Electrolytic Preparation and Characterization of Cuprous Oxide Nano Powder

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Abstract-- **Cuprous oxide (Cu2O) has been prepared using electrochemical cell consisting of two compartments separated by ceramic diaphragm. Two copper sheets have be used as cathode and anode materials. The effect of KOH concentration ,Glycerin, PVA, and SDS on the particle size and roughness of surface have been studied and analyzed using atomic force microscopy. The results indicated that grain size increases with increasing current density and PVA addition gives lower value .the roughness is decreased dramatically from 1.82 to 0.0991nm when PVA was added therefore it recommended to use this additive in preparation of Nano Cu$_2$O. The effect of addition other additives (Glycerin and SDS) is similar to PVA addition but with lower extend.**

Index Term-- **Cuprous oxide, electrodeposition, atomic force microscopy, roughness**

1- INTRODUCTION

Cuprous (Cu$_2$O) oxides (cuprite) is the most important stochiometric compounds in the copper-oxygen (Cu-O) system. Both materials are intrinsic p-type stoichiometry with narrow energy band gaps (2.1 eV for Cu$_2$O, 1.2 eV for CuO) and exhibit a variety of interesting properties that can be fully exploited is several fields. Applications have been envisaged in solar cells [1], Li-ion battery systems (negative electrode material) [2], superconductors [3], magnetic storage systems [4], gas sensors [5], photothermal [5] and photoconductive systems [6].Copper oxides are known to be ideal compounds in the study of electron-correlation effects on the electronic structure of transition metal compounds in general and in high Tc superconductors. Changes in the electronic structure of these semiconductor materials at the nanometer scale significantly influence their properties due to quantum confinement effects [7].

The literature is not very rich in papers dealing with the production of Cu2O. For instance, Wei *et al.* [8] synthesized cuprous oxide via a simple solvothermal reduction route, whereas Musa *et al.* [9] produced copper oxide by thermal oxidation and studied its physical and electrical properties. Other synthesis methods include for instance electrochemical deposition [10], sonochemistry [11], sol-gel [12], RF reactive sputtering [13] and chemical vapour deposition (CVD) [14].

Electrodepostion of Cu2O can be performed either in the potentiostatic mode or, galvanostatic mode. In potentiostatic mode, a potentiostat will accurately control the potential of the counter electrode (CE) against the working electrode (WE) so that the potential difference between the working electrode and the reference electrode (RE) is well defined. In galvanostatic mode, the current flow between the WE and the CE is controlled. The potential difference between the RE and WE and the current flowing between the CE and WE are continuously monitored [15-18].

Rakhshani et al. [15] prepared *p*-Cu2O film onto conductive substrates in each three different modes, they used a solution of cupric sulphate, sodium hydroxide and lactic acid and the composition of the films deposited under all conditions was *p*-Cu2O with no traces of CuO. Rakhshani et al. [19] also showed that the size of grains could be controlled by the rate of deposition in the galvanostatic mode. Mukhopadhyay et al. [17] galvanostatically deposited *p*-Cu2O at 40–60 °C on copper substrates in solution of cupric sulphate (0.3 M), NaOH (3.2 M) and lactic acid (2.3 M) at pH 9. The deposition kinetics was found to be independent of deposition temperature and linear in the thickness up to about 20 μm. The electrical conductivity of *p*-Cu2O films was found to vary exponentially with temperature in the 145–300°C range with associated activation energy of 0.79 eV. Golden et al. [20] electrodeposited *p*-type cuprous oxide by reduction of copper (II) lactate in alkaline solution of 0.4 M cupric sulfate and 3 M lactic acid and concluded that the surface texture of electrodeposited Cu2O films in bath is affected by bath pH and current density. Wang et al. in a narrow pH range, 9.4-9.9 obtained a third preferred orientation namely (110) [21]. In pH range 8-9, the preferential orientation of Cu2O deposited film is (200) and as the pH decreases further below 8, the film composition changes from Cu2O to mix phase of Cu and Cu2O at pH 7 and to Pure Cu below pH 5 [22].Zhou and Switzer [23] conducted similar experiment and obtained similar results. They obtained pure four-sided pyramids Cu2O films at bath pH 9 with applied potential between -0.35 and -0.55 vs. saturated calomel electrode (SCE) or at bath pH 12. Georgieva & Ristov [24] deposited the cuprous oxide (Cu2O) films using a galvanostatic method from an alkaline CuSO4 bath containing lactic acid and sodium hydroxide at a temperature of 60 °C. Authors obtained polycrystalline films of 4–6 μm in thickness with optical band gap of 2.38 eV. The first *n*-type behavior of Cu2O by electrodeposition was reported by Siripala and Jaykody [25]. They cathodically deposited *n*-Cu2O on various metal substrates in solution containing 1mM CuSO4 and small amount of NaOH. Tang et al. [26] investigated the *n*-type electrochemical deposition of

