ISSN : 2393-8188 (print)
2393-8196 (online)
www.milliyasrcollege.org.journal.php

SYNTHESIS OF CuS BY HYDROTHERMAL METHOD FOR THE SUPER CAPACITOR APPLICATION

J R Nagarale[a], S N Kulkarni[b], K Y Rajpure[c], S B Madake[d]

[a] Department of Physics, Doodhsakhar Mahavidyalaya, Bidri, 416202, India

[b] Department of Physics, Doodhsakhar Mahavidyalaya, Bidri, 416202, India

[c] Department of Physics, Shivaji Univerisity Kolhapur, Kolhapur, 416004,India

[d] Department of Physics, Shivaji Univerisity Kolhapur, Kolhapur, 416004,India

jyotinagarale20@gmail.com

ABSTRACT: Copper sulphide an important compound is prepared by hydrothermal method to study its super capacitive behavior. CuS was prepared by using simple source of copper as copper foil and sulphur powder as sulphur. 0.49g copper foil is used with 0.19g of sulphur and was put into the autoclave and maintained at 140 ^{0}C throughout. At this temperature reaction time is varied as 6hrs, 12hrs and 13hrs respectively to get CuS. The XRD confirms the phase formation. The lattice parameters were calculated (a (Å): 3.796, b (Å):3.796, c (Å): 16.36). SEM gives surface morphology of prepared CuS. CV, GCD and EIS were obtained to study electrochemical behavior of copper sulphide powder. Contact angle calculated which comes out to be 53.6 ^{0}C.

KEYWORDS: Supercapacitor; hydrothermal; autoclave; XRD; SEM; CV.

1. INTRODUCTION

Nowadays, supercapacitors are the creator of this globalizing world. Increasing requirement thus creating increased interest in field of supercapacitor. Supercapacitors are also known as ultracapacitors or electric double layer capacitor. Supercapacitor has high energy density than capacitors but much lower than that of batteries. Supercapacitor have longer life time than battery which means that they exhibit nearly thousands of cycles of charging and discharging. Properties of supercapcitor are mainly determined by their performances as the electrode material.

CuS is an important member of sulphide family. It shows a great application in terms of semiconducting nature such as photocatalysis, solar cell, batteries etc. As it is a material with great potential it took out interest of various researchers to study its supercapacitive behavior [1,2].

2. EXPERIMENTAL PROCEDURE

In this article copper sulphide were prepared by simple hydrothermal method. To Prepare copper sulphide Copper foil is used as a copper source and sulphur powder as sulphur source. 0.49g of copper foil were weighed accurately and 0.19g of sulphur powder were used. The precursors with distilled water were placed into an autoclave. The autoclave is maintained at 140^{0}C throughout and reaction is carried for 6, 8, 12 and 13hrs. Obtained powder were collected from the autoclave and washed carefully with water and ethanol. Further, prepared powder is used to make film of CuS. Using “Doctor blade method” CuS film is prepared by

help of a binder. Binder preparation takes place by following steps;

Mixture of 45ml DDW and 5ml ethanol, then add 5gm of PVA in above solution. Then this solution is kept at 60^0C with stirring for nearly 1hr. Using this solution and powder of CuS, thin film is prepared and it is annealed at 150^0C for 1hr within vacuum.

3. CHARACTERIZATION

X-ray diffraction patterns of prepared samples were recorded using a X-ray powder diffractometer (Bruker AXS analytical instruments Pvt, ltd., Germany, Model: D2 phaser). Morphology of prepared samples is examined by scanning electron microscopy (Model JEOL-JSM-6360, Japan), operated at 18kV. The electrochemical measurements were performed in an electrolyte of Na_2SO_4 in a conventional three electrode arrangement comprising a graphite counter electrode and saturated calomel electrode (SCE) serving as the reference electrode, by using potentiostat.

