Cu-doped tunguston oxide nanocomposite gas sensor for acetone sensing

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Abstract - **Cu-doped WO_3 was preparing a nano composite for sensing acetone by solvo thermal chemical method. The surface morphology, dopant distribution, Crystal phase structure and electric properties was characterized by SEM, TEM, XRD. The gas sensing propeties was investigated as function of the amount of cu element, concentration of acetone. The 3mol% Cu dope WO_3 nanocomposite give high response and good selectivity to acetone. The response of the nanocomposite to 20ppm of acetone was 5.43, which could be recognized to their high surface to volume ratio and structure. This is a low regularity, large dipole moment and strong interaction with acetone molecules and good selectivity to acetone gas. Therefore Cu doped WO_3 based material show the potential application for semiconducting gas sensor in the asthmatics. Exposure of low concentration of acetone causes irritation to the eye nose throat. It may also cause difficulty in breathing for some asthmatics**

Keywords* — *Copper, Tunguston oxide,* solvo thermal chemical method, *Sensitivity, Response time

I. INTRODUCTION

Metal oxide nanocomposite thin film have been used for different application because their unique properties such as electrical propeties, optical properties, electronic properties, physicochemical properties. Now days the demand of highly sensitive sensor towards gases is used for various applications such as industrial process control environment protection food safety healthcare and security has increase [1]. They says that certain disease in human health are associated with specific inorganic and organic gases and volatile organic compound existing in human breath. For example inhaling volatile acetone compound cause of oral malodour. Acetone is important breath maker [2]. Acetone seems to have antibacterial affect against the bacteria that cause acne.it also might help promote the loosening and shedding of skin. So, acetone as important breath maker of diabetes could be used to reflect metabolic product of diabetes. Diabetes is harmful for human health and there are about 100 million patients shall over the world and number is continuously increases. The medical survey has shown that acetone concentration in exhaled breath from a healthy human body is lower than 0.6 ppm but diabetic patient is higher than 1.6 ppm [3]. So, accurate analysis of acetone gas is extremely helpful to diabetes treatment and is highly desirable. Acetone produced mainly decay of organic matter .it release from sewage, liquid manure and with natural gas .it is a byproduct in many industries such as waste water treatment agriculture silos ,pits textile manufacturing pulp and paper processing food processing hot asphalt paving mining petroleum production and refining sewer.

For fast sensitivity and exact analysis of of acetone in human breath is important method for diagnosis of diabetes. The traditional detecting apparatus is expansive and needed special knowledge for operation. The principle of metal oxide gas sensor is changing resistance of nanocomposite due to the surface absorption and desorption of gas molecule and the related space charge effect . The sensing properties can be increase by increasing the surface to volume ratio and decreasing grain size.SnO_2,CuO,ZnO are metal oxide semi conductive sensor have certain advantage including high sensitivity ,fast response and easy operation[4].Now a day one dimensional nano material is generally used in fabrication of gas sensor due to high specific surface area which provide more active site for gas adsorption . WO_3 has attracted much attention for gas sensing application and has been considered as the most favorable material for detecting gas like NO_2, H_2S, SO_2 and NH_3.In order to improve the sensitivity and selectivity of WO_3 by doping, dimension control and phase transition [5].

In this paper Cu dope tunguston oxide have been successfully prepare by solvo thermal chemical method and their acetone sensing properties were investigate in detail. Gas sensing properties such as sensitivity, response, and recovery time have been evaluated for possible gas sensing mechanism [6]. So, the key point to improve the gas sensing performance. By improving the interaction between the gas molecules and sensing surface to decrease operating temperature and improve expose surface which leads to allow detection in gas sensors. The effect of crystal structure and possible gas sensing mechanism were also discussed.

II. MICROSTRUCTURE AND PROPERTIES

Copper is one of the oldest metals used by human because it has useful metallurgical properties and it is a native metal. Which means it can be found naturally in a useable form. It also occur naturally in a useable form. It also occurs in the minerals cuprite, azurite, bornite, and chalcopyrite. The

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chemical element symbol for copper is Cu, with the atomic number 29. Copper has many useful properties making it ideal for a wide verity of application. The main properties of copper are high electrical conductivity, high ductility, good heat conductivity, corrosion resistance, good machinability, antimicrobial properties/befouling resistance, non-magnetic [7]

Tungsten has the highest melting point (1473^0c) of all metals and is therefore also suitable for very high-temperature applications. It is also characterized by a uniquely low coefficient of thermal expansion and a very high level of dimensional stability.WO_3 nano powders are available high surface area and its particles exhibiting magnetic properties. Other forms in which these particles are available are discrete, transparent, high purity and coated forms. Tungsten belongs to block d, period 6 while oxygen belongs to block p, period 2 of the periodic table. The chief applications of tungsten oxide nanoparticles are the manufacture of conducting and semiconducting materials, in optics and mechanochemical applications.

