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Synthesis of Graphene Oxide Coating on $ZnCo_2S_4$ Using Hydrothermal Method for Electrochemical Capacitors Applications

S. Deepalakshmi[1,2], M.S. Revathy[1*], J. Richards Joshua[3], L. Saravanan[4], S. Thanikaikarasan[4+], R. Jansi[1], M.A. Majeed Khan[5] and O. Savadogo[6]

[1] Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil-626126, Tamil Nadu, India.
[2] Department of Computer Science, Rajapalayam Rajus College, Rajapalayam - 626 117, Tamil Nadu, India.
[3]Department of Physics, P.G and Research Department of Physics, Chikkaiah Naicker College, Erode - 638 004, Tamil Nadu, India
[4]Department of Physics, Saveetha School of Engineering,Saveetha Institute of Medical and Technical Sciences, Chennai – 602 105, Tamil Nadu, India.
[5]College of Science, King Saud University, Riyadh, 11451, Saudi Arabia.
[6]Laboratory of New Materials for Electrochemistry and Energy, UNESCO Chair for Sustainable Engineering-Solar Cell Technology, Polytechnique Montréal, Canada.

Corresponding Author: [+]s_thanikai@rediffmail.com;[*]revz27vijay@gmail.com

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ABSTRACT

Due to the manufacturing and utilization of innovative electric devices which need energy storage systems using edge-cutting technologies as electrochemical capacitors in many areas including mobility, there is an increased demand for research and development on new materials for energy storage devices. In this research, a bimetallic sulfide as $ZnCo_2S_4$ with graphene oxide was identified and developed as electrode material for an electrochemical capacitor. Synthesis of $ZnCo_2S_4$ and $ZnCo_2S_4$@GO(1%) was elaborated by hydrothermal method. Characterization of materials was achieved using X-ray diffraction, Field Emission Scanning Electron Microscopy, Cyclic Voltammetry, and galvanostatic charge-discharge analysis. From the result, it is observed that the specific capacitance of $ZnCo_2S_4$@GO(1%) is 1060 Fg^{-1} at the current density of 1 Ag^{-1} was greater compared with $ZnCo_2S_4$. $ZnCo_2S_4$@GO(1%) has a power density of 8500 W Kg^{-1} with an energy density of 43 Wh Kg^{-1}. Due to the addition of GO the electrochemical performance was improved on $ZnCo_2S_4$. From the excellent result, it is observed that $ZnCo_2S_4$@GO(1%) is the right choice for the fabrication of energy storage devices.

NOMENCLATURE

Symbols

V	Voltage
J	Current density, Ag-1,
Cg	Specific Capacitance, Fg-1
T	Time, S
˚C	Degree Celcius
Nm	Nano Meter
Ag-1	Ampere per Gram
Fg-1	Farad per Gram
S	Second

Abbreviations

$Zn(NO_3)_2{\cdot}6H_2O$	Zinc Nitrate
$Co(NO_3)_2{\cdot}6H_2O$	Cobalt Nitrate
$ZnCo_2S_4$(ZCS)	Zinc Cobalt Sulfide
ZnCo2S4@GO(ZCS@GO)	Zinc Cobalt Sulfide with Graphene Oxide
GO	Graphene Oxide
XRD	X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
CV	Cyclic Voltammetry
GCD	Galvanostatic Charge-Discharge
JCPDS	Joint Committee on Powder Diffraction Standards
AgCl	Silver Chloride

1. INTRODUCTION

In this world, most people use a lot of devices with energy storage devices which increases the flexibility of the product usage. Resource utilization, compatibility, flexibility, and being environmentally friendly are the main purpose of a lot of manufacturing companies. Manycompanies introduce innovative devices with long time storage forhome appliances and medical purposes. So they require long time usage with large energy storage. In recent decades, energy storage is the challenging because of demand in various applications such as smartphones, wearable devices, medical appliances, home appliances, etc.[1] The usage of these products grows day to day by consumers around the world. While concentrating on

the next version of devices, the enhancement of energy storage device performance will be concentrated. A recent study of many articles highlighted the enhancement of the capacity of energy storage in materials. As already know, batteries have large storage capacity and long life compared with other energy storage devices as shown in Table 1. However, supercapacitors have a short duration of life for energy storage but have high performance for small device applications. Energy storage devices such as supercapacitors, capacitors, batteries, etc. should be improved by choosing novel materials for the fabrication of devices shown in Table 1 [2] Metal oxides and Metal sulfides[3] are good choices for energy storage devices. Nowadays researchers have their choice of graphene oxide for enhancing the electrochemical performance of the metal oxides or metal sulfides[4]. By adding graphene oxide with metal oxide/metal sulfides, the morphology nature of the material does not change instead it enhances the performance of the material. Choosing the right dopant is also challenging for the perfect material. Metal oxides are utilized by many researchers. The same performance can be achieved while referring to many articles in the journal. From the reference, the following experimental preparation has been done for analyzing the electrochemical performance of the sample material [2,5,6].

Table 1 Comparision of Various Energy Storage Devices

Parameter	Capacitors	Supercapacitors	Batteries
Energy Storage	Watt –Sec	Watt –Sec	Watt-Hour
Energy Density	0.01-0.05 $WhKg^{-1}$	1-5 $WhKg^{-1}$	8-600 $WhKg^{-1}$
Power Density	High,>5000 WKg^{-1}	High, >4000WKg^{-1}	Low, 100-3000WKg^{-1}
Lifetime	>100K cycles	>100K cycles	150-1500 Cycles
Power Delivered	Rapid Discharge Linear/Exponential Voltage Decay	Rapid Discharge Linear/Exponential Voltage Decay	Constant Voltage over long time period
Charge/Discharge Time	Pico Seconds to Milli Seconds	Milli Seconds to Seconds	1-10 Hours
Charge Method	Voltage across Terminals	Voltage across Terminals	Current & Voltage
Form Factor	Small to Large	Small	Large
Weight	1 Grams-10 Kilograms	1-2 Grams	1 Grams to >10 Kilograms
Operating Voltalge	6V-800V	2.3V-2.7V/Cell	1.2V-4.2V/Cell
Operating Temparature	-20 to +100˚C	-40 to +85˚C	-20 to +65˚C

2. EXPERIMENTAL METHODS FOR THE SAMPLE PREPARATION AND CHARACTERIZATION

2.1 Hydrothermal method for preparation of $ZnCo_2S_4$

The chemical has been bought from inside Tamilnadu without purity. During synthesis, a solution with a transparent pink color was obtained by stirringa well of 99% Sigma Aldrich 10 mL of glycerol(Merk, 99%), 50 mL of isopropanol, 0.08 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 0.15 g of $Co(NO_3)_2{\cdot}6H_2O$. After the added Thioures as a sulfide source was liquified well with the above solution and maintained at a temperature of 160 °C for a period of 18 hours in the Teflon-lined autoclave. The resultant solid substance was purified with ethanol and water until reached room temperature and then evaporated to 80 °C in a vacuum oven. Finally, ZCS ($ZnCo_2S_4$) was obtained.

2.2 Hydrothermal method for preparation of $ZnCo_2S_4$@GO

The above procedure was followed for GO coating on $ZnCo_2S_4$ by adding 0.2g of $ZnCo_2S_4$ and GO 1% in 50 ml of the liquified solution for the time of 2 hrs. A temperature of 140 °C for 12 hrs was maintained at the Teflon-lined autoclave. The previous procedure was followed for evaporating the solution. The resultant sample was ZCS@GO(1%). The experimental procedure is shown in Figure 1.

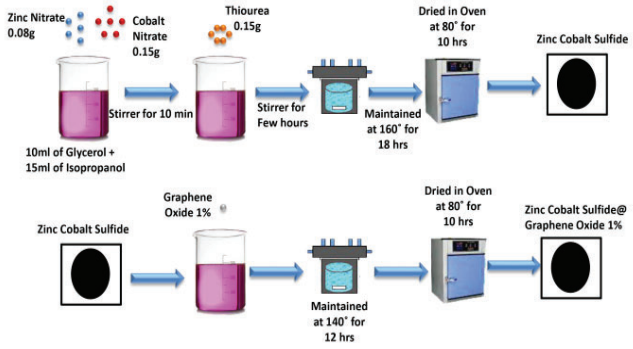


Figure 1: Experimental Procedure for preparation of $ZnCO_2S_4$ and $ZnCO_2S_4$@GO 1% using Hydrothermal Method

2.3 Chararterisation of the Samples Using XRD , FESEM, CV, and GCD Methods

2.3.1. XRD(X-ray Diffraction) characterisation method

The XRD patterns of the samples were obtained using Rigaku powder diffractometer. The wavelength of the Cu K radiation utilised in the experiment was 0.154 nm, and the range of the angle 2 theta was 10 degrees to 80 degrees, in 0.2 degree increments.

2.3.2. FESEM(Field emission scanning electron microscopy) charaterisation method

The morphology information of the sample was analyzed using SEM-EDS (ZEISS-EVO/18, Germany) to get FE-SEM and EDX pictures.

2.3.3. CV(Cyclic Voltammetry), and GCD (Galvanostatic charge/discharge) charaterisation methods

The electrochemical analysis was performed using Bio-logic 350 (France). The CV analysis was performed at the voltage range of about 0 – 0.6 V . The galvanostat charge/discharge analysis was performed at the voltage range 0- 0.5V at different current densities(1 – 20 Ag^{-1}).

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

XRD was investigated to analyze the crystallographic structure of the sample. Figure 2 shows the XRD investigation of the prepared material. The peaks of $ZnCo_2S_4$ and

$ZnCo_2S_4$@GO(1%) are same aslocated at 15.9°, 26.22°, 30.83°, 37.86°, 46.19°, 49.12°, 53.87°, 63.86°, 67.34°, 69.69°, 73.56, 75.92° that corresponds to the miller indices (040), (044), (111), (131), (151), (202), (246), (422), (444), (533), (701), (731) planes. From XRD patterns were taken and referred with JCPDS (47-1656) data which confirms that there are purity peaks were observed and proves that the nature of the sample was pure crystalline. The outer surface of $ZnCo_2S_4$ contains the coating of graphene oxide which proves that the sample has good electrochemical performance with enhancement of electron transport.

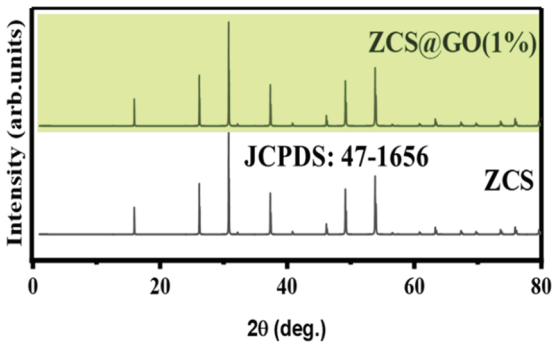
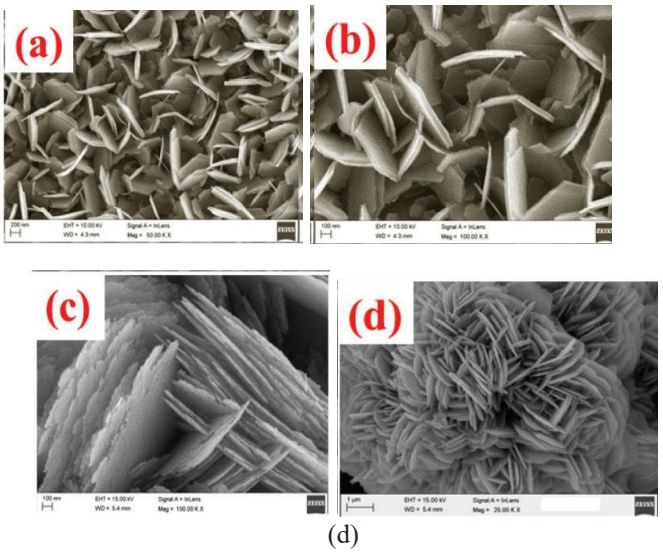


Figure 2: X-Ray Diffraction Analysis of ZCSand ZCS@GO(1%)

3.2. FESEM Analysis

The Microstructure Analysis of $ZnCo_2S_4$ and Graphene Oxide with coated $ZnCo_2S_4$ was shown in the Figure 3(a),(b),(c) and (d). Figure 3(a) & (b) shows the FESEM results of $ZnCo_2S_4$. It shows that there are flakes-like petals randomly appearing all over the sample. The Petal diameter is about 50-60 nm. Figure 3(c) and (d) describes the FESEM results of $ZnCo_2S_4$@GO(1%). Due to the addition of 1% of Graphene Oxide, flower-like flakes appeared and Graphene oxide distributes as a thin layer on the outer surface of $ZnCo_2S_4$. While comparing with $ZnCo_2S_4$ and $ZnCo_2S_4$ @GO(1%), the diameter and morphological structure were changed from flakes-like petals to flower-like flakes because of the increasing ratio of GO coating. The thickness of $ZnCo_2S_4$@GO(1%) is 2-4 nm.