4. RESULTS AND DISCUSSION

a) Structural analysis(XRD)

Fig. (1.1) displays XRD patterns of prepared powder at 140^0C with varying time from 6hrs, 8 hrs, 12hrs and 13hrs respectively. All pattern shows pure CuS phase with hexagonal crystal structure (P63/mmc). The four intense peaks observed at 29.25^0, 31.75^0, 32.82^0 and 47.88^0 with d_{hkl} along (102), (103), (006) and (110) planes correspond to CuS. The d values (interplanar spacing) of XRD were compared with standard d values taken from JCPDS card (01-074-1234) for CuS. The peak intensities in XRD patterns of prepared CuS material are showing nanocryastalline nature. The crystallite size was calculated by the X-ray line broadening method using

Material	2 θ (degree)	FWHM (degree)	Interplanar distance (d) A°	Crystalline size (D) A^0
CuS	47.9683	0.1574	1.89660	21.48895

Scherrer formula.

$$D = \frac{0.9\,\lambda}{\beta cos\theta}$$

where,

λ is the wavelength of radiation used, k is the Scherre constant (0.9), β is full width at half maximum (FWHM) intensity of the diffraction peak for which the particle size at to be calculated, θ is the diffraction angle of the concerned diffraction peak and D is the crystallite size.

Table 1.1

b) Scanning Electron Microscopy (SEM)

Surface morphology of CuS material is investigated by SEM. fig. (1.2) shows SEM for CuS at magnification X5000 [a] and X15000 [b] and 20kV potential it clearly reveals that CuS nanoparticles are uniformly and poly-dispersed (nature shows particles of varied sizes in the dispersed phase) with porous nature. This porous nature of our CuS nanoparticles gives rise to high surface area which is the beneficial criteria for electrochemical properties.

4.3 Electrochemical performance of CuS:

4.3.1 Cyclic voltammetry:

The electrochemical set up for the supercapacitive studies of CuS films consists of film electrode, a counter electrode and an aqueous electrolyte. The electrochemical analysis of the CuS films onto stainless steel substrate were carried out by recording cyclic voltammograms (CV) on the 263A EG & G, applied Research Potentiostat. The charging-discharging behavior of the electrode was studied using chronopotentiograms (CP).

The cyclic voltammetry (CV) experiments were performed using 263-A EG & G, Applied Research Potentiostat to determine the specific capacitance of the CuS electrode in 1M Na_2SO_4 electrolyte at 50mV/s, 80mV/s and 100mV/s scan rate in between potential range 0.0 to 0.4V vs SCE as shown in fig.(1.3).

We can calculate capacitance of our prepared CuS film by following formula,

$$\boldsymbol{c = \frac{\int Idv}{m\,X\,v\,X\,dv}}$$

where $\int \boldsymbol{Idv}$ is area under the curve, m is deposited mass, v is scan rate, dv = potential window.

4.3.2 Galvanostatic charge discharge:

The charge-discharge behavior of CuS electrode is studied in GCD measurements. Fig. (1.4) shows the charge-discharge curve for CuS electrode measured in 1M Na_2SO_4 solution in between potential range 0 to 0.5 V vs SCE. The specific capacitance is calculated by using formula,

$$C_{sp} = \frac{I_d \times T_d}{m \times dV}$$

Where, I_d is the discharge current, T_d is the discharge time, m is deposited mass and dv is potential window.

4.4 Contact angle:

For further potential applications contact angle is determined and the hydrophobic or hydrophilic properties of CuS films were studied. In our brief theory of supercapacitor, the hydrophobic solid surface has low surface energy and hydrophilic solid surface has high surface energy. The contact angle of the CuS electrode was tested using water as an aqueous solution shown in fig (1.6). It is found that surface of CuS substrate is hydrophilic (water lovable) in nature with water contact angle of 53.6 ± 2° resp. which is beneficial for supercapacitive performance

Contact angle of 0° means complete wetting of surface, and contact angle of 180° corresponds to non-wetting of surfaces. It is found that the surface of CuS substrates is hydrophilic with water contact angle of 53.6± 2° respectively. Low water contact angle increases the electrochemical performance, where inbetween contact at electrolyte-electrode is important [13]. It is beneficial for improvement in the supercapacitor behavior because hydrophilic substrates refers ionic diffusion process and reduces the electrolyte into electrode [3,4].

5. REFERENCES:

[1]. Ke-Jing Huang, Ji-Zong Zhang, Yun Fan, One-step solvothermal synthesis of different morphologies CuS nanosheets compared as supercapacitor electrode materials, Journal of Alloys and Compounds (2014).