The microstructure of tungsten oxide and copper oxide is shown in figure

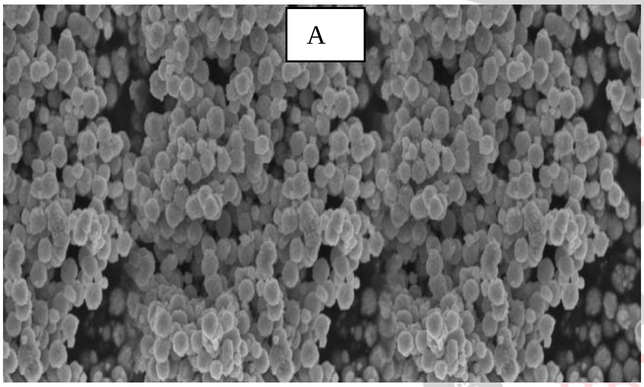

Figure 1 (A)show microstructure of copper oxide

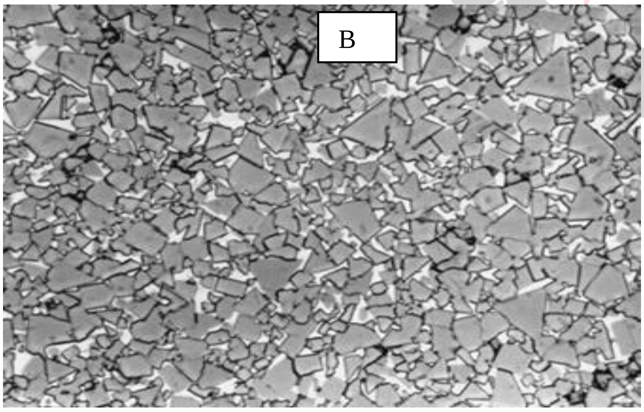

Figure 1 (B) show microstructure of tunguston oxide

III. EXPERIMENTAL

Preparation of cu dope tunguston oxide nanocomposite

In our experiment, a solvo thermal chemical method for synthesized Cu doped WO_3 nanocomposit.They Cu doped WO_3 is prepare at different temperature 100 , 400^0c and room temperature. The tunguston chloride (30mg) was slowly dissolved in 10ml of cyclohexane to obtain a identical solution with the help of magnetic stirrer. Then the solution was centrifuged and washed with distilled water until to reach neutral PH of the solution. After the centrifuge , the solution was subjected to ultrasonification, Which increase the porosity of the material and after the solution was subjected to slow evaporation to remove the excess solvent present in the solution at room temperature. After the evaporation we got WO_3 nanoparticle. To prepare copper doped WO_3 nanoparticle, We used the paste preparation method .In paste preparation method the paste was produce by mixing of 2.0 g of Cu anatase powder and 5g of WO_3 nanoparticle with a mixture consisting of 10.0 g of α-terpineol, 1g of cellulose, and 25 mi of ethanol, Which was petitioned for 48 hrs. at 1200 $WCm^{2.}$ By using the prepare paste thin film were prepared by coating the paste on the glass plate using the doctor blade technique. After the coating two electrodes fitted at both end of copper electrode.

Microstructure analysis and gas sensing properties test

The structural feature of the synthesis Cu dope nanocomposite was investigated using FESEM and transmission electron microscopy. The crystalline structure including the phase purity was examined by X-ray diffraction. Thermal analysis including thermo gravi metric and differential scanning calometric was used to determine the calcination temperature. The acetone sensing properties of gas sensor measure in a static gas system connected with a computer Which used to measure the resistance of the sensor. The response of acetone was define as

$$Response = \frac{Ra}{Rg}$$

Where Ra and Rg were the electric resistance in air and test gas respectively .the resistance measure was carries out at 300℃ which were controlled by adjusting the heating voltage.

