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Effect of temperature on the wettability of CuO nanowires

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Abstract:*CuO has been prepared by a thermal method in different temperature 300-600°C, the water contact angles of CuO film were measured by the contact angle goniometer; the contact angles were investigated to see the effect of temperature on the wettability of the CuO film which was found to be hydrophilic in nature. The copper before treatment is hydrophobic then, it changed to hydrophilic after the treatment in different temperature.*
Keywords: *copper oxide,Contact Angle, hydrophobicity, hydrophilic.*

I. Introduction

The contact angle is one of the most common reasons for measuring the wettability of a surface or material. Wetting is based to the study of the way a liquid deposited onto a solid substrate (or liquid) spreads or the capacity of liquids to form boundary surfaces with Solid States. The interaction between the different liquids and the surface of the film was evaluated from contact angle measurements. The contact angle values vary with the surface charge of the film and with the polarity of the liquid.

CuO is a semi-conductor with a monoclinic crystal structure**.** It can be widely used in applications such as solar energy, V. Dhanasekarana, T. Mahalingam**[1],**found that transmission spectra (T) of CuO thin film at normal incidence revealed that the films exhibit indirect transitions and can be adapted for the passage of selected frequency bands visible near IR range, and also found that the activation energy is estimated at about 0.29 eV**.** Batteries, for example; copper oxide microflowers (CuO-MFS) synthesized by ZhongliHuaHongdong Liu **[2],** by thermal conversion in the solid state of Cu $(OH)_2$ precursors, showed excellent electrochemical performance in lithium-ion batteries, the initial discharge capacity is 785 mA h g^{-1}, and the reversible capacity is maintained at 350 mA h g^{-1} after 50 cycles. And in three dimensions CuO-MFS provide new insight into the development of anode materials for high-performance next-generation lithium-ion batteries. Sensors, Kima Sang Hoon and al **[3]**, synthesized nanostructures rose-like CuO by hydrothermal process easier at low temperatures to produce chemical glucose sensors. The chemical glucose sensor fabricated shows a very high sensitivity of ~ uA 4.640 mM-1 cm-2 and an experimental detection limit of ~ 0.39 mM with a correlation coefficient (R) of 0.9498. The linear dynamic range observed for the manufactured chemical sensor was 0.78 mM to 100 mM, and in catalysisChao Yang and al [**4**],have synthesized CuO nanosheets dendrites by a microwave hydrothermal method.Synthesized CuO nanostructures were active in the direction of the thermal decomposition of ammonium perchlorate (AP), and allowed the decomposition temperature of AP to decrease. Furthermore, nanostructures CuO are very active inphotodegradation of organic dyes as rhodamine B and methyl orange.

CuO films have been deposited with several methods namely: electrodeposition; A.S.M. SayemRahman, M. A. Islam, K. M. Shorowordi**[5],** have electrodeposited of CuO on the copper substrate and gold plated glass substrate in an electrolyte bath containing 0.2 M $CuSO_4.5H_2O$, 3 M lactic acid and NaOH. They used for electrodeposition a potentiostat / galvanostatic with silver chloride electrode (Ag / AgCl) and a reference electrode. During deposition, the bath temperature and pH were maintained 60°C and 12-12.5 respectively. Copper oxide was deposited at different deposition times and different potentials**.**Dip coating; S.S. Shariffudinand al **[6],**have prepared CuO by dissolving copper acetate powder into isopropanol with molarity of 0.25M. Then they made preheating and annealing the solution at temperature 250 ° C and 600 ° C respectively. Nanostructured CuO thin films were deposited onto quartz substrates by dip coating technique**.** Spin coating; H. Hashimand al **[7]**, have prepared CuO by sol gel technique and they used spin coating technique to deposit the CuO onto quartz substrate, and they have prepared 5 samples of CuO with different coating speeds of 1000, 1500, 2000, 2500 and 3000 rpm were annealed at 600°C for 30 minutes**, by** direct thermal oxidation **[8-9].**
In this work, we will study the wettability of Cu and CuO as well as CuZn and ZnO, by measuring the contact angle and we will be based on textural and structural properties of CuO and ZnO.

II. Materials and methods

The sheets of copper (Cu) and (CuZn) of 2cm×2cm size was firstly rinsed by acetone followed by de-ionized water several times, to remove the oxides from the surfaces. Then, the cleaned foilsit had been dried using an air gun. Finally the Cu and CuZnplates were annealed in the furnace (Thermolyne Furnace 6000) at 300°C, 400°C, 500°C and 600°C for 24 h in air.The wettability of CuO is measured by contact angle using the sessile drop method at ambient temperature. The three liquids used are usually water formamid and hexane.