[2]. Qing-Li Huanga,∗ , Hu Chenb, Yong Cai Zhangb, Chang Le Wua, CuS nanostructures prepared by a hydrothermal method, Journal of Alloys and Compounds 509 (2011) 6382–6387.

[3]. Alok Singh, R. Manivannan, S. Noyel Victoria, http://dx.doi.org/10.1016/j.arabjc.2015.03.013.

[4]. Anat Itzhak, Eti Teblum, Olga Girshevitz, Sivan Okashy, Yury Turkulets, Luba Burlaka, Gili Cohen-Taguri, Efrat Shawat Avraham, Malachi Noked, Ilan Shalish, and Gilbert Daniel Nessim, Digenite (Cu9S5): Layered p-Type Semiconductor Grown by Reactive Annealing of Copper, Chem. Mater. 2018, 30, 2379−2388.

Figures and data:

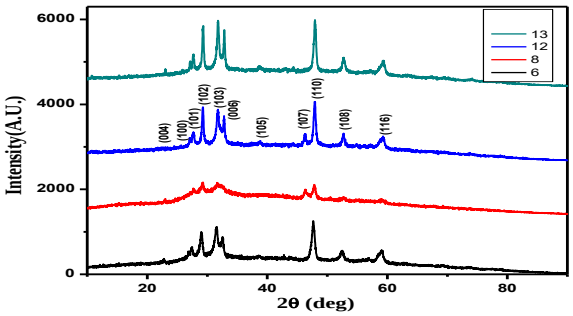

Fig.1.1. XRD Pattern of CuS prepared by hydrothermal method

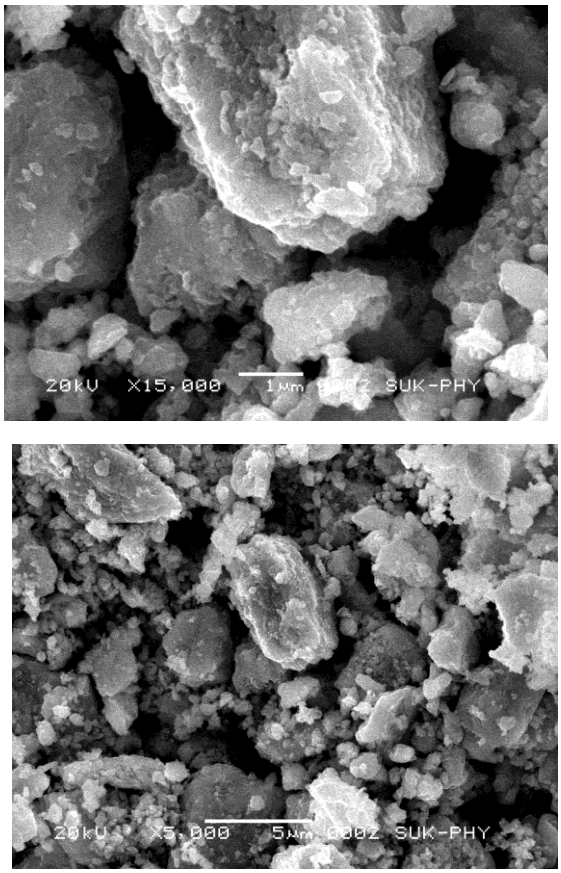

Fig 1.2. SEM images of CuS prepared by hydrothermal method at 12hrs with 140^0 C temperature

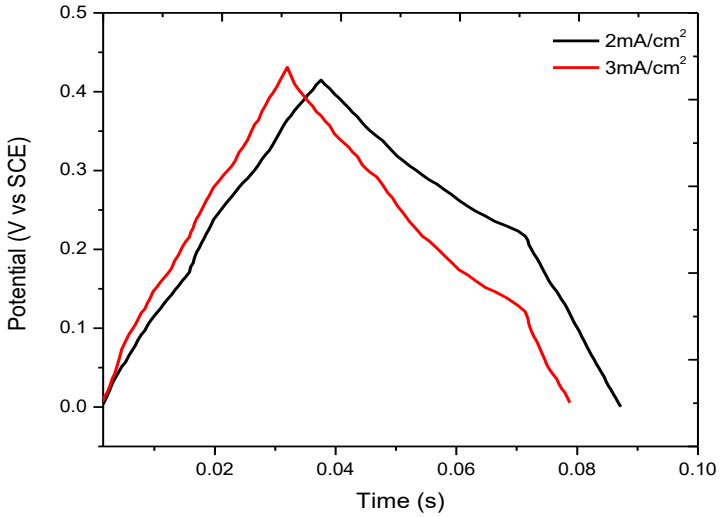

Fig 1.3. Cyclic Voltammetry curve of CuS prepared by hydrothermal method at 12hrs with 140^{0}C temperature