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nanocrystalline Cu2O thin films on TiO2 films coated on transparent conducting optically (TCO) glass substrates by cathodic reduction in solution consisting of cupric acetate 0.1 M sodium acetate and 0.02 M cupric acetate. The effect of bath temperature was investigated at bath temperature at 0, 30, 45, and 60 °C. Authors found that that growth rates also exhibit significant temperature dependence and the film thickness increases with increasing temperature for the same deposition time. Wijesundera et al. [27] showed that that the single phase polycrystalline Cu2O can be deposited from 0 to -300 mV (SCE). While at more negative potential co-deposition of Cu and Cu2O starts and at the deposition potential from -700 mV (SCE) and more negative a single phase Cu thin films are produced. They carried the electro deposition in an aqueous solution containing sodium acetate and cupric acetate. Jayathileke et al. [28] electrodeposited cuprous oxide thin film in aqueous acetate baths and discovered not only the pH value but also the cupric ion concentration of acetate bath determines the conduction type of the Cu2O films.

Most of previous work were conducted in aqueous solution of NaOH or sodium acetate, to the best of authors knowledge no previous work was conducted using KCl as electrolyte therefore the aim of present work is to prepared nano particle Cu_2O using KCl electrolyte and characterization using atomic force microscopy. The effect of several additives like Glycerin, Polyvinyl alcohol, and Sodium dodecyl sulphate on AFM structure were studied.

2- EXPERIMENTAL WORK

The electrochemical system consists of electrolytic cell [glass beaker 250 ml, two cupper electrodes (anode and cathode) separated by a fine silica diaphram to prevent the precipitate Cu2O moving toward the cathode electrode and reduced to cupper powder. the distance between the electrodes was 80mm. A power supply (DC current, Maximum voltage 30 V,5 amp .china) was used to provide and measure with more accuracy current. figure (1)shows the system under study..

Fig. 1. The Electrochemical System.

Different electrolyte solutions were used for Cu2O electrochemical deposition ,these were aqueous solution of KCl at different concentrations ranges (50,100,150,200,250, g/l) with and without additives like Glycerin, Polyvinyl alcohol, and Sodium dodecyl sulphate .All chemicals were from commercial sources. They were used without further purification. All solutions in this study were prepared from de-ionized water.

At the end of the experiment, electrodes were removed quickly and the cell was disconnected, the suspension was filtered quickly ultra-fine porous filter bag was used, the washing of the cuprous oxide slurry after its withdrawal from the cell is a very important step in the process. It is necessary to effect the fast and thorough removal of impurities, especially chlorides, and to prevent the oxidation of cuprous oxide, [29, 30] recommended that the cuprous oxide slurry be treated with a solution of neutralized invert sugar at 3% concentration before washing in order to reduce the tendency towards oxidation during washing and drying, and the cuprous oxide slurry be separated from the electrolyte within 12 hrs. To avoid the formation of a greenish copper oxychloride layer. The slurry should always be covered with distilled water during washing and before stabilization. After the cuprous oxide slurry, together with the electrolyte, was withdrawn from the cell, the precipitate of cuprous oxide was allowed to settle. As soon as a good settling of the cuprous oxide was reached, as much of the clear electrolyte as possible was decanted. Afterwards, the cuprous oxide powder was washed repeatedly with distilled water through the cycles of stirring settling and decanting for several times, or until no precipitation occurred in the supernatant solution upon the addition of a few drops of silver nitrate

solution. then centrifuged, washed several times with de-ionized water, repeat also several washing with absolute ethanol, filtration again with ultra-fine porous bag finally store the deposited Cu2O in tightly closed vials, to prevent the oxidation of Cu2O particles, store in evacuated desceature contain a silica gel powder . The AFM analysis was performed using SPM-AA3000 (Angestrom Advanced Inc., USA) in contact mode. AFM images were recorded over scan area (2µmx2µm).

