Journal of Engineering and Applied Sciences 13 (1): 150-156, 2018
ISSN: 1816-949X

The Preparation of Nano thin Films of Poilyaniline/Carbon Nanotubes and Studying their Reaction to Some of the Organic Materials

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Abstract: A quartz crystal microbalance sensor coated with a thin film of pollyaniline/carbon nanotubes was used as a sensitive method for the determination of a number of following vapours: Ethyl acetate, chloroform, ammonia. The detections were based on the absorptions of vapours of these organic compounds into the film by using gas cell room. The detection of vapours were obtained in part per million ppm. The research includes the use of polyaniline films with different thickness 64, 94, 124 and 186 nm where thickness of the (Poly aniline/MWCNT) films was controlled by spin coater. Results show that increasing of sensitivity with increase of the concentration of injected analyte when the (Poly aniline/MWCNT) nano-film-coated QCM was exposed to the vapours of ethyl acetate, chloroform, ammonia. Best sensitivity to ammonia were obtained with film thicknesses 94 nm while in the case of.

Key words: Chloroform, ammonia, QCM, sensitivity, crystal, quartz

INTRODUCTION

Quartz crystal microbalance: Quartz material is piezoelectric materials used to detection of mass variation due to piezoelectric properties. "QCM" Quartz Crystal Microbalance is a particularly sensitive mass frequency biosensor mass. Using quartz crystal microbalance technique is considered as an electric method suitable for mass and viscoelastic analysis of adsorbed layers at the solid/water or solid/air interface. It measures a mass per unit surface by measuring the variation in frequency of a quartz crystal sensor (Voinova *et al*., 2004).

The quartz crystal microbalance is basically a mass sensing device that has the ability to measure minor mass changes on a quartz crystal resonator in real-time. Quartz crystal microbalance sensitivity is approximately over than 10^2 time an electronic fine balance with a sensitivity of 1 mg. That means that quartz crystal microbalance technique are ability for measuring the changes of mass are very small such as a fraction of a single layer or monolayer of atoms (Li *et al*., 2007).

QCM has sensitivity its very high and the same time monitoring of mass changes on the sensor crystal make it very smart technique for a large range of applications. Especially, the development of "QCM" systems is used in fluids or with visco-elastic deposits has dramatically bigger the interest towards this technique (Baldini *et al*., 2006; Shinen *et al*., 2014).

MATERIALS AND METHODS

Polyaniline: In the family polymer famous world, polyaniline consider one of the very important conducting materials. The conditions variations of aniline polymerization makes it has ability to synthesize polymer materials production with the properties and desired structures. Therefore, it at important materials used in various fields of the sciences and engineering. Thomas and Parks (2006) special devotion is given to the matrix synthesis of (PANI) as the main approach to obtain electro active and conducting composite materials. And also, we can use Polyaniline (PANI) and composite materials in polymer electronics is analyzed in short time. (Alam *et al*., 2013).

During the past 15 years, a wide range of diverse methods in the field of synthesis of polyaniline that provide ways to control its structure physic and chemical properties development (Heeger, 2001).

The selection of synthesis procedures is largely determined by the tasks and application of polyaniline in a given a big field of organic electronics using. High wide spectrum of properties made a polyaniline is used in different applications material such as a sensors in field effect transistors, solar batteries, lithium ion batteries, fuel cells, super capacitors, actuators and many other purposes (Peng *et al*., 2007; Boeva and Sergeyev, 2014; Al-Mashhadani *et al*.,

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2014). With the use of the methods of template polyaniline synthesis, various composite materials combining mechanical, physics and chemical properties of the PANI. (pH sensitivity, electron conductivity, various kinds of chromism and the ability to absorb electromagnetic radiation in a wide wavelength range) may be synthesized (Shinen *et al*., 2014; Gao *et al*., 2008).

The commercial value of the discovery of aniline has been involved in many industries such as the dye industry. In addition, to being used as a primary compound of dyes, it is the primary compound for the manufacture of many drugs (Shinen *et al*., 2014).

Carbon nanotubes: We can summarize some of the major achievements in the carbon nanotube of the experimental and theoretical researches in connection with the possible industrial applications of the nanotubes. The nanotubes has an amazing mechanical and electronic properties of the stem in their semi-one dimensional structure such as the graphite arrangement of the carbon atoms in the network. Therefore, the nanotubes have high Young's factor and tensile strength which makes them preferable for composite materials with good mechanical properties (Bachtold *et al*., 2001). The nanotubes maybe metallic material or semiconducting material that depending on their some structural parameters. This properties makes the nanotubes have more applications as a basics elements in electronic devices. Such as a transistors and correcting diodes (Popov, 2004). The probability for using of the nanotubes as high capacity hydrogen storage media were also considered important information are derived by electrical, mechanical and thermal measurements (Dresselhaus *et al*., 2001).

Carbon nanotube is used in many areas such as automotive fuel tanks industry, Tennis rackets, golf, skiing and sticks on the snow and the coating of military weapons that are not detected by radar and its can be applied this characterizes on a variety of areas including touch screens and displays foldable (Dresselhaus *et al*., 2001).

Ethyl acetate: Ethyl acetate organic composite, write in $C_4H_8O_2$ formula, the form of a colorless liquid with a distinctive smell reminiscent of the smell of the adhesive. Ethyl acetate is chemically classified as citrate has significant practical uses. Has some physical significant properties such as 897 kg/m density, 77.1°C boiling point, 88.11 g/mol molecular mass, -83.6°C melting point, viscosity 0.426 cp at 25°C and soluble in water (Seader and Henley, 2006).

Ethyl acetate is used in several applications as solvent in ink, adhesives and pharmaceutical substances, as a solvent for medicinal herbs. High purity ethyl acetate is used in the electronics across many industries, industry including in surface coating and thinners, flavors and essences, flexible packaging, occurrence in wines and miscellaneous (Kirbaslar *et al*., 1997). High exposure causes heartburn, nose and throat an anesthetic in the body and inflammation of the skin.

Chloroform: Chloroform is a colorless liquid, non-flammable, easy to volatilize with a distinctive odor. It has a melting point of -63°C and its boiling point at atmospheric pressure is 61.3°C. Chloroform has a greater density than water 7.2-9.3 at 25°C, density at 25°C 1.48 g/cm^3 which is not mixed with it (not mixed with water). Chloroform disintegrates as a result of ultraviolet light where phosgene, gaseous chloride and hydrogen chloride form. Therefore, commercial containers of chloroform such as ethanol are added to a concentration between 0.5-1.0% to avoid the formation of poisonous phosgene gas.

The packagings are often dark in color to reduce the diffractive effect of light. Chloroform fumes cause loss of consciousness and relieve pain. However, chloroform has toxic effects on the heart, liver, internal organs, nausea, vomiting and renal disorders. It has a severe vasodilator effect, decreases arterial pressure and has a direct inhibitory effect on the heart muscle. Therefore, chloroform is not used as an anesthetic at present. Chloroform is industrially prepared to heat chlorine gas with CH_4 when the temperature between 400-500°C, a radical substitution reaction occurs in a phased manner until complete replacement and access to carbon tetrachloride (Karellas and Chen, 2013).

Chloroform hazard maybe causes in different risks at a human such as harmful if swallowed, causes skin irritation, causes serious eye irritation, toxic if inhaled in this case maybe cause dizziness or drowsiness, suspected of causing cancer or damaging the unborn child, maybe causes damage to organ's human through prolonged or repeated exposure (Anonymous, 1999).

Ammonia: Ammonia gas is lighter than air and is symbolized by the chemical symbol NH_3, a colorless element has a pungent odor when it's concentration above 50 ppm. Ammonia has special properties at normal atmospheric pressure his highly soluble in water, melting point -78, molecular weight 17.03, boiling point of -33.5°C and a freezing point of -107.86°C (Phillips, 1995).

Inhaling large amounts of this poisonous gas, leads to irritating to the eyes, nose and mouth. When NH_3 gas inhalation consider is very danger is that it is explosive when mixed with air in certain proportions, approximately one volume of ammonia to two volumes of external air and more that when ammonia and oxygen mixing (Phillips, 1995).

The tremendous development in the field of various industries led to the production of many organic compounds, a section of these compounds beneficial and some of them dangerous. Ammonia gas is one of the most part dangerous toxic compounds that threaten human life at inhalation operation. These include are many fields applications such as the coke manufacture, livestock management, fossil fuel combustion, fertilizer manufacture industry and refrigeration methods. The main reason for the emission of ammonium gas is from the mismanagement of the recycling of livestock waste and the production of fertilizers such as nitrogen fertilizers, urea manufacture, ammonium nitrate and nitric acid. They account of the totalammonia emissions at 90% (Gomaa and Cindric, 1991).

Synthesis of thin film: Different nano thickness of polyaniline/carbon nanotubes films were deposited on both sides of the quartz crystal microbalance by using spin coating. Polyaniline/Carbon nanotubesnano films obtained were 64, 94, 124 and 186 nm and thickness measurements were achieved by using ellipsometry. Gas-cell chamber was used to the sensitivity of the QCM measure when exposed to different analysts of ammonia, chloroform and ethyl acetate. The QCM was exposed to air after the absorption of each analyte. The backshift of the crystal frequency to its initial value was taken as an indication of every desorption. All measurements were carried out at room temperature. We can be defined sensitivity is a ability of a sensor to produce a signal when low concentrations of a target analyte are present. We can defined the sensitivity of a sensing material is a concentration of analytesorbed on to the sensing material divided by the total concentration of the analyte (Thomas and Parks, 2006).

RESULTS AND DISCUSSION

FTIR: Figure 1 shows the frequency of the bonds of effective aggregates sites for pure polyaniline film. The emergence of a summit in the 3153.61 cm^{-1} this indicates the presence of C-H aromatic is an important feature of the reference to the polyaniline, the emergence of values between 1487-1566.20 cm^{-1} these values back to the presence of Yle group C = C aromatic ringed in the polyaniline. When vaccination with carbon nano-tube as in Fig. 2 are seeing the emergence of value at 3210 cm^{-1} and this is clear evidence of a C-H Aromatic attributable to polyaniline this ccorresponds to approximately the same value that appeared when you reference the value of which 3153.61 cm^{-1} as in Fig. 1, the emergence of value at 2958.80 cm^{-1} this returned to CH_3 in carbon nanotubes as referred to in the basic material as in Fig. 3. The emergence of value at 2927.94 cm^{-1} returning to Yle group CH_2 in carbon nanotubes and also the emergence of value at 2779.42 cm returning stretchable (CH) in carbon nanotubes he emergence of values between 11635.64-1486 cm^{-1} evidence of a C = C aromatic attributable to polyaniline (Stewart, 2011).

These results indicated to the presence of each of the polyaniline and carbon nano-tube which indicates to their presence together.

AFM: The results of the tests (AFM) of the nano films for pure (PANI) and doped of (MWCNTS) films which prepared by spin coating which showed a uniform granular surface morphology as in Fig. 4 and 5. Where we note that the roughness increased with increasing the ratio of doped. As well the Root Mean Sequare (RMS) increased with increasing of ratio of doped, the average grain diameter also it exhibits the same behavior. This is consistent with the findings of the researchers (Stewart, 2011).

Figure 6-8 shows that increasing of sensitivity with increase of the concentration of injected analyte when the polyaniline/carbon nanotubes films coated quartz crystal microbalance was exposed to the one of the vapours of chloroform, ethyl acetate and ammonia. This is expected since when more vapor molecules are provided in the test atmosphere, more molecules would be absorbed into the polyaniline/carbon nanotubesnanofilms coating on the quartz crystal microbalance. After each addition for the concentration of vapor, the frequency of the crystal was back shifted to its initial value by drying the electrode using air which indicates full desorption of vapor from the electrode surface. This behavior confirms that the sensing interaction between the imine and amine sites of polyaniline/carbon nanotubesnano films chains coating and vapor is a physical absorption properties through a dipole/dipole interaction or hydrogen bonding. The presence of hydrogen in the electronegative nitrogen in all of the polymers allow for hydrogen bonding (Thomas and Parks, 2006).

Figure 1shows increasing of sensitivity with increase of the concentration of injected ethyl acetate and Chloroform. The resistivity is increase for the sensor on exposure to ethyl acetate is thought to be caused by an interaction via. dipole/dipole moment of ether molecules and the nitrogen atoms of polyaniline/carbon nanotubesnanofilms, leading to the hindrance in conformational rearrangements of the macromolecules

