Facile synthesis of hierarchical agglomerated cauliflower-like ZnWO₄@NiO nanostructures as an efficient electrode material for high-performance supercapacitor applications

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Abstract: Hierarchical agglomerated cauliflower-like ZnWO₄@NiO nanoparticles were successfully prepared using the facile chemical bath deposition method for supercapacitor applications. The electrochemical studies revealed a higher value of specific capacity as 225.131 mA h g⁻¹. Further, the ZnWO₄@NiO electrode possesses a higher rate capability of 83.78% and good cycling stability of 94.27% after 4000 cycles, respectively. The impressive electrochemical studies and their morphology reveal that the as-prepared ZnWO₄@NiO composite electrode possess high energy storage performance.

Keywords: Cauliflower, agglomerated, chemical bath deposition, supercapacitor.

Introduction

The rapid growth of energy demand and the effect of global warming on the environment created a need to replace fossil fuels with more reliable and efficient renewable energy sources such as solar, wind and tidal energy, etc. This energy is stored in various energy storage devices.

Hence, in the phenomenon of energy storage, supercapacitors (SCs) play an important role in the energy supply when compared to batteries and possess high energy density when compared to conventional capacitors. In addition, SCs have unique features such as an improved life cycle, safer operation and require a simple charging circuit [1, 2].

There are some pseudocapacitive materials obtained from various transition metal oxides (TMOs) such as MnO_2 , NiO , MoO_3 , Co_3O_4 considered as potential electrode materials for SC applications because of their high theoretical capacities. NiO has its own high specific capacitance because of the mobility-regulated electrochemical redox reactions with electrolyte ions. They are less cost, possess good chemical and thermal stability. The NiO nanostructure morphology affects its electrochemical behavior. NiO as a SC electrode material exhibits different morphologies such as nanoflakes, nano/microspheres, and nanosheets hollow type spheres, and quasi-nanotubes, were majorly reported [3].

Very recently, great research was conducted on ternary metal oxides that yield higