



# Article Facile Synthesis of Coral Reef-Like ZnO/CoS<sub>2</sub> Nanostructure on Nickel Foam as an Advanced Electrode Material for High-Performance Supercapacitors

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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Abstract:** Nanocomposite electrodes receive much attention because of their excellent energy storage nature. Electrodes for supercapacitors have come a major source of interest. In this pursuit, the current work elucidates binder-free coral reefs resembling ZnO/CoS<sub>2</sub> nanoarchitectures synthesized on the surface of Ni foams employing the cost-effective hydrothermal route. The Zno/CoS<sub>2</sub> nanocomposite demonstrated excellent battery-type behavior, which can be employed for supercapcitor application. Various analyses were carried out in the current study, such as X-ray diffraction and high-resolution scanning electron microscopy, which allowed defining the crystalline nature and morphology of surface with ZnO/CoS<sub>2</sub> nanoarchitectures. Electrochemical measures such as cyclic voltammetry, galvanostatic charge discharge, and potentiostatic impedance spectroscopy confirmed the battery-type behavior of the material. The synthesized precursors of binder-free ZnO/CoS<sub>2</sub> nanostructures depicted an excellent specific capacity of 400.25 C·g<sup>-1</sup> at 1 A·g<sup>-1</sup>, with a predominant cycling capacity of 88. 2% and retention holding of 68% at 10 A·g<sup>-1</sup> and 2 A·g<sup>-1</sup>, even after 4000 cycles, representing an improvement compared to the pristine ZnO and CoS<sub>2</sub> electroactive materials. Therefore, the electrochemical and morphological analyses suggest the excellent behavior of the ZnO/CoS<sub>2</sub> nanoarchitectures.

**Keywords:**  $ZnO/CoS_2/NF$  nanostructures; supercapacitors; cyclic voltammetry; galvanostatic charge–discharge; electrochemical impedance spectroscopy

# Highlights:

✤ Coral reefs like nanostructure ZnO/CoS<sub>2</sub>/NF was synthesized using a hydrothermal technique.

 $rac{1}{2}$  ZnO/CoS<sub>2</sub>/NF nanocomposite displayed an excellent electrochemical performance than bare ZnO/NF and CoS<sub>2</sub>/NF.

♦ Prepared composite electrode exhibits a high specific capacity of 400.25 C g<sup>-1</sup> at 1 A g<sup>-1</sup>. ♦ ZnO/CoS<sub>2</sub>/NF nanocomposite shows a superior rate capability and cycling stability than ZnO/NF and CoS<sub>2</sub>/NF.

# 1. Introduction

Energy storage devices such as batteries and supercapacitors are considered the major sources to store electrochemical energy for sustainable energy due to their efficiency and flexibility [1–4]. Li-ion batteries are emerging sources of energy storage devices, for rechargeable, durable, and greater voltage applications. In this context, supercapacitors are also considered major sources of energy due to their high power density, cost-effectiveness,

and longer life span [5,6]. At the time of charging, electrons are accumulated at the electrode by reversible electrochemical reactions, responsible for electron flow in the circuit. Hence, it is quite essential to fabricate an optimal electrode custom-made structure with outstanding reactivity [7].

SCs can be classified as follows on the basis of the storage process: pseudocapacitors (faradaic charge transfer) and electrochemical double-layer capacitors (EDLCs) (nonfaradaic charge transfer, e.g., graphene, CNTS, and AC) [8–12]. Carbon-derived materials generally suffer from drawbacks such as long ion diffusion length, unregulated pore shape, and dimensions limiting the accumulation of charge in the EDLC, leading to lower storage values. In contrast, they have enhanced potential windows and higher stability during electrochemical calibrations. On the other hand, pseudocapacitors have been widely investigated and reported to store enhanced energy because of continuous reversible redox reactions in the electrodes.

Until now, there have been various diverse electrode materials fabricated on the basis of their promising features, which can be summarized as metals (Cu), metal oxides (NiO, ZnO, MnO<sub>2</sub>, etc.), carbon-derived compounds (single-walled/multiwalled carbon nanotubes, activated carbon, carbon black, bioderived carbon), metal hydroxides (Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, etc.), and various polymeric materials (conducting polymers, MXenes, etc.) [13–15].

Among these materials, various electrodes demonstrate battery-type behavior, such as  $Co_3O_4$ , CoS,  $ZnCo_2O_4$ , and CuS, demonstrating enhanced storage behavior when compared to pseudocapacitor materials such as  $MnO_2$  and  $RuO_2$  because of their structural features, i.e., elemental valences, structural nature, good conductivities, greater capacities, and swift redox cycles.

Very recently, potential and feasible nanocomposites and ternary metal oxides/sulfides  $(ZnCo_2O_4, CoMoO_4, CoO@CoS/Ni_3S_4, CuCo_2O_4, etc.)$  were found to have greater energy storage with excellent energy storage behavior when compared to metal oxides and sulfides [16]. These fabricated nanocomposites have predominant features such as numerous oxidation and reduction states, wide potential windows, enhanced conductivity, and ability to perform prominent redox reactions at the time of electrochemical reactions.

Today, cobalt sulfide (CoS<sub>2</sub>) attracts great attention due to its thermal stability and electrochemical conductivity, which allow prominent capacitance and greater cycling stability in SCs [17]. Jinmi Tian et al. [17] fabricated an NiFe-LDH@CoS<sub>2</sub>@Ni electrode and achieved an exceptional specific capacitance of 11.28 F·cm<sup>-2</sup> at 2 mA·cm<sup>-2</sup> in a three-electrode setup.

Yihing et al. generated an CoO@Ni-Co-S electrode by employing the facile hydrothermal phenomenon, and the electrode demonstrated 2507  $\text{F} \cdot \text{g}^{-1}$  at  $1 \text{ A} \cdot \text{g}^{-1}$  of specific capacity [18]. Chandu et al. [19] fabricated hierarchical flower-like nanocomposites of NiMoO<sub>4</sub>– CoMoO<sub>4</sub> nanosheet arrays using the facile one-step chemical bath deposition method, showing an excellent specific capacity of 236.86 m·A·h·g<sup>-1</sup> at 2 A·g<sup>-1</sup> [19].

Moreover, to benefit from the desirable thermal stability and electrochemical conductivities of  $CoS_2$  and the excellent capacity of ZnO, researchers have turned to promising composite materials for SCs [20]. There are some drawbacks of ZnO such as poor electronic conductivity and inadequate active sites, which reduce the electrode capacity; this can also be addressed by combining ZnO with  $CoS_2$ .

Following the above discussion, in the current work, we fabricated coral reef-like  $ZnO/CoS_2$  binder-free nanostructures demonstrating excellent battery-type behavior as electroactive materials for SCs. The  $ZnO/CoS_2$  electrode led to enhanced electrical conductivity, an increased number of active sites with an electrochemical response, and a significant increase in cycling performance and specific capacity. The as-synthesized  $ZnO/CoS_2$  nanostructure displayed an excellent specific capacity of 400.25 C·g<sup>-1</sup> at 1 A·g<sup>-1</sup>, with exceptional cycling stability.

### 2. Experimental Section

# 2.1. Synthesis of ZnO and ZnO/CoS<sub>2</sub> on Nickel Foam

Current collector design in the supercapacitor plays a major role in yielding enhanced performance. Recently, various substrates of commercial grade have been employed in SCs, such as nickel foam, carbon cloth, stainless steel, copper sheet, and PET. Among them, nickel foams have potential benefits such as greater conductivity, 3D structure durability, flexibility, light weight, and an excellent charge carrier nature for greater energy storage [21]. Prior to the synthesis of ZnO/CoS<sub>2</sub>, 1 cm<sup>2</sup> nickel foam was ultrasonicated with 2 M HCl, acetone, and ethanol, before being washed with double-deionized water and dried. ZnO NRs were made using a two-step chemical bath deposition method. The ZnO seed layer was layered on Ni-foam as described in our latest article [22].

Then, the scattered Ni-foam substrates were perpendicularly submerged into a 0.015 M zinc nitrate hexahydrate and hexamethylenetetramine solution, which was maintained at 95 °C for 15 h to produce the ZnO NRs. After cooling to room temperature, the ZnO NR-covered Ni-foam was prepared and dried at 70 °C overnight in a vacuum oven. To prepare ZnO/CoS<sub>2</sub>/NF, 0.1 M CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.8 M thiourea were dissolved in 40 mL of ethylene glycol, before adding 0.2 M 3-MPA and stirring for 60 min to obtain a standardized solution. The homogenous mixture was moved to a Teflon-lined autoclave, and then the arranged ZnO NRs/NF was steeply submerged, which was maintained 150 °C for 10 h. Subsequently, the ZnO/CoS<sub>2</sub>/NF was rigorously sanitized with ethanol and double-deionized water before drying at 70 °C for 12 h. The mass loading of the active electrodes was  $4 \pm 1.5$  and  $6 \pm 1.5$  mg·cm<sup>-2</sup> for ZnO and ZnO/CoS<sub>2</sub>/NF. The surface morphology and phase structures were studied using high-resolution scanning electron microscopy (HR-SEM, S-2400, and Hitachi) and X-ray diffraction (XRD, D/Max-2400 Rigaku) analysis.

#### 2.2. Electrochemical Measurements

A three-electrode setup (Pt wire as the counter electrode, Ag/Cl as the reference electrode, and the above-synthesized material as the working electrode) was designed using the electrochemical Biologic SP- 150 workstation. The electrolyte employed was a 3 M KOH homogeneous solution. Cyclic voltammetry measurements were performed at various scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV·s<sup>-1</sup>) in a potential range between -0.5 and 0.6 V. Equation (1) from galvanostatic charge–discharge analysis was used to calibrate the specific capacity of the synthesized nanocomposite, where  $C_S$  is the specific capacity in C·g<sup>-1</sup>, *I* denotes the discharge current in A,  $\Delta t$  is the discharge time difference in s, and *m* denotes the mass of the electroactive material in g.

$$C_S = \frac{I \times \Delta t}{m}.$$
 (1)

#### 3. Results and Discussion

The crystallinity of the composite was determined using XRD analysis. The XRD spectrum of the synthesized composite of ZnO/CoS<sub>2</sub>/NF (Figure 1) exhibited strong Bragg peaks (44.9°, 52.2°, and 76.8°) due to the NF substrate, whereas the peaks located at  $2\theta \approx 31.8^{\circ}$ ,  $34.5^{\circ}$ ,  $47.6^{\circ}$ ,  $63.0^{\circ}$ , and  $68.1^{\circ}$  could be indexed to the lattice fringes of (1 0 0), (0 0 2), (1 0 2), (1 0 3), and (1 1 2) plateaus of ZnO (ICSD No: 75-0576). The peaks located at  $2\theta \approx 46.47^{\circ}$ ,  $49.46^{\circ}$ ,  $62.91^{\circ}$ , and  $77.17^{\circ}$  Bragg angles corresponded to the lattice fringes of (2 2 0), (2 2 1), (3 2 1), and (4 2 0) planes (ICSD No: 043715). The ZnO/CoS<sub>2</sub>/NF nanostructures showed all the major diffraction peaks exhibited by ZnO and CoS<sub>2</sub>, representing that the nanocomposite had a pristine crystal-like structure.



Figure 1. XRD pattern of ZnO/CoS<sub>2</sub>/NF nanocomposite.

Morphological analysis was carried out using HR-SEM of the prepared ZnO and  $ZnO/CoS_2/NF$  nanocomposite. HR-SEM (Figure 2a–c) images of ZnO/NF showed a nanorod (NR)-like assembly with few void spaces. The HR-SEM image of the ZnO/CoS<sub>2</sub>/NF composite is shown in Figure 2e, presenting a coral reef-like nanostructure with a great number of redox-active sites, which would facilitate the conductivity of the material. The coral reef-like nanostructure was dispersed consistently across the NF substrate, delivering a great superficial area that was accessible to the KOH electrolyte solution with a healthy transfer resistance associated with ZnO NRs.



Figure 2. Low- and high magnification HR-SEM images of the ZnO/NF (a-c) and ZnO/CoS<sub>2</sub>/NF nanocomposite (d-f).

The pseudocapacitor feasibility study was aimed at interpreting the synthesized precursors by evaluating the electrochemical behavior in terms of CV, GCD, and EIS, using the three-electrode setup with a 3 M KOH homogeneous electrolyte solution. Figure 3a depicts the ZnO/NF,  $COS_2/NF$ , and ZnO/ $COS_2/NF$  CV plots within the broad potential window of 0.6 to -0.5 V at a scan rate of 30 mV·s<sup>-1</sup>. The redox peaks and the wide integral area suggest that the active species exhibit a predominant charge storage phenomenon and a battery-type nature.



**Figure 3.** (a) CV curves of the ZnO, CoS<sub>2</sub>, and ZnO/CoS<sub>2</sub>/NF nanocomposite in 3 M KOH at a scan rate of 30 mV·s<sup>-1</sup>. CV curves of (b) ZnO, (c) CoS<sub>2</sub>, and (d) ZnO/CoS<sub>2</sub>/NF nanocomposites at various scan rates (20, 40, 60, 80, and 100 mV·s<sup>-1</sup>).

The ZnO/CoS<sub>2</sub>/NF nanocomposite was found to possess a predominant integral area with reduction and oxidation potential in both positive and negative regions, depicting the enhanced and prominent charge storage phenomenon. The excellent electrical behavior of the ZnO/CoS<sub>2</sub>/NF nanocomposite can be validated by the ZnO and CoS<sub>2</sub> materials which represent enhanced redox-active species for swift electrochemical reactions [20]. Figure 3b–d show that the CV curves of all three samples varied with scan rate in the range 20–100 mV·s<sup>-1</sup>. As the scan rates increased from 20–100 mV s<sup>-1</sup>, the shifting was offset by the escalated peak current densities, suggesting reversible conditions and an excellent behavior compared to synthesized precursors [21–24].

Simultaneously, the CV shape with respect to reduction and oxidation potentials revealed enhanced current densities, indicating the excellent energy storage behavior of as-synthesized  $ZnO/CoS_2/NF$  nanocomposite. Figure 4a depicts an increase in the spread of redox peaks for both positive and negative potentials as the scan rate increased from 20 to  $100 \text{ mV} \cdot \text{s}^{-1}$ , illustrating a greater ion diffusion rate and lower resistance of  $ZnO/CoS_2/NF$  at the time of electrochemical reaction [25–27]. The mechanism involved in the excellent

electrochemical behavior and greater energy storage behavior of ZnO and CoS<sub>2</sub> can be demonstrated using the electron release equations in KOH electrolyte solution [20].

$$ZnO + K^+ + e^- \leftrightarrow ZnOK.$$
 (2)

$$CoS + OH^- \leftrightarrow CoSOH + e^-.$$
 (3)

$$CoSOH + OH^- \leftrightarrow CoSO + H_2O + e^-.$$
 (4)

In Figure 4b, the correlation between the cathodic peak response ( $i_p$ ) and the CV scan rate (V) is shown as a function of the power law ( $i_p = a * v^b$ ), thereby elucidating the charge storage mechanism of the ZnO/NF, CoS<sub>2</sub>/NF, and ZnO/CoS<sub>2</sub>/NF nanocomposites. Here, *a* and *b* are constants, whereby *b* can be calculated from the slope of the log (v)–log ( $i_p$ ) plot, with values between 1 and 0.5; *b* = 0.5 represents a diffusion-controlled current and *b* = 1 indicates that the current is capacitive [28,29]. The calculated *b* values for the ZnO/NF, CoS<sub>2</sub>/NF, and ZnO/CoS<sub>2</sub>/NF nanocomposites were 0.53, 0.54, and 0.51, respectively. Clearly, the *b* value was close to 0.5 for the prepared electrodes, indicating a diffusion response or battery-type behavior. The obtained outcome values agree with previous reports on the behavior of battery-type materials [19].



**Figure 4.** (a) Linear relationship of oxidation and reduction vs. scan rate for nanocomposite; (b) *b* values obtained from the log (i) vs. log (v) plot for the cathodic peaks of ZnO/NF,  $CoS_2/NF$ , and  $ZnO/CoS_2/NF$  nanocomposites.

The GCD plots in Figure 5a evaluate the ZnO/NF and ZnO/CoS<sub>2</sub>/NF nanocomposites employed at a current density of 1 A·g<sup>-1</sup>, showing a nonlinear GCD characteristic of battery-type behavior. Persistently, the ZnO/CoS<sub>2</sub>/NF nanocomposite illustrated enhanced GCD periods when compared to ZnO/NF, demonstrating greater capacity storage values, in line with the CV plots. The capacities of the as-synthesized precursors of ZnO/CoS<sub>2</sub>/NF and ZnO/NF were 400.25, 356.16, 340.80, 330.96, 308.06, 288.58, and 272.18 C·g<sup>-1</sup> and 366.01, 320.85, 295.35, 264.43, 231.91, 200.24, and 191.27 C·g<sup>-1</sup> at current densities of 1, 2, 3, 4, 6, 8, and 10 A·g<sup>-1</sup>, respectively.

Upon gradually increasing the current density to  $10 \text{ A} \cdot \text{g}^{-1}$ , the synthesized ZnO/CoS<sub>2</sub>/NF nanocomposite illustrated an excellent capacity retention of 68%, which was greater when compared to ZnO/NF (52.25%), as depicted in Figure 5d. The synergy between ZnO and CoS<sub>2</sub> led to excellent availability of active species and mass loading on the surface of the electroactive material, thereby giving rise to excellent capacity values.



**Figure 5.** (a) Charge–discharge curves of ZnO/NF and ZnO/CoS<sub>2</sub>/NF nanocomposites at  $1 \text{ A} \cdot \text{g}^{-1}$ ; charge–discharge plots of (b) ZnO/NF and (c) ZnO/CoS<sub>2</sub>/NF at various current densities. (d) Specific capacity of the prepared electrodes as a function of the current density. (e) Long-term cycling stability of the ZnO/NF and ZnO/CoS<sub>2</sub>/NF at  $2 \text{ A} \cdot \text{g}^{-1}$  for 4000 GCD cycles. (f) EIS curves.

Figure 5e demonstrates the cycling stability of ZnO/NF and ZnO/CoS<sub>2</sub>/NF in the three-electrode setup following repetitive GCD cycles at an appreciable current density of 2 A·g<sup>-1</sup> over 4000 cycles. The coral reef-like structures of synthesized ZnO/CoS<sub>2</sub>/NF nanocomposites depicted a predominant cycling stability of 88.2% over 4000 cycles with a capacitance fading percentage of 11.8%, showing an improvement to bare ZnO/NF (27.5%). The mechanism involved during fabrication and operation of the electrode material plays a crucial role in the elevated cycling behavior. The electrolyte ions facilitating the electrode also aid in enhancing the performance of the electroactive material. Low charge transfer and excellent conductivity are the two main reasons for the improved capacity values of CoS<sub>2</sub> [30].

Table 1 compares the performance of the  $ZnO/CoS_2/NF$  nanocomposite with electrodes from the recent literature [10,20,31–37]. As shown in Figure 5f, the synthesized electroactive materials resulted in the impedance of  $ZnO/CoS_2/NF$  nanocomposite being more aligned vertically in the low-frequency area compared with ZnO/NF. The EIS plot

showed a lower resistance of the  $ZnO/CoS_2/NF$  nanocomposite, illustrating the potential conductivity and swift electron movement at the areal interface of the electrode/electrolyte.

**Table 1.** Comparison of specific capacitance for various composite electrode materials in aqueous electrolyte as reported in the literature.

Electrode Material	Electrolyte	Current Density	Specific Capacitance	Ref
ZnO/CoS <sub>2</sub> /NF nanocomposite	3 M KOH	$1 \text{ A} \cdot \text{g}^{-1}$	$400.25  \mathrm{C} \cdot \mathrm{g}^{-1}$	This study
ZnO/CoO@NiCoS	3 M KOH	$1 \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$934 \mathrm{C}{\cdot}\mathrm{g}^{-1}$	31
ZnO/NiO:rGO (ZNR/NF)	1 M KOH	$1 \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$622.3 \ { m F} \cdot { m g}^{-1}$	32
3 D PCSMs	1 M Na <sub>2</sub> SO <sub>4</sub>	$1 \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$313 \ \mathrm{F} \cdot \mathrm{g}^{-1}$	33
ZnO@CoS Electrode	3 M KOH	$3 \mathrm{mA}\mathrm{cm}^{-2}$	898.9 $C \cdot g^{-1}$	20
CoS (SFC)	$6 \text{ mol } \mathrm{L}^{-1}$	$1 \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$350.4 \ { m F} { m g}^{-1}$	34
NiCoP@CoS NAs/NF	-	$2 \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$1796  \mathrm{F} \cdot \mathrm{g}^{-1}$	35
Ag@CoS/rGO	6 mol/L KOH	$0.5 \ \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$1582  \mathrm{F} \cdot \mathrm{g}^{-1}$	36
ZnWO <sub>4</sub> @WS <sub>2</sub>	КОН	$3 \mathrm{A}{\cdot}\mathrm{g}^{-1}$	$1280.7 \ { m F} { m \cdot} { m g}^{-1}$	37
CuS@PbS	3 M KOH	$2.85 \mathrm{A} \cdot \mathrm{g}^{-1}$	$1004.42 \text{ F} \cdot \text{g}^{-1}$	10

### 4. Conclusions

The current study fabricated a ZnO/CoS<sub>2</sub>/NF nanocomposite employing a costeffective hydrothermal approach for applications in SCs. The efficient ZnO/CoS<sub>2</sub>/NF composite showed a predominant electrochemical performance with improved capacity of 400.25 C·g<sup>-1</sup> at a density of 1 A·g<sup>-1</sup>, with a good cycling performance of 88.2% over 4000 cycles at 2 A·g<sup>-1</sup>, while even maintaining 272.18 C·g<sup>-1</sup> at 10 A·g<sup>-1</sup> current density. Furthermore, the excellent capacitance retention and EIS characteristics characterized the greater performance of ZnO/CoS<sub>2</sub>/NF by establishing synergy with electron release. Hence, the ZnO/CoS<sub>2</sub>/NF nanocomposite was proven to have promising electrochemical and surface morphological properties, showing great potential for use in SCs.

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