3- RESULTS AND DISCUSSION
3-1 Effect of current density

Figs. 2-3 show the current density and voltage transients during cuprous oxide preparation for 60 mints at different concentration of KOH. A gradual increase of current density or voltage at near steady state was obtained as the concentration of KCl increase. The current density was increased as the concentrations of KCl increases. Figure (4) shows the relation between the average of grain size of Cu_2O and the current density. It can be seen that grain size decreases with increasing of current density at different additives, the grain size is increased with addition of PVA higher than that was observed for SDS or Glycerin.as a general guide, the grain size results can be arranged as PVA < SDS < Glycerin.
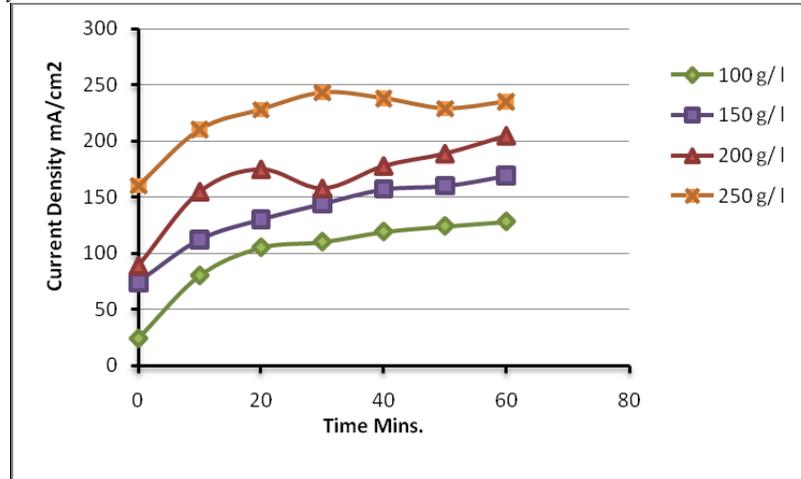

Fig. 2. the Influence of Current Density on the Reaction Time at Different KCl Concentrations.
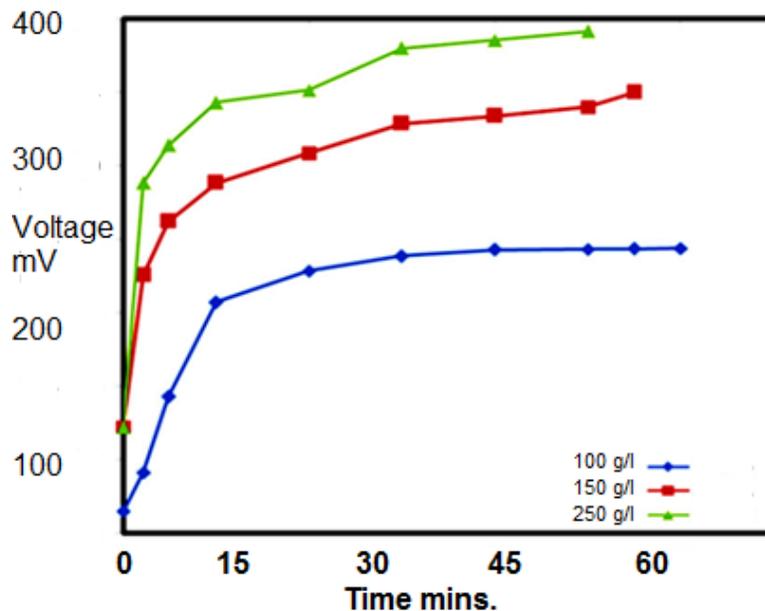

Fig. 3. the Influence of Cell Voltage on The Reaction Time at Different KCl Concentration.

3-2 AFM analysis

Atomic force microscopy (AFM) is an excellent tool to study morphology and texture of diverse surfaces. The knowledge of the surface topography at nanometric resolution made possible to probe thin film surfaces. The versatility of this technique allows meticulous observations and evaluations of the textural and morphological characteristics of the films, showing better facilities than other microscopic methods

[31].table (1) illustrate the experiments achieved for studding the AFM in which the effect of concentration of different electrolyte species and additive have been studied .the AFM results are shown in table (2) and figure (5)
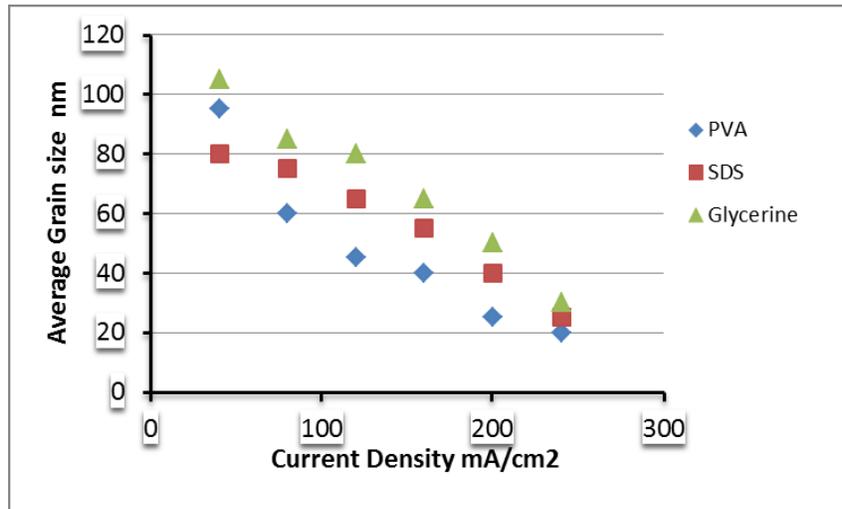

Fig. 4. the Influence of Current Density on The Grain Size at Different Additive Type

Table I
Conditions and materials used in the experiment of Cu2O powder electrodeposited at different KCl solutions

| Chemicals	1	2	3	4	5	6	7
KCL	250 g/L 200 ml	250 g/L 100 ml	250 g/L 100 ml	250 g/L 100 ml	250 g/L 100 ml	250 g/L 100 ml	250 g/L 100 ml
KOH	5 g/100 ml 2-3 ml	5 g/100 ml 1-2 ml	5 g/100 ml 1-2 ml	5 g/100 ml 1-2 ml	5 g/100 ml 1-2 ml	5 g/100 ml 1-2 ml	5 g/100 ml 1-2 ml
$K_2Cr_2O_7$	1g/100ml 2 ml	1g/100ml 1ml	1g/100ml 1ml	1g/100ml 1ml	1g/100ml 1ml	1g/100ml 1ml	1g/100ml 1ml
Citric acid	5 g/100 ml 2 ml	5 g/100 ml 1 ml	5 g/100 ml 1 ml	5 g/100 ml 1 ml	5 g/100 ml 1 ml	5 g/100 ml 1 ml	5 g/100 ml 1 ml
Glycerin	....	....	1g/100ml 1ml	1g/100ml 10 ml	....	....	....
SDS	....	....	....	....	....	1g/100ml 5ml	1g/100ml 20ml
PVA	....	....	....	....	1g/100ml 20ml	....	....
PH	8 - 9	8 - 9	8 - 9	8 - 9	8 - 9	8 - 9	8 - 9
Temperature	70 - 80 c°	70 - 80 c°	70 - 80 c°	70 - 80 c°	70 - 80 c°	70 - 80 c°	70 - 80 c°
General CD	500 A /m²	500 A /m²	500 A /m²	500 A /m²	500 A /m²	500 A /m²	500 A /m²
Anode area	12 cm²	8 cm²	8 cm²	8 cm²	8 cm²	8 cm²	8 cm²
current density	0.60 mA	0.40 mA	0.40 mA	0.40 mA	0.40 mA	0.40 mA	0.40 mA
Voltage	7.1 mv	5.4 mv	19.7 mv	7.9 mv	13.7 mv	15.3 mv	8 mv

Table II
AFM measurements of Cu2O powder electrodeposited at different KCl solutions