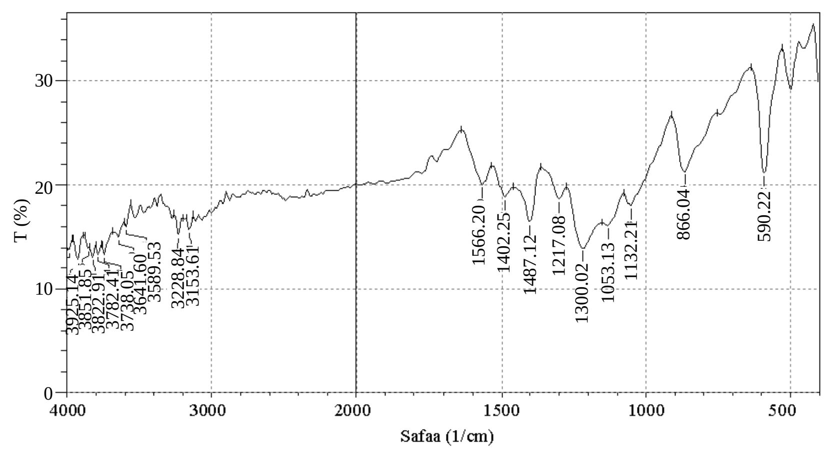

Fig. 1: FTIR for pure polyaniline

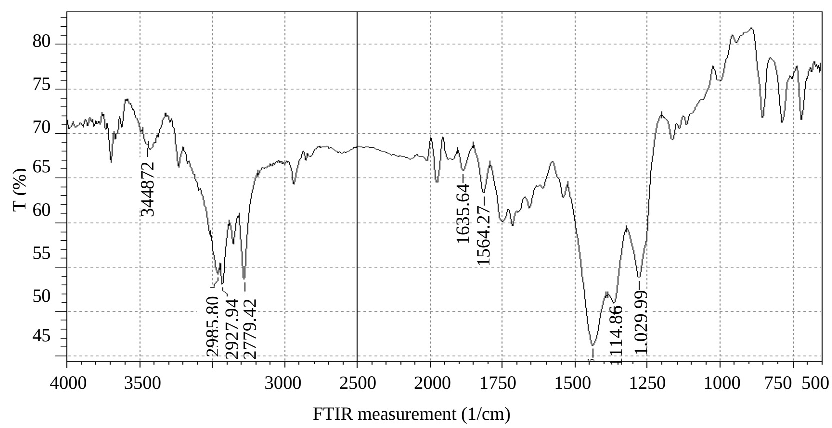

Fig. 2: FTIR for polyaniline/MWCNTS

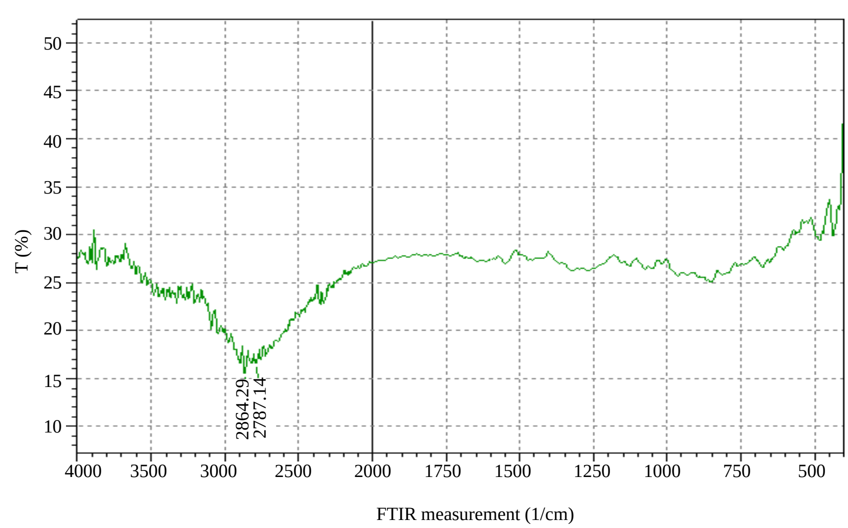

Fig. 3: FTIR for carbon nanotubes (MWCNTS)

