UGC MAJOR RESEARCH PROJECT

FINAL REPORT

(F.NO: 43-533/2014(SR) dated 09.04.2015)

Development of Surfactant Stabilized Transition Metals Doped Porous Copper Sulfide – Composite Materials for Energy Sources

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PERFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE MAJOR RESEARCH PROJECT

1.	Title of the Project	DEVELOPMENT OF SURFACTANT STABILIZED TRANSITION METALS DOPED POROUS COPPER SULFIDE – COMPOSITE MATERIALS FOR ENERGY SOURCES
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3.	Name and Address of the Institution	Department of Physics Annamalai University, Annamalainagar-608 002. Tamilnadu, India.
4.	UGC Approval Letter No. and Date	F.No. 43-533/2014 (SR) Dated: 09.04.2015
5.	Date of Implementation	01.07.2015
6.	Tenure of the project	01.07.2015 **to** 30.06.2018
7.	Total Grant Allotted	**Rs. 11,75,500.00**/-
8.	Total Grant Received	1st Installment : Rs. 8,02,500.00/- 2nd Installment : Rs. 2,91,200.00/- Total : Rs. 10,93,700.00/-
9.	Final Expenditure	**Rs. 10,93,338.00/-**

10. OBJECTIVE OF THE PROJECT

- Developing an electrical vehicle is a solution to save fossil fuel. Supercapacitor is a challenging charge storage device owing to its high power density and longer life cycle compared to batteries and it has better energy than conventional capacitors.
- Carbon materials (CNT), nano metal oxides (R_2O_2, V_2O_5) are in the use as electrode materials in EDLC and Pseudocapacitors. There is always a demand in the development of novel electrode materials for supercapacitors.
- Most of the metal sulfides are good metallic conductors and also undergo redox transitions among different states of the metal ions. Therefore, it is extremely important to develop alternate metal sulfide electrode material with a combination of low cost, larger capacitance and excellent electrochemical stability.
- Among the metal chacogenides CuS has better electrochemical properties, so it can used in lithium iron batteries and electrochemical bio sensors.
- The goal of this project is to prepare copper sulfide (CuS) that has received considerable attention owing to its wide stoichiometric composition, diverse morphology and non-linear optical properties. Only limited studies have been attempted towards pseudocapacitance application. The existence of two or more valence states of metal constituents present in the sulfides and high theoretical capacity of the sulfur compounds can provide better capacitance behavior than oxides. Hence surfactant stabilized CuS and transition metals doped (Co/Ni/Zn/Mn)-CuS were planned to synthesis.
- The synthesis technique and the reaction medium play a significant role in controlling the shape, size and phase of the products which determines their structural, optical and electrical properties. Compared with other approaches, hydrothermal method has several advantages: (1) the solvent is ethylene glycol which is non-toxic, low-cost and environmental friendly; (2) the reactant metal copper and sulfur powder are both inexpensive and easy to be prepare; (3) the process is facile and low temperature. A power conversion efficiency of hydrothermal synthesis as a potential method with the advantages of large-scale production and low-temperature synthesis. So the samples were prepared by this method at 130˚C.

- Composite materials consisting of ionic surfactant with CuS for supercapacitor have rarely reported. Hence it was aimed to synthesis and to characterize the samples various techniques have been adopted viz., XRD, XPS, SEM/EDS, FESEM, TEM and BET.
- The porous structure of the samples can provide fast ion/electron transfer leads to improved reaction kinetics and high performance.

11. WHETHER OBJECTIVES WERE ACHIEVED: YES

12. ACHIEVEMENTS FROM THE PROJECTS

As per the objective, surfactant stabilized metals doped copper sulfide nanocomposites were successfully prepared using hydrothermal technique. CTAB stabilized metals doped CuS nanocomposites were successfully prepared and used as active electrode material in the cyclic voltameter. The electrochemical behavior was examined and compared with the earlier reports. Enhanced specific capacitance values confirm the betterment of the samples. It is in the order of

CuS < Co-CuS < Ni-CuS < Zn-CuS< Mn-CuS.

The morphology (spheres, flower like, cube and branched plant like dendrite etc.) of the synthesized samples with porous nature may be the reason for larger specific capacitance. Among the samples Mn-CuS shows excellent specific capacitance. It may be best alternative electrode material in future supercapacitors.

The nanopores present in the electrode materials offer a 3D pathway for electrolyte ion diffusion and electron transport which is highly important for enhancing the electrochemical performance. The mesopores in CuS can supply immerous catalytically active sites, facilitating the oxygen diffusion and electrolyte throughout the electrode.Macroporous formed between the loosely interconnected nano compounds can provide more useful space to accommodate the discharge products to increase the specific capacity.

Obtained results were published in reputed journals with good impact factor which shows the acceptance of research community. It will defiantly replace the electrode material in supercapacitor with high energy density and cyclic stability.

Also, project fellow submitted the part of the work as Ph.D thesis.

13. SUMMARY OF THE FINDINGS

In this project work, to improve the electrochemical performance of porous copper sulfide MCuS (M = Co/Ni/Zn/Mn) have been prepared using cationic surfactant (CTAB) by adopting facile mild hydrothermal method at 130˚C. Materials, so obtained, were carefully characterized physico-chemicaly by XRD, XPS, SEM/EDS, FESEM, TEM/SAED, and BET techniques. Then the prepared nanostructures were used for electrochemical measurements, to modify the glassy carbon electrode (GCE) using a sulfide slurry coating technique. Electrochemical properties of the prepared material have been characterized by cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance tests. The complete details of the results obtained are summarized as follows.

Initially, various concentrations of CTAB templated CuS nanostructures by cost-effective and facile one step hydrothermal route for electrochemical performance were investigated. The hexagonal structures were confirmed by XRD analysis. When the synthesized samples were used as electrode materials for supercapacitor application and the electrochemical tests reveal that (0.1mM) CTAB-CuS electrode achieves the high specific capacitance than that of other samples.

Co-CuS nanostructures have been prepared using CTAB and their structural and electrochemical performances were systematically studied. The chemical composition of the synthesized (0.15mM) Co-CuS nanostructures was analyzed by XPS. The surface area calculated from BET analysis is $13.59 m^2/g$. Electrochemical studies demonstrate that the pseudocapacitive type energy storage behaviors and with specific capacitance of 586 Fg^{-1} at $5mAcm^{-2}$ for (0.15mM) Co-CuS.

Structural and electrochemical performances of porous Ni-CuS nanostructures were studied. The hexagonal structure was confirmed by powder XRD characterization. XPS analysis gives the evidence for sulfide vacancy, sulfide states of Ni-CuS compounds. The cube like (0.30mM) Ni-CuS nanostructures was investigated through SEM, FESEM, and TEM analysis. The surface area calculated from BET analysis is $19.63 m^2/g$. The specific capacitance of cube-like (0.30mM) Ni-CuS electrode is 753 Fg^{-1} at $5mAcm^{-2}$.

Porous Zn-CuS nanostructures have been prepared using CTAB and their structural and electrochemical performances were systematically studied. The flower-like (0.05mM)Zn-CuS nanostructures was investigated through SEM, FESEM, and TEM analysis The surface area calculated from BET analysis is $21.23 m^2/g$. Electrochemical studies demonstrate that the pseudocapacitive type energy storage behaviors and with specific capacitance of 826 Fg^{-1} at $5mAcm^{-2}$ for Zn-CuS.

Mn-CuS dendrites have been prepared and characterized. Electrochemical properties of Mn-CuS dendrites were successfully investigated. Powder X-Ray diffraction pattern reveals that the CuS and Mn-CuS nanomaterials were crystallized in hexagonal system. XPS studies confirm the presence of Cu, S and Mn elements in Mn-CuS compounds. The surface area calculated from BET analysis is $28.63 m^2/g$. At $5mAcm^{-2}$ current density, the specific capacitance was 1173 Fg^{-1} for dendrite-like (0.15mM) Mn-CuS.

From the present investigation, porous metals doped copper sulfide MCuS (M=Co/Ni/Zn/Mn) nanocomposites were prepared using CTAB to improve supercapactive performance. In an overview, the morphology differs with one another based on the surfactant and dopent in the same synthesis route. Among the different metal sulfide doped CuS nanostructures has shown the better performance for electrochemical properties. The enhanced specific capacitance of Mn-CuS compounds mainly due to the size, shape, and porous nature of the materials.

The specific capacitance of as-synthesized samples were in the order of

Mn-CuS > Zn-CuS > Ni-CuS > Co-CuS > CuS> Pure CuS

From the present investigation, it was observed and confirmed that the physico-chemical properties, porous nature, morphology of as-synthesized samples play an important role to act as an electrode materials for supercapacitor. Performance characteristics of all the cells were characterized using electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge techniques. All fabricated cell shows good capacitive values along with acceptable energy and power density values in present studies. The above results were published in International reputed journals with good impact factor.