CSPM Imager surface roughness analysis	1	2	3	4	5	6	7
Roughness average (sa) nm	1.5000	0.4020	1.0700	0.1210	0.0824	0.1470	0.3230
Root mean square (sq) nm	1.8200	0.5000	1.3200	0.1460	0.0991	0.2030	0.3950
Surface skewness (Ssk) nm	-0.5830	-0.6020	-0.4770	-0.3900	-0.8640	0.2990	-0.4530
Surface kurtosis (sku) nm	2.4700	2.9900	2.7500	2.4200	2.4000	4.5000	2.630
Peak-peak (sy) nm	8.9700	2.7000	6.6200	0.6710	0.4610	1.6900	2.0500
Ten point height (sz) nm	5.8100	1.6100	4.7700	0.4190	0.2720	0.8590	0.9910
Root mean square slope (sdq) [1/nm]	0.0795	0.0230	0.0529	0.0071	0.0055	0.0071	0.0224
Surface area ratio (sdr)	0.3130	0.0260	0.1390	0.0025	0.0015	0.0025	0.0249
Surface bearing index (sbi)	2.4500	1.3500	1.2000	2.9600	2.0600	0.4310	0.8000
Core fluid retention index (sci)	1.2400	1.3100	1.3100	1.3300	1.3400	1.7800	1.3100
valley fluid retention index (svi)	0.1440	0.1430	0.1320	0.1310	0.1220	0.1270	0.1330
Reduced summit height (spk) nm	0.5180	0.2460	0.9630	0.0368	0.0382	0.3220	0.1790
Core roughness depth (sk) nm	4.3700	1.1800	3.2800	0.3970	0.2630	0.3840	1.0300
Reduced valley depth (svk) nm	2.5300	0.6740	1.6000	0.1710	0.1050	0.2590	0.4600

The most important parameters in AFM measurements are **Roughness average (Sa), Root mean square Roughness (Sq), Surface skewness (Ssk)** and **Surface kurtosis (Sku)** .The roughness average (Sa) is the arithmetic average of the absolute values of the measured profile height deviation taken within the sampling length and measured from the graphical center line. The roughness average can be the same for surfaces with roughness profile totally different because it depends only on the average profile of heights. The Root-mean square roughness (Sq) is defined as the standard deviation of the surface height profile from the mean height. It is the most commonly reported measurement of surface roughness, and is given by:

$$Sq = \left[\frac{1}{N} \sum_{i=1}^{N} (h_i - (h_{av}))^2 \right]^{1/2}$$

Where N is the number of pixels in the image (or data points), h_i is the height of the pixel, and h_{av} is the mean height of the image. Although the (Sq) evaluations are useful, they provide information only on the height variation, i.e., in the direction perpendicular to the substrate. The (Sq) is more sensitive to peaks and valleys than the average roughness due to the squaring of the amplitude in its calculation. Skewness (Ssk) is the third moment of profile amplitude probability density function and is used to measure the profile symmetry about mean line. When the height distribution is symmetrical (Ssk) *is* zero. If the height distribution is asymmetrical, and the surface has more peaks than valleys the Skewness moment is positive and if the surface is more planar and valleys are predominant the Skewness is negative. Kurtosis moment (Sku) is the fourth moment of profile amplitude probability function and corresponds to a measure of surface sharpness.
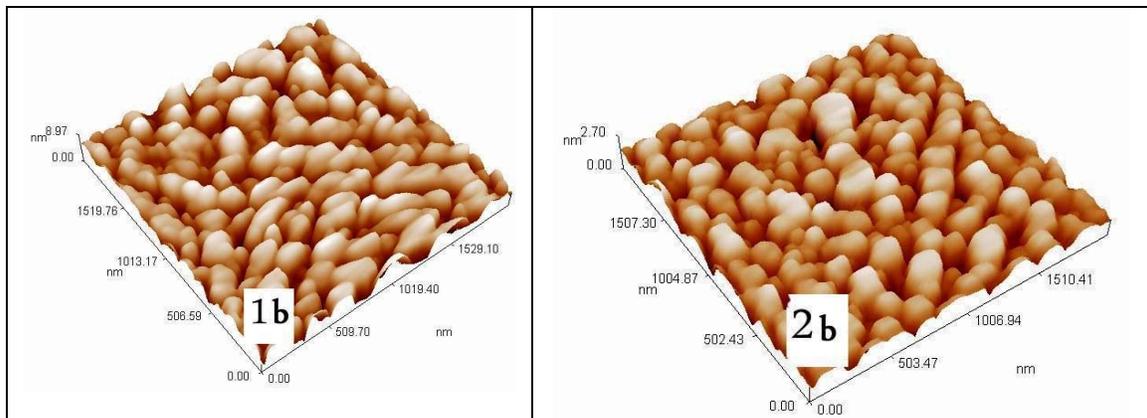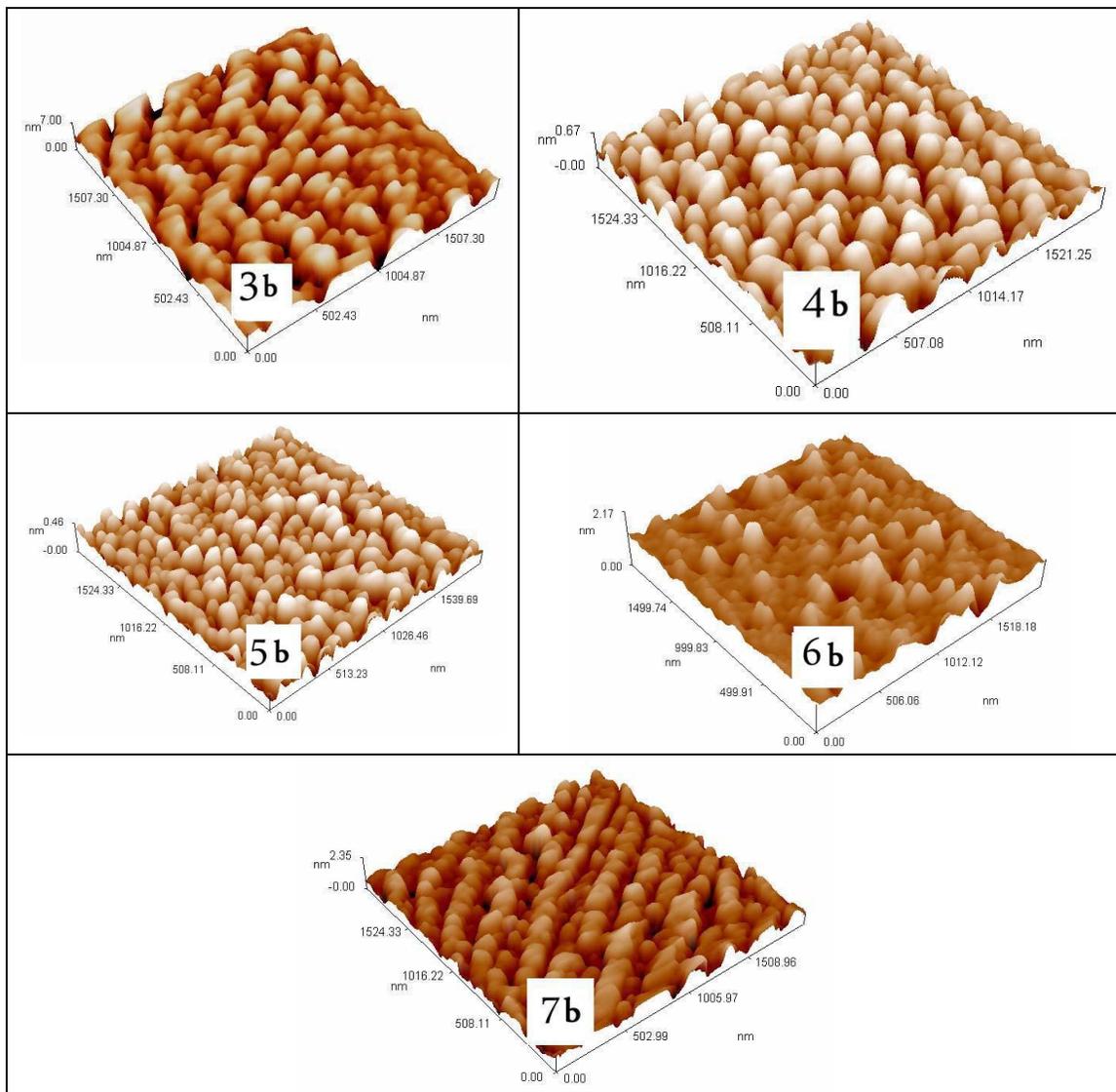
Fig. 5. AFM image for different cu2o particles prepared according to condition in table (1)

When (Sku) is 3 indicates a Gaussian amplitude distribution, and the surface is called Mesokurtic, but if Kurtosis is smaller than 3 the surface is flat and called Platykurtic. If the Kurtosis is higher than 3, the surface has more peaks than valley.

The root-mean square surface roughness values are determined to be 1.82 ,0.5,1.31, 0.146,0.0991,0.203 ,0.395 nm for Sample,1,2,3,4,5,6,and 7 respectively ,Accordingly the roughness profile of the powders may be arranged as follows: 1 > 3 > 2 > 7 > 6 > 4 > 5

Increasing amount of kcr2o7 or cetric acid led to higher roughness of powder. Also increasing amount of glycerin led to higher roughness of powder while increasing amount of SDS led to lower roughness. The most important result is the addition of PVA which give the lowest value of roughness. The roughness results can be arranged as PVA < Glycerin < SDS. The results refer that all powders have negative surface skewness except the addition 5ml of SDS which means that surface has more valleys than peaks. Surface kurtosis (sku) for all samples are lower than 3 while addition 5ml of SDS is only higher than 3 indicating that this addition gives more flat surface.

4- CONCLUSIONS

Cu2O nano-powder was successfully deposited from an alkaline electrolyte solution containing 250 g/l KCl ,citric acid ,potassium dichromate ,using three different type of additives as emulsifiers agent (SDS ,PVA , glycerin) at current density 500 A/m2 . The results indicate that addition of PVA gives Nano powder having the lowest grain size and roughness. The dramatic decrease of roughness from 1.82 nm to 0.0991 engorges the using of PVA in the preparation of Nano Cu_2O particles. Increasing of current density higher than 500 A/m^2 is not recommended because of lowering the current efficiency than 50% in spite of giving lower particles size.

REFERENCES

[1] A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi. "Heterojunction solar cell with 2% efficiency based on a Cu2O substrate". Applied Physics Letters, 88, 163502, (2006).

[2] D. Zhang, Y. Tang-Hong, Chun-Hua Chen, "Cu nanoparticles derived from CuO electrodes in lithium cells", Nanotechnology, 16, 2338–2341, (2005).

[3] J. B Goodenough, "Bond-length fluctuations in the copper oxide superconductors," Topical Review J. Phys.: Condens. Matter, 15, R257–R326,(2003).

[4] R.V. Kumar, Y. Diamant, A. Gedanken, "Sonochemical synthesis of cerium oxide nanoparticles effect of additives and quantum size effect", Chem.Mater., 1**2**, 2301, (2000).

[5] S.T. Shishiyanu,T S. Shishiyanu and O. I. Lupa, "Novel NO2 gas sensor based on cuprous oxide thin films", Sensors and Actuators B: Chemical,113,[1],468-476,(2006)

[6] J. Herion, E.A. Niekisch and G. Scharl, "Investigation of metal oxide/cuprous oxide heterojunction solar cells", Solar Energy Materials, vol. 4, [1], 101-112,(1980).

[7] M. Wei, N. Lun, X. Ma and S. Wen, "A simple solvothermal reduction route to copper and cuprous oxide", Materials Letters, Vol. 61, [11-12**]**, 2147-2150,(2007).

[8] Musa A.O, Akomolafe T, Carter M.J., "Production of cuprous oxide a solar cell material, by thermal oxidation and study of its physical and electrical properties," Solar Energy Mater Solar Cells, 51, 305–316, (1998).

[9] J.K. Barton, A.A. Vertegel, E.W. Bohannan, J.A. Switzer, "Epitaxial

[10] Electrodeposition of Cuprous Oxide onto Single-Crystal Copper," Chem.

[11] Chapter 1. Introduction 16 Mater., 13, 952, (2001).

[12] R.V. Kumar, Y. Mastai, Y. Diamant, A. Gedanken, "Sonochemical synthesis of amorphous Cu and nanocrystalline Cu2O embedded in a polyaniline matrix", J. Mater. Chem., **11**, 1209, (2001).

[13] L. Armelao, D. Barreca, M. Bertapelle, G. Bottaro, C. Sada, E. Tondello, "A sol-gel approach to nanophasic copper oxide thin films", Thin Solid Films,442, 48–52, (2003).

[14] S. Ghosh, D.K Avasthi, P. Shah, V. Ganesan, A. Gupta, D. Saransgi, R.Bhattacharya, W. Assmann, "Deposition of thin films of different oxides byRF reactive sputtering and their characterization". Vacuum, **57**,377–385,(2000).

[15] P.R. Markworth, X. Liu, J.Y. Dai, W. Fan, T.J. Marks, R.P.H. Chang,"Coherent island formation of Cu2O films grown by chemical vapourdeposition on MgO(110)", J. Mater. Res., **16**, 2408, (2001).

[16] A. E. Rakhshani, et al., "Electrodeposition and characterization of cuprous oxide," Thin Solid Films, vol. 148, pp. 191-201, 1987.

[17] M. T. S. Nair, et al., "Chemically deposited copper oxide thin films: structural, optical and electrical characteristics," Applied Surface Science, vol. 150, pp. 143-151, 1999.

[18] A. E. Rakhshani and J. Varghese, "Galvanostatic deposition of thin films of cuprous oxide," Solar Energy Materials, vol. 15, pp. 237-248, 1987.

[19] A. K. Mukhopadhyay, et al., "Galvanostatic deposition and electrical characterization of cuprous oxide thin films," Thin Solid Films, vol. 209, pp. 92-96, 1992.

[20] A. E. Rakhshani and J. Varghese, "Surface texture in electrodeposited films of cuprous oxide," Journal of Materials Science, vol. 23, pp. 3847-3853, 1988/11/01 1988.

[21] T. D. Golden, et al., "Electrochemical Deposition of Copper(I) Oxide Films," Chemistry of Materials, vol. 8, pp. 2499-2504, 1996/01/01 1996.

[22] L. C. Wang, et al., "Electrodeposited copper oxide films: Effect of bath pH on grain orientation and orientation-dependent interfacial behavior," Thin Solid Films, vol. 515, pp. 3090-3095, 2007.

[23] T. Mahalingam, et al., "Galvanostatic deposition and characterization of cuprous oxide thin films," Journal of Crystal Growth, vol. 216, pp. 304-310, 2000.

[24] Y. Zhou and J. A. Switzer, "Electrochemical deposition and microstructure of copper(I) oxide films," ScriptaMaterialia, vol. 38, pp. 1731–1738, 1998.

[25] V. Georgieva and M. Ristov, "Electrodeposited cuprous oxide on indium tin oxide for solar applications," Solar Energy Materials and Solar Cells, vol. 73, pp. 67-73, 2002.

[26] W. Siripala and J. R. P. Jayakody, "Observation of n-type photoconductivity in electrodeposited copper oxide film electrodes in a photoelectrochemical cell," Solar Energy Materials, vol. 14, pp. 23-27, 1986.

[27] Y. Tang, et al., "Electrodeposition and characterization of nanocrystalline cuprous oxide thin films on TiO2 films," Materials Letters, vol. 59, pp. 434-438, 2005.

[28] R. P. Wijesundera, et al., "Growth and characterisation of potentiostatically electrodeposited Cu2O and Cu thin films," Thin Solid Films, vol. 500, pp. 241-246, 2006.

[29] K. Jayathileke, et al., "Electrodeposition of p-type, n-type and p-n Homojunction Cuprous Oxide Thin Films," Sri Lankan Journal of Physics, vol. 9, pp. 35-46, 2008.

[30] V.F. Vetere and R. Romagnoli, Ind. Eng. Chem. Prod. Res.Dev. 23, 656, (1984).

[31] J. W. C. COOPER, Electrochemical preparation of cuprous oxide powder:Part I. Basic electrochemistry, *JOURNAL OF APPLIED ELECTROCHEMISTRY* 20 , 818-825 , (1990).

[32] M. Raposo*, Q. Ferreira and P.A. Ribeiro, A Guide for Atomic Force Microscopy Analysis of Soft-Condensed Matter, Modern Research

[33] and Educational Topics in Microscopy. A. Méndez-Vilas and J. Díaz (Eds.) ©FORMATEX 2007.

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