IV. RESULT AND DISCUSSION

The morphology of the 3 mol% Cu dope WO_3 nanocomposite shown in figure (2). The porous feature of nanocomposite was characterized by acetone adsorption method and result shown that the surface area of 3 mol% Cu doped WO_3 nanocomposite makes them have more active adsorption site and more gas diffusion channel compare to solid fiber. The gas can be absorb on inside and outside surface of nanocomposite simply and the gas sensing properties can improve accordingly.

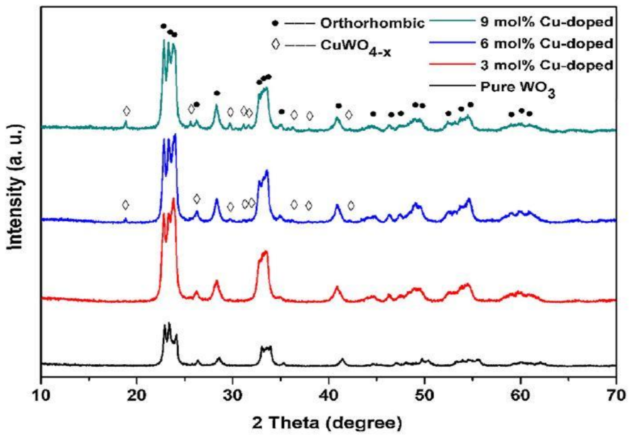

Fig :- (2) X-ray diffraction pattern of pure 3, 6 and 9 mol % Cu doped WO_3 nanocomposite

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Figure (2) Show the X- ray pattern of the pure and Cu doped WO_3 (3, 6 and 9%) nanocomposite at 500 degree Celsius. The pattern of pure and 3 mol % Cu doped WO_3 nanocomposite show peaks those are in good agreement with the orthorhombic WO_3 phase with increasing of the Cu doping content the diffraction peak of $CuWO_4$ phase appear and become increase in intensity.

The resistance of nanocomposite is increase a shown in figure 3 (B).The resistance of WO_3 nanocomposite increase with doping 3 mol % Cu element compare to pure WO_3 , with increase of the Cu content resistance of nanocomposite is decrease a little and increase with further increasing of copper content because in addition of Cu content concentration of electron in composite will increase as well as crystal structure of WO_3 is much disorder, Which will hinder the electron movement and led to increase of resistance of nanocomposite.

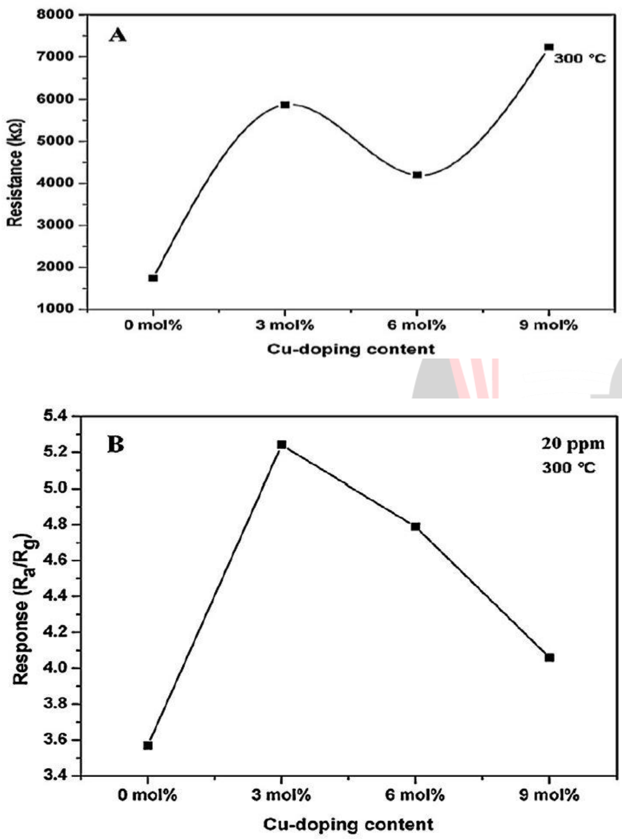

Fig 3:- Original resistance of Cu dope WO_3 nanocomposite vs. Cu doping content curve (A) and response value of the pure 3, 6 and 9 mol % Cu doped WO_3 nanocomposite to 20ppm of acetone (B) at 300 degree Celsius.

