour of the sensors are provided by the nature of the I-V characteristics which are experienced by the operational sensor<sup>[14]</sup>.

## CONCLUSIONS

Addition of CNTs to PANI for the formation of PANI/CNTs composite resulted in an upgrade in the electrical conductivity indicated by an increase in  $J$ . This reveals a well formed CNTs network inside PANI. In the liquid type sensing, it was found that with the increase of HCl concentrations, the value of  $J$  could be raised and found pronounced at 3000 ppm and 4000ppm concentration along with PANI/0.5 wt %CNTs and PANI/1 wt% CNTs sensors. The reason behind that may be the enhancement of more efficient transfer of charges. Upon using different concentrations of  $\text{NH}_3$ , results showed a reduction in  $J$  with increasing concentration and found apparent with 1000 ppm and 2000 ppm concentrations along with PANI/0.5wt %CNTs and PANI/1wt % CNTs sensors. The enhancement of the deprotonation process could have been the governing factor in this process.

## REFERENCES

- [1]. Inzelt, G. E. Csahok and V. Kertesz, "preparation and characterization of polyaniline electrode modified with diamino: methylbenzoate", *Electrochimica Acta* 46:pp3955-3962, (2001).
- [2]. Grimes, C.A. C. Mungle, D. Kouzoudis, S. Fang, P.C. Eklund, "The 500MHz to 5.5GHz complex permittivity spectra of single wall carbon nanotube-loaded polymer composite" *Chem Phys Lett* 319:pp 460-464(2000).

- [3]. Breuer and U. Sundararaj, O. "Big Returns from Small Fibers: A Review of Polymer/Carbon Nanotube Composites", *Polymer Composites*, 25, pp 630-645 (2004).
- [4]. Sun, Y. S.R. Wilson, D.I. Schuster, "High dissolution and strong light emission of carbon nanotubes in aromatic amine solvents", *J. Am. Chem. Soc.* 123):pp 5348- (2001).
- [5]. Sittig. M. "Handbook of Toxic and Hazardous Chemicals and Carcinogens. 2nd ed. Noyes Publications, Park Ridge, NJ. (1985).
- [6]. Bochenkove and G. B.sergeev, V. E. "sensitivity ,selectivity ,stability of gas sensitive metal-oxide nanostructure",*Amirican scientific publishers*,Edited by Ahmed Umer and Yoon Bong Hahn,Vol.3 pp.31-52;(2010).
- [7]. Quillard, S. G. Louarn, S. Lefrant, A.G. MacDiarmid,"Vibrational analysis of polyaniline. A comparative study of leucoemeraldine ,emeraldine, and pernigraniline bases", *Phys Rev B* 50:12496(1994).
- [8]. Trchova, M. J. Stejskal, J. Prokes sit in "Jin Shi, Zhe Wang, Hu-lin Li" "Electrochemical fabrication of polyaniline/multi-walled carbon nanotube composite films for electrooxidation of methanol";*J Mater Sci* 42 : pp539–544;(2007).<sup>1</sup>
- [9]. Chuizhou Meng. Changhong Liu, Shoushan Fan,"flexiblecarbon nanotube/polyaniline paper-like films and their enhanced electrochemical properties", *Electrochemistry communications* 11:pp.186-189 ;(2009).
- [10]. Mazloun-Ardakani and M.A. Shiekh-Mohseni, M. "Carbon Nanotubes in electrochemical sensors", edited by Mohammed Naaghi, Intech: pp.395-411; (2011).
- [11]. Bard and L.R. Faulkner, A.J. "Electrochemical methods fundamentals and applications", John Wiley and Sons, 3rd edition New York ;(2001).
- [12]. Jin, Z. Y.X Su, Y.X. Duan, "Development of a polyaniline-based optical ammonia sensor". *Sens. Actuators B* 72: pp 75-79 ;(2001).
- [13]. Hau Bai and Gaoquan Shi,"gas sensors based on conducting polymers", *sensors*, 7, pp.267-307 ;(2007).
- [14]. Thamir Hassan, A.A. M. Izzat Al-Essa, A.Al-Ajaj Ekram and M. Ali Abdul Kareem;"Current-Voltage of Polyaniline Nanofibers and Polyaniline /MWNTs Nanofibers Fabricated By Electrochemical Polymerization", *IJIRST-ISSN2229-3116*, Vol. 4 No.2 (2013).