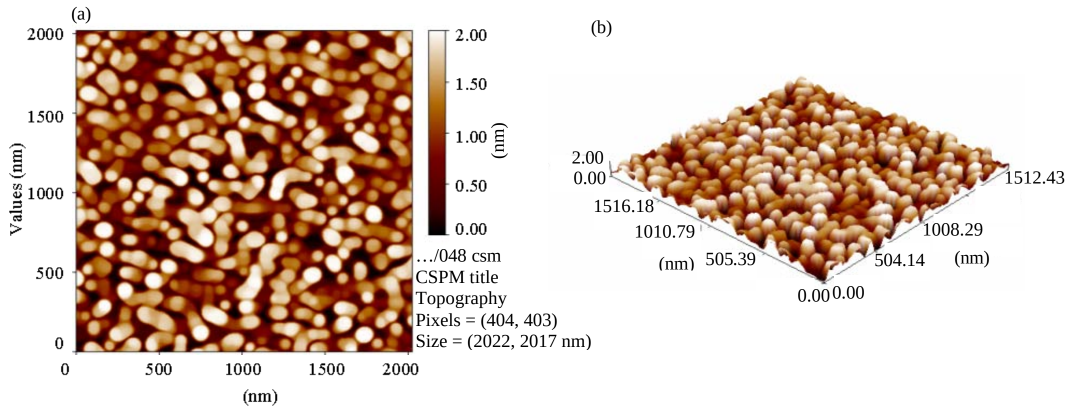

Fig. 4: AFM images of pure PANI nano films for; a) 2-D and b) 3-D

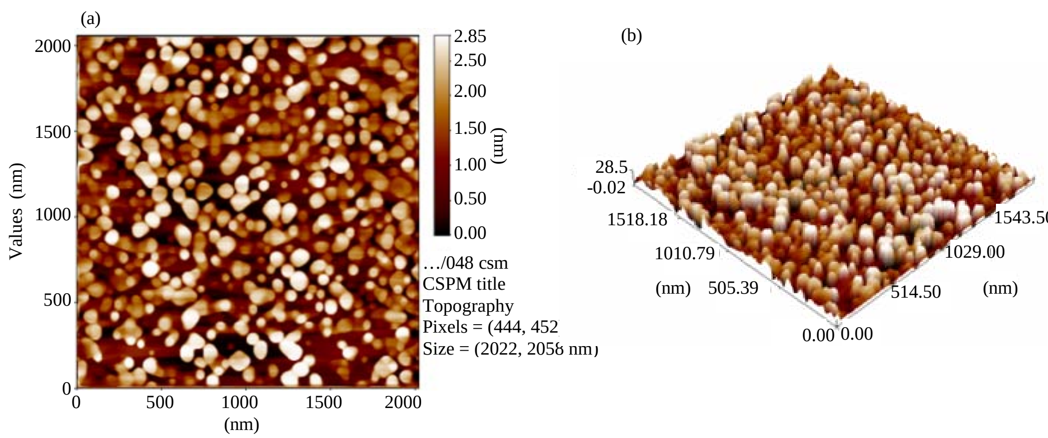

Fig. 5: AFM images of PANI/ MWCNTS for 2%; a) 2-D and b) 3-D

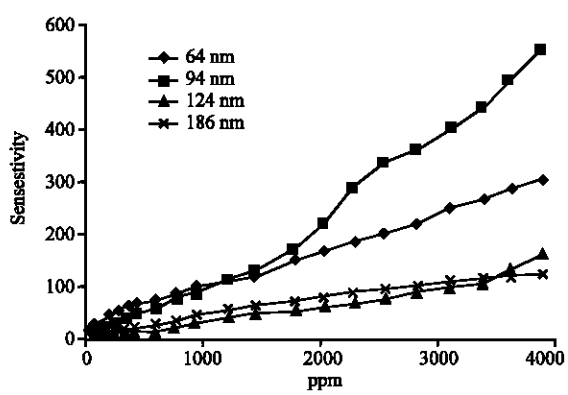

Fig. 6: Sensitivity of QCM coated with different thickness of poly aniline/MWCNT) nano composite exposed to ethyl acetate

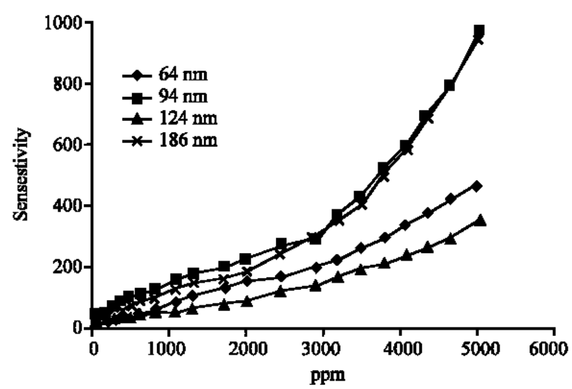

Fig. 7: Sensitivity of QCM coated with different thickness of (Poly aniline/MWCNT) nano composite exposed to chloroform

that resist to change in the electron delocalization and charge transport through the polymer chain (Stewart, 2011). Best sensitivity was obtained with film thicknesses 86 nm at high and low concentration of ethyl acetate. So, it is found that the polyaniline/carbon nanotubesnano films would affect the sensitivity of the sensor. This can be assigned to the increased active sites of the polyaniline/carbon nanotubesnano films as the film