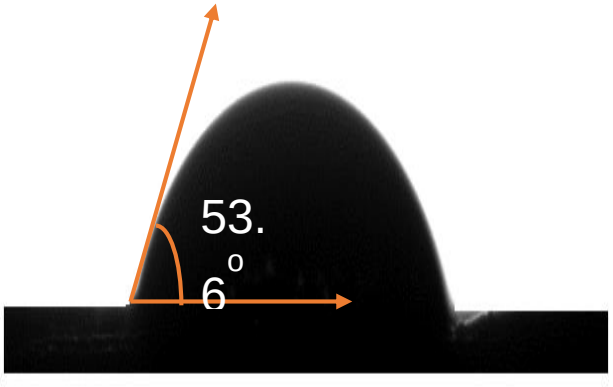

Fig 1.5 EIS of prepared CuS by hydrothermal method

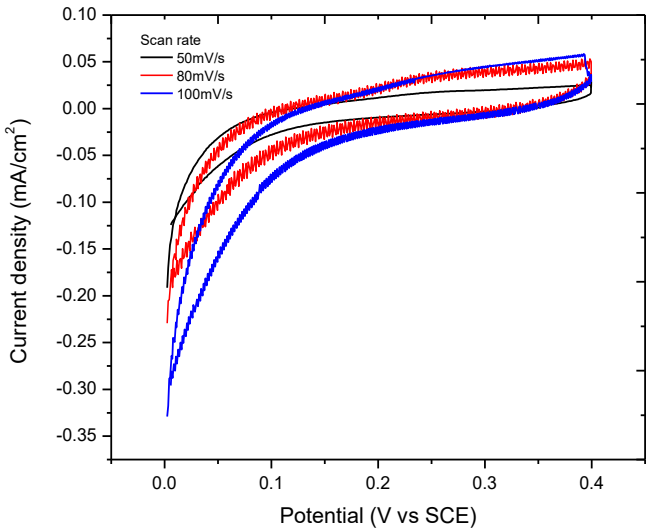

Fig 1.4. GCD curve of CuS prepared by hydrothermal method at 12hrs with 140^0 C temperature

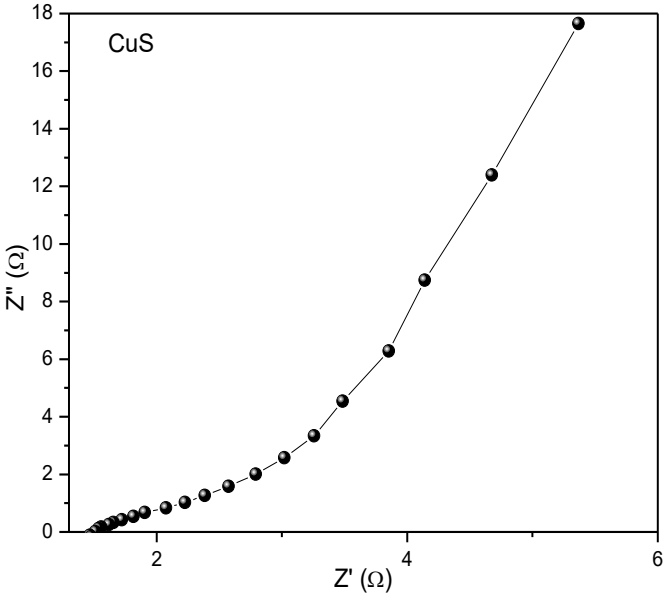

Fig 1.6 Contact angle of CuS prepared by hydrothermal method at 12hrs with temperature 140^{0}C