Table1: Comparison of Over all Data Observed for Synthesized Best samples

Technique	**(0.1mM) CTAB-CuS**	**(0.15mM) Co-CuS**	**(0.30mM) Ni-CuS**	**(0.05mM) Zn-CuS**	**(0.15mM) Mn-CuS**
XRD	14nm	8nm	8nm	7nm	5nm
XPS	Cu, S	Co, Cu, S	Ni, Cu, S	Zn, Cu, S	Mn, Cu, S
SEM	Nano flakes	Nano flower	Nano cube	Nano flower	Nano sheets
EDX	Cu, S	Co, Cu, S	Ni, Cu, S	Zn, Cu, S	Mn, Cu, S
FE-SEM	Nano sphere	Nano flower	Nano cube	Nano flower	Nano sheets
TEM	Nano flower	Nano flower	Nano cube	Nano flower	branched plant like dendrite
BET	8.32 m^2/g 0.0281 cm^3/g 6.39 nm	13.59 m^2/g 0.0358 cm^3/g 9.75 nm	19.63m^2/g 0.062 cm^3/g 12.79 nm	21.23m^2/g 0.074 cm^3/g 13.75 nm	28.63m^2/g 0.0863 cm^3/g 21.67 nm
CV	328 F/g at 5$mAcm^{-2}$	586 F/g at 5$mAcm^{-2}$	753 F/g at 5$mAcm^{-2}$	826 F/g at 5$mAcm^{-2}$	1173 F/g at 5$mAcm^{-2}$

14. CONTRIBUTION OF THE SOCIETY

Supercapacitors (SCs) are also called electrochemical capacitors (ECs) have attracted significant attention and are considered to be one of the promising potential system among a variety of emerging energy-storage systems. Supercapacitors, a family of electrochemical capacitors has been explored as one of the most ideal candidates for the next generation of prevailing high performance energy-storage devices and technologies due to its great advantages of short charging/discharging time, high power density, superior cycle life and relatively low cost compared to other energy storage devices, which are mostly applied in power source application such as hybrid electric vehicles, aircraft, and electronic devices. Supercapacitors have a number of benefits such as high power density, good pulse charge/discharge process and long life span, compared to batteries.

Copper sulfide (CuS) is an important transition-metal chalcogenide p-type semiconducting material and also Cu and S are less toxic, inexpensive and relatively abundant material with widespread applications. The covellite CuS is one of the most intensively studied copper sulfides due to its unique physical and chemical properties and its great potential applications in many fields. Transition metals doped with copper sulfides have been synthesized and employed as active electrode material for excellent electrochemical supercapacitors, which is higher than that of pure CuS. Hence to improve the specific capacitance it is worth to carry out the research on surfactant templated transition metals (Co/Ni/Zn/Mn) doped with copper sulfide.

In this project work the prepared CuS and used transition metals are low cost as well as non toxic and environment friendly. Surfactant templated metals (Co/Ni/Zn/Mn) doped copper sulfide nanocomposites were prepared and used as electrode material. Among these metals, Mn doped CuS electrode found to have very high specific capacitance value may be due to the morphology is in nanosheets like also are interconnected by a network to form dendrite structure may influence the charge-discharge process in a very good way.

The synthesized metals doped CuS dendrites, nano flowers, nano cubes with porous structure, hence large surface area will create fast diffusion paths for ions, which will obviously enhance ion transmission and electrode utilization rate. The weight fraction of supercapacitive M-CuS is high because the nano sheet is thin and light, so high energy and power densities will achieve because of high specific capacitance. The porous nanosheets, nano flowers and nano cubes ordered pore passages and high conductivity are mainly responsible for the much improved supercapacitive performance of the MCuS indicating these materials are promising materials for SCs than that of pure CuS and other metal sulfides also can be replaced by these materials to get better energy density. The synthesis strategy of electrode materials reported in this study can be used for other metal sulfides that will be very promising for various electrochemical devices such as batteries and sensors.

15. WHETHER ANY PH.D. ENROLLED/ PRODUCED OUT OF THE PROJECT

Produced : YES

Candidate Name : Surekha Podili

16. LIST OF PUBLICATIONS

1. **D. Geetha,** P. S. Ramesh, **(2017)**. "Highly stable low cost anode interfacial material preparation and characterization via hydrothermal route for organic solar cell". *Materials Today: Proceedings* 4, 4319–4328.

2. Surekha Podili, **D. Geetha,** P. S. Ramesh, **(2017)**. "Preparation and Characterization of Porous hollow Sphere of Ni doped CuS nanostructures for electrochemical supercapacitor electrode material". *Springer Proceedings Phys*., Vol. 189, 277-288.

3. Surekha Podili, **D. Geetha,** P. S. Ramesh, **(2017)**. "One-Pot Synthesis of CTAB stabilized mesoporous Cobalt doped CuS nano flower with enhanced Pseudocapacitive behavior". *J Mater Sci: Mater Electron. 28:15387–15397.*

4. Surekha Podili, **D. Geetha,** P. S. Ramesh, **(2018)**. "A report on CTAB stabilized CuS nanostructures with enhanced structural, morphological and electrochemical properties". *International journal for research in Applied science and Engineering technology*, 6(2), 2313-2319.

5. Surekha Podili, **D. Geetha,** P.S. Ramesh, **(2018)**. "Electrochemical Studies on Ni doped CuS Nanostructures with Cationic Surfactant Synthesized through a Hydrothermal Route". *J Mater Sci: Mater Electron*, 29:11167-11177.