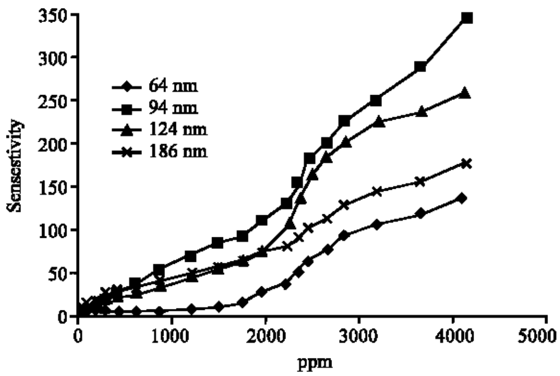

Fig. 8: Sensitivity of QCM coated with different thickness of (Poly aniline/MWCNT) nano compositeeexposed to ammonia

thickness increases (Mirmohseni and Oladegaragoze, 2004; Choudhury, 2009, 2004). Therefore, polyaniline/carbon nanotubesnano films of 86 nm considered suitable thickness to create active sites and but ethyl acetate molecules only physically absorb on the the polyaniline/carbon nanotubesnano films surface. On the other hand it was found that thickness of 124 and 164 nm gave low sensitivity at high and low concentration to ethyl acetate as shown in Fig. 7 due to poor physically absorb on the polyaniline/carbon nanotubesnano films surface.

Figure 7 illustrates the effect of polyaniline/carbon nanotubesnano films thickness on sensitivity of QCM with increase of the concentration of injected analyte of chloroform. Therefore, this result showed the increasing in analyte concentration the sensitivity increases which could be attributed to the interaction via dipole/dipole moment of chloroform molecules and the nitrogen atoms of polyaniline/carbon nanotubesnano films. Figure 7 shown best results were obtained with thickness of 124 and 86 nm. By comparison of Fig. 1 and 2 it can be seen that QCM with PANI film of thickness 124 nm has more sensitivity to chloroform because more physical absorption take place. This is because low molecular weight alcohols vapors decrease the conductivity of the polyaniline/carbon nanotubesnano films faster than higher molecular weight alcohols. Finally, these results are acceptance with the literature scientific researches.

For example Bartlett and Ling-Chung (1989) and Hussien and Shinen (2013) observed a much slower response for ethanol vapor when compared to methanol vapor. It was interpreted that the electrons in the polyaniline/carbon nanotubesnano films. were much more tightly bound in the presence of the low molecular weight alcohol. Figure 6 and 8 demonstrates behavior of quartz crystal microbalance towards increase of the concentration of injected analyte, carbon tetrachloride and ethyl acetate respectively which both are non-polar molecular. This would t indicate that polarity is not the only factor in generating a response on the nanosensors (Yang, 2010; Bartlett and Ling-Chung, 1989; Yang, 2010; Hussien and Shinen, 2013). Elucidation of the exact mechanisms would require extensive research with a variety of substances and possible development of structure activity relationships. Also, it can be seen that best sensitivity to carbon tetrachloride was obtained with polyaniline/carbon nanotubesnano films film thicknesses 86 nm. Figure 7 shows that thickness of 64 and 184 nm gave very good sensitivity to ethyl acetate. It is obvious from Fig. 3 that QCM has more sensitivity to ethyl acetate.

CONCLUSION

Construction of “QCM” sensor by coating the surface of a quartz crystal electrode pole with a film capable of interaction with the interest environments. The interaction between the sensing materials with the surface of a quartz crystal coated and the target materials considers is principle of “QCM” sensors (Baldini *et al*., 2006; Shinen *et al*., 2014)

Polyaniline (PANI) coated “QCM” gas sensor has often been investigated. Therefore, we attempted to make a highsensitivity, lowcost and rapid response of “QCM” interaction gases sensor. The performance of the sensor was investigated (Shinen *et al*., 2014; Thomas and Parks, 2006).

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