Figure (B) show the response of pure , 3 mol % , 6 mol % and 9 mol % Cu doped WO_3 nanocomposite to 20 ppm of acetone at 300 degree Celsius. Compare with the pure WO_3 nanocomposite, The response of all the other sample are found to increase with copper doping element, Which attain the maximum (4.240) At 3% Cu doping and decrease with a further rise of the Cu doping content. This show that Cu doping can increase the gas sensing properties of WO_3 gas sensor to acetone and 3 mol % Cu dope WO_3 exhibits the best gas sensing properties compare with another sample. When a proper content (3 mol %) of Cu^{2+} are introduce. Cu^{2+} will substitute W(+6) in WO_3 crystal lattice Which will change the electrum atmosphere and crystal structure, that means more active absorption site for oxygen are formed, thus the gas sensing properties of WO_3 nanocomposite are improve.

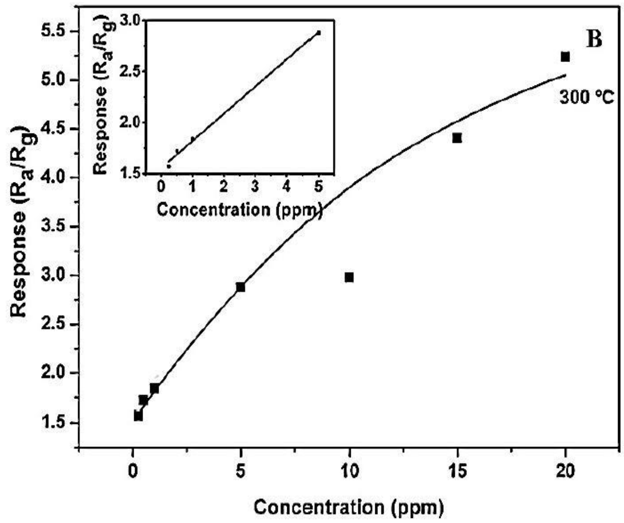

Fig :- (4) Dynamic response recovery curve (A) and response (B) of the sensor based on the prepared 3 mol% Cu doped WO_3 nanocomposite to acetone with concentration ranging from 0.25 ppm to 20 ppm at 300 ℃

Figure 4(A) show the response verses time curve of 3 mole% cu dope wo3 nanocomposite to different concentration of acetone at 300 degree Celsius. It shows that the sensor response is increases with increase the acetone concentration. When the sensor is open to acetone gas, the resistance drops instantly. When the acetone supply is stopped and air is introduce, the resistance fully recovers to the initial value rapidly, which is a characteristic of n-type semiconductor. When expose to 0.25 ppm of acetone, the response of the sensor is about 1.57, which indicates that the sensor has the capacity to detect acetone even at low concentration down to sub ppm level. For 5, 10, 15 and 20 ppm of acetone, the response are about 2.88, 2.98, 4.41and 5.24 respectively.

The gas response of Cu dope WO_3 nanocomposite to acetone is shown in figure 4(b). The response is increase abnormally with the increase of acetone concentration. At relatively low acetone concentration, the response increases nearly linearly with the acetone concentration in the range of 0.25 to 5 ppm, and when the acetone concentration is more than 10 ppm, it change non-linearly. Reducing hydrogen species in acetone are bound to carbon, which disturb the disconnection step to be oxidized. When more acetone molecule is introduced as shown in fig. 4(A, B). The acetone molecule could only be moderately oxidized. So, the resistance of the fiber decrease and the response increase more slowly then low acetone concentration. However, the high response for low acetone concentration is attractive for practical use in breath diagnosis.

V. CONCLUSION

In summary, Cu doped WO_3 nanocomposite with different phase structure successfully synthesized by solvo thermal chemical method. The gas sensing indicated that the sensor

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based on 3 mol% Cu doped triclinic WO_3 nanocomposite exhibited high gas response (6.43), good selectivity, fast response (5s) and recovery times (20s) at 20 ppm of acetone. These could be recognized by their high surface to volume ratio, junction structure and triclinic phase structure Which facilitated the adsorption of oxygen species and strengthened the interaction strength between acetone and WO_3 on the surface, As a result this type of sensor can be a good for diabetes, diagnosis based n human breath analysis.

But this type of gas sensor also sense NO_2 and N_2 for future scope.

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