(d)

Figure 3. FESEM Analysis, **(a) & (b)** $ZnCo_2S_4$ **(c) & (d)** $ZnCo_2S_4$@GO(1%)

3.3. Cyclic Voltammetry

The electrochemical efficiency analysis was studied by using a three-electrode setup. The prepared electrode materials were $ZnCo_2S_4$ and $ZnCo_2S_4$@GO(1%). A 3.0M KOH was used as electrolyte for the CV analyses. The CV curves of both $ZnCo_2S_4$ and $ZnCo_2S_4$@GO(1%) were taken with a scan rate of 1 mV sec^{-1} and are given in Figure 4(a) and (b).

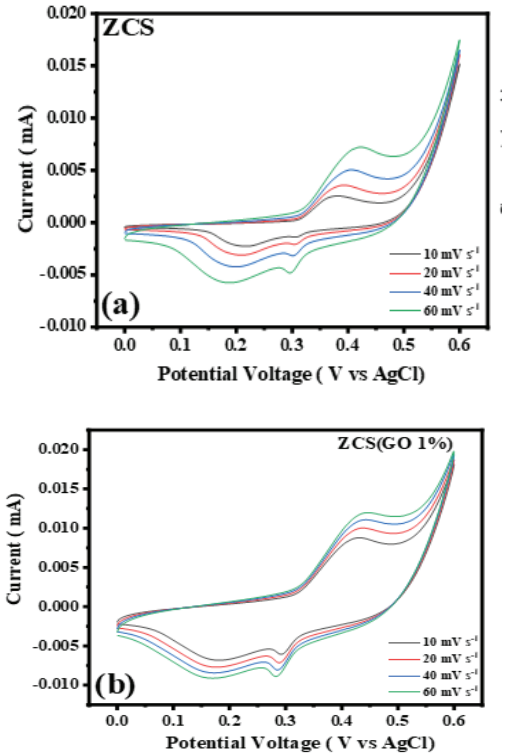


Figure 4. Cyclic Voltammetry Curves (a) $ZnCo_2S_4$(ZCS) (b) $ZnCo_2S_4$@GO(1%)(ZCS@GO(1%))

The rising and falling appearance of outstanding redox current peaks in the identical location. The properties of faradic reaction sharpening and pseudo-capacitance may be deducted from the appearance of the curves that are analyzed using prepared electrode materials. The electrochemical performance analysis shows that the curve of $ZnCo_2S_4$@GO(1%) was a higher region than that of the curve of $ZnCo_2S_4$. It was observed that the electrochemical performance of $ZnCo_2S_4$@GO(1%) was higher than $ZnCo_2S_4$.

3.4.Galvanostatic Charge-Discharge

The Galvanostatic charge-discharge patterns with various current densities are given in Figure 5(a-b). The electrode material $ZnCo_2S_4$@GO(1%) has taken a short discharge time, showing that the current density is significantly greater than that of $ZnCo_2S_4$. From this, it is observed that $ZnCo_2S_4$@GO(1%) in the electrode involves less time in the redox reaction. Due to the shorter time for redox reaction the transport of electrons having velocity is significantly faster than the electrochemical reaction rate. 1060 Fg^{-1} is the specific capacitance of $ZnCo_2S_4$@GO(1%) at the current density of 1 A g^{-1}. . As a result, the $ZnCo_2S_4$@GO(1%) electrode material has a specific capacitance (Cg) of 1060 Fg^{-1} at a current density of 1 A g^{-1} with a power density of 8500 W Kg^{-1} at the energy density 43 Wh Kg^{-1}.

A $ZnCo_2S_4$-based electrode exhibited specific capacitance 989 Fg^{-1} at a current density of 1 A g^{-1}. Since it is lower compared to the specific capacitance of $ZnCo_2S_4$ @GO(1%), the power density and energy density were calculated only for $ZnCo_2S_4$@GO(1%). Due to the low value of the specific capacitance of the $ZnCo_2S_4$-based electrode in comparison to that of $ZnCo_2S_4$@GO(1%), it is expected that the power density and the energy density of the $ZnCo_2S_4$-based electrode are lower than those of the $ZnCo_2S_4$@GO(1%) electrode. This is supported by the surface area of the curves voltage vs time at the current density of 1 A g^{-1} A of Figure 5(a) and Figure 5(b) . For a current density of 1 $A.g^{-1}$, the surface area of the curve voltage vs time is lower for $ZnCo_2S_4$-based electrode(Fig.5(a)) than that of $ZnCo_2S_4$@GO(1%), based electrode (Fig.5(b)).

Effectively, the comparison of the graph of Figure5(a) and Figure 5(b) indicates that performance of the ZnCo2S4@GO(1%) electrode has improved at higher current densities. During the exchange between electrons and ions at the electrode/electrolyte interface, the efficiency of the electron transfer is higher in the case of the ZnCo2S4@GO(1%) electrode than that of the ZnCo2S4 electrode. This can be attributed to the presence of more electrochemically active sites on the ZnCo2S4@GO(1%) electrode due to the graphene oxide coating.

Then, as expected, the specific capacitance of the $ZnCo_2S_4$(ZCS) electrode is lower than that of the $ZnCo_2S_4$@GO(1%) electrodes which has higher specific capacitance compared to that of $ZnCo_2S_4$.

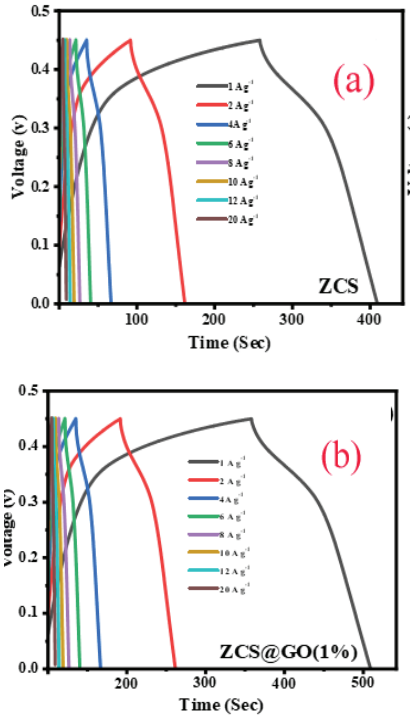


Figure 5. Galvanostatic Charge-Discharge for various current densities: (a) $ZnCo_2S_4$ (ZCS) (b) $ZnCo_2S_{4@}$GO(1%)(ZCS@GO(1%))

4. CONCLUSIONS

Thus the $ZnCo_2S_4$ and $ZnCo_2S_4$@GO(1%) materials were synthesized using the hydrothermal method. The materials characterization methods such as XRD, FESEM, CV, and GCD were used to analyze both electrode materials. From the analysis of XRD, the morphological structure does not change while adding GO in $ZnCo_2S_4$ and it is matched with JCPDS (47-1656). From the analysis of FESEM, it is observed that flower-like flakes appeared due to the addition of GO in $ZnCo_2S_4$. From the analysis of CV, it is observed that pseudo capacitance and faradic reaction were deducted and $ZnCo_2S_4$@GO(1%) has a higher region compared to $ZnCo_2S_4$.which shows excellent electron transfer and electrochemical performance. From the analysis of GCD, $ZnCo_2S_4$@GO(1%) has a current density that is significantly greater than $ZnCo_2S_4$. As a result, it is concluded that $ZnCo_2S_4$@GO(1%) electrode material has greater specific capacitance (Cg) 1060 Fg^{-1} at a current density of 1 A g^{-1} with a power density of 8500 W Kg^{-1} at the energy density 43 Wh Kg^{-1} whereas the $ZnCo_2S_4$(ZCS) based electrode exhibited a specific capacitance (Cg) of 989 $A.^{g-1}$ at a current density of 1 A g^{-1} with a power density. And the enrgy density so it is recommended for the fabrication of Asymmetric supercapacitor as energy storage devices.

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