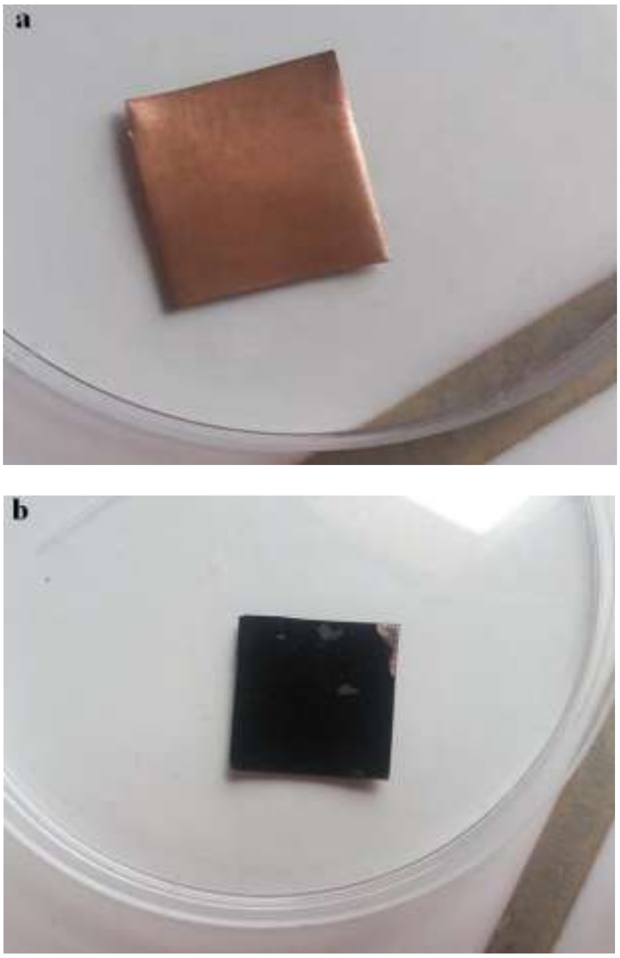

Figure 1: copper a) before and b) after heat treatment

III. Characterization method

In our previous works, we prepared CuO at different temperatures **[9]**.Weconclude the presence of CuO by XRD diffraction and found the monoclinicstructures, and we also showedpresence of the nanowires by AFM analysis.

3.1-Measuring the contact angle (MAC):

The contact angle measurements were performed using a goniometer (GBX instruments, France) by the sessile drop method. A drop of liquid was deposited on a substratum. Three to six contact angle measurements were performed on each substrate surface for the liquid sensor including water, Formamide and Hexane.

***Surface free energy*:**

The surface free energy cannot be measured directly. The area of the energy is performed by measurement of the contact angle with a test liquid deposited on the solid surface.Good approach, Van OSS and CHAUDHURY (acid-base theory) are used in this study. The components of the surface energy of a surface (γ_s^+, γ_s^-andγ_s^{LW}) were determined by carrying out contact angle measurements using three probe liquids (one non polar and two polar) with known surface tension parameters (γ_s^+, γ_s^-andγ_s^{LW}) and using Young's equation **[10]**(1):

$$\cos\theta = -1 + 2(\gamma_s^{LW}\gamma_L^{LW})^{1/2} / \gamma_L + 2(\gamma_s^+\gamma_s^-)^{1/2} /\gamma_L + 2(\gamma_s^-\gamma_L^+)^{1/2} /\gamma_L \qquad (1),$$

Where θ is the measured contact angle, $\gamma^{LW}$is the Van der Waals free energy component γ^+ is the electron acceptor component, γ^-component is the electron donor and the indexes (S) and (L) denote solid surface and the liquid phase respectively.

The Lewis component acid-base, of the surface tension is defined by: $\gamma_S^{AB} = 2(\gamma_S\text{-}\ \gamma_S +)^{1/2}$.

The surface free energy is expressed as: $\gamma_s=\gamma_s^{LW} + \gamma_s^{AB}$ where $\gamma_s=\gamma_s^{LW} + \gamma_s^{AB}$ is the energy component without acid-base.

The surface hydrophobicity was estimated by the Van Oss approach(Van Oss, Good and Chaudhury 1988; Van Oss, 1995)**[11-12]** and by contact angle measurements. This approachconsidersthedegree of hydrophobicityof a material (i) asthe free energy ofinteractionbetween the two entitiesin thismaterialwhileimmersed in water(w): ΔGiwi. If the interaction between the two entities is lower than the interaction of each entity with water, the material is considered hydrophilic ΔGiwi> 0; conversely, for a hydrophobic material, (ΔGiwi<0).ΔGiwi is calculated through the surface tension components of the interacting entities, according to the following formula **[13]:**

$$\Delta Giwi= -2\gamma_{iw}= - 2[((\gamma_i^{Lw})^{1/2} - (\gamma_w^{LW})^{1/2})^2 + 2((\gamma_i^+\gamma_i^-)^{1/2} + (\gamma_w^+\gamma_w^-)^{1/2} – (\gamma_i^+\gamma_w^-)^{1/2} – (\gamma_w^+\gamma_i^-)^{1/2})] \qquad (2)$$

3-Interpreting the results of the contact angle:

The surface physicochemical characteristics of Copper before and after treatment thermal of 24h with various temperatures are shown in **Table1**. We observed that the lowest contact angle was obtained with hexane which was the most dispersive liquid, and the highest contact angle was obtained with the more polar liquid that is water.Important variations in electron donor were detected after contact of the copper with various temperatures. The electron donor for Cu (99, 99% of impurity), increase after the thermal treatment. The level of this increase depends on temperature. The high value is obtained when the sample is treated at 600°C.
On the other side the electron donor for (CuZn) decrease after the treatment,it’s very lowerwhen the sample is treated at 600°C.

The levels of these characteristics after treatment seem to be depending on the type of substrates and temperatures.According to van Oss (1997), it’s possible to determine the degree of absolute hydrophobicity by calculatingthe free energy of interactionΔG_{iwi} between substrate and water. The Cu and CuZnsurfaces are hydrophobic (ΔG<0). Jing Xiao and al (2009) show that the Wettability could be controlled by controlling the concentration of amphiphilicmoleculecetyltrimethylammonium bromide (CTAB) and polyethylene glycol-6000(PEG); they found that adsorption of this amphiphilic molecule transforms hydrophilic surface to superydrophilic**[14]**. Sheng-Hung Tuand al (2014), show that the wettability can be reversible by using H_2O_2oxidation and vacuum-oxidation**[15]**.

For the purpose of finding the effects of the temperatures on CuO nanowire structures, the contact angle measurements of copper (Cu) and CuZn at different temperatures are shown in **Fig. 2**. This latter clearly shows that a copper is hydrophobic before the thermal treatment and at 300°C. The contact angles are higher than 90° for the two types of copper. After the heat treatment can see the decrease of contact angle for the two types of substrate, for Cu attained a valueless than 20° but for (CuZn) less than 70° at 600°C.

Finally, we can deduce that there is a relationship between the degree of temperature and the physicochemical properties of copper substrate.

Table1: Surface tension components and free energy interaction of Cu and CuZntreated and no treated with various temperatures

Substratum	**contact angle**					
	Θ_W	Θ_F	Θ_H	γ^{LW}	γ^+	γ^-
Cuwitness	117,8	125,4	17,0	17,6	8,5	8,3
Cu 300	115,1	46,1	20,7	17,2	22,6	19,7
Cu 400	36,8	19,8	21,0	17,2	12,0	32,3
Cu 500	22,9	25,9	16,2	17,7	8,3	50,0
Cu 600	18,1	25,8	18,6	17,5	8,1	54,0
CuZnwitness	109,6	124,3	20,4	17,3	9,5	16,3
CuZn 300	141,7	66,3	26,8	17,2	17,2	14,9
CuZn 400	54,1	21,6	23,1	17,0	15,4	13,7
CuZn500	71,1	48,2	25,4	16,7	8,7	7,9
CuZn600	68,6	22,1	20,4	17,3	19,0	2,7

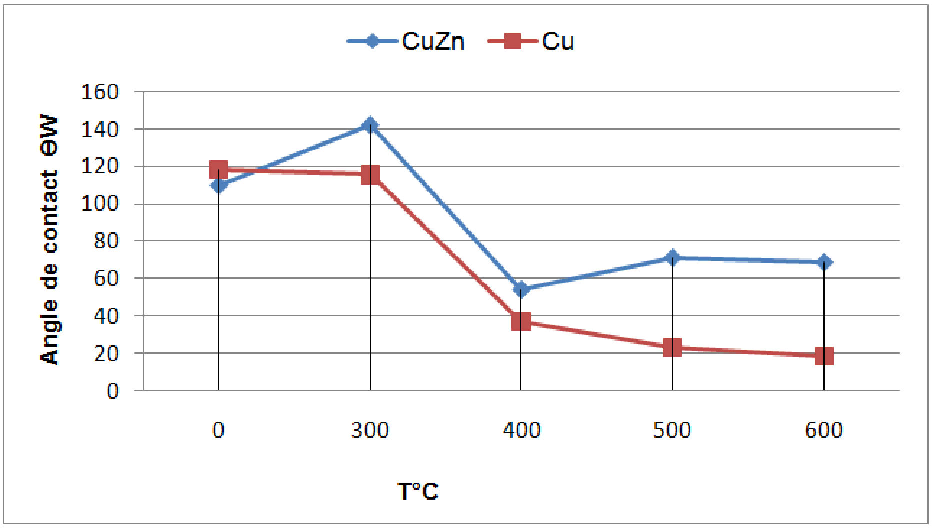

Figure 2: The contact angles for Cu and CuZn surfaces modified with different temperatures

The characteristics of the components of the surface energy of the untreated and treated substrates at different temperature values that have been then used to provide a quantitative measure of the importance of their hydrophobicity or hydrophilic character (ΔG_{iwi}) in international scientific units (mJ m^{-2}) are shown in the**fig.3 and 4.**The results of the **Fig.3**indicates a substantial change in the wettability of the copper film surface from the highly hydrophobic surface untreated (negative valueΔG_{iwi}= -18, 96)to the hydrophilic surface treated with temperatureat 600 °C(positive value, of ΔG_{iwi}= 19, 79).

In 300 °C after 24h, copper crystals were observed with the formation of a few crystals of Cu_2O, explains the hydrophobic nature ofthe substrate with a contact angle 115.1°.By against at high temperatures, for example 600 °C, it's observed the formations of the crystal of CuO with a large amount resulting the change of wettability in more hydrophilic surface with a contact angle 18.1°, This results confirms that the CuO film is hydrophilic in nature as explaining by Feng-Ming Chang and al (2010) **[16].**The material surface characteristics including high surface free energy and chemical composition play a key role in increasing the hydrophilic character of the surface.

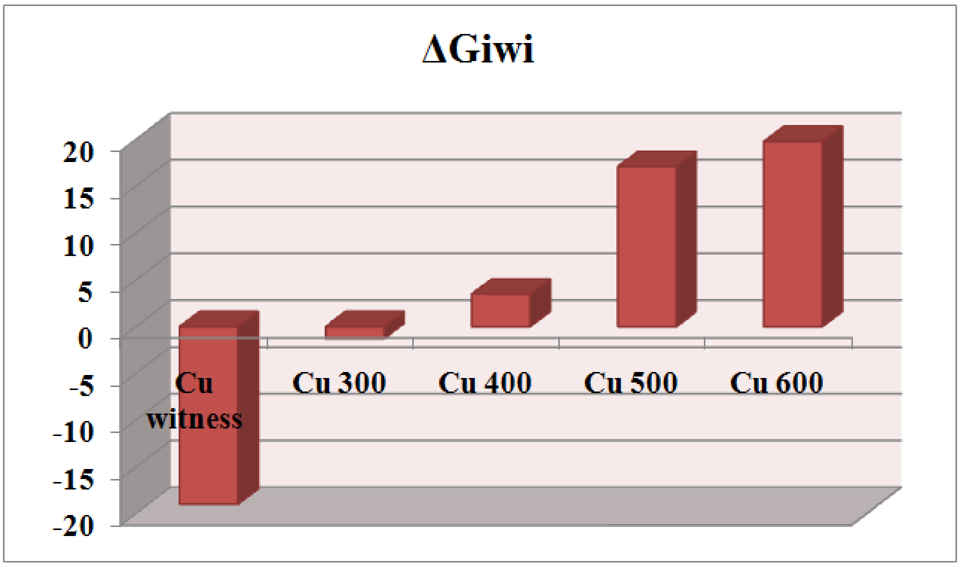

Figure 3: Calculate the free energy of interaction for red Cu surfaces modified with different temperature

WhenCuZn is treated at different temperature we observed, in **Fig.4,** the increase in the surface hydrophobicity with temperatures, the level of this hydrophobicity ranged fromΔG_{iwi}= -8.48mJ/m^2 to ΔG_{iwi}=9.93mJ/m^2. After the treatment of CuZn at different temperature 400-600°C we observed the formation of crystals of ZnO which explains the hydrophobic nature of the substrate**[9-17].**So the temperature rendered hydrophobic surfaces for copper (Cu) hydrophilic and hydrophobic surfaces for (CuZn) more hydrophobic.

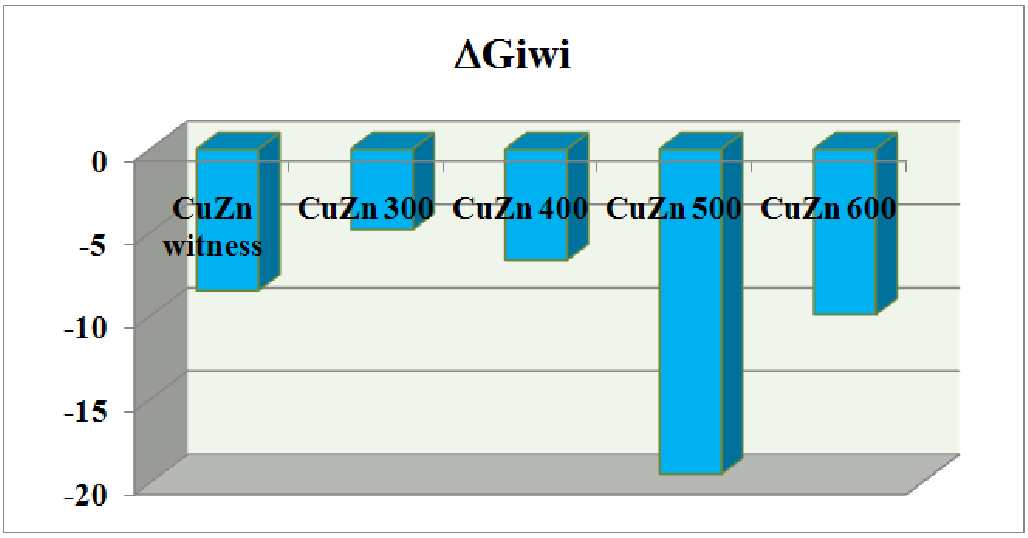

Figure 4: Calculate the free energy of interaction for CuZn surfaces modified with different temperatures

As we can see in**Table2,** after treatment the no-dispersive component increases for copper (Cu). Untreated copper films have a very low in no-dispersive component of the surface energy. After treatments, the no-dispersive component is strongly increased. The no-dispersive component, of all the copper's substrate, is ranging from 16.79 to 41.82mJ m^{-2}.By againstwe observe the decrease in the no-dispersive component for thesubstrate (CuZn). Untreated CuZn films have a low in no-dispersive component of the surface energy. After the heat treatments and more precisely at 500 °C, the no-dispersive component is strongly decreased. The no-dispersive components of all substrateof (CuZn), ranging from 24.88 to14.32mJ m^{-2}.

The values of the dispersive component ofthe surface energy of the prepared copper (Cu) and CuZnfilms are very small in comparison to the non-dispersive component of the surface energy.

The increasing and decreasing in no-dispersive component for (Cu) and (CuZn) respectively, bind to the increase in temperature.

Table 2: Dispersive and non-dispersive components of Cu and CuZn untreated and treated at different temperatures.

	Cu witness	Cu 300	Cu 400	Cu 500	Cu 600	CuZn witness	CuZn 300	CuZn 400	CuZn 500	CuZn 600
no-dispersive components	16.79	42.20	39.37	40.74	41.82	24.88	32.017	29.050	16.58	14.32
dispersive components	17.6	17.2	17.2	17.7	17.5	17.3	17.2	17	16.7	17.3

With these results, we believed that the change in temperature affects the topography of the surface microstructure of CuO. The superstructure of the film and its hierarchical surface structure is directly responsible for the wettability.

IV. Conclusion

The preparation of CuO by a thermal method in different temperature 300-600°C, and the study of the wettability of Cu and CuO, by measuring the contact angle, they show a transition of Cu from hydrophobicity to hydrophilic metal, which explains the formation of CuO. So, there is a relationship between the degree of temperature and the physicochemical properties of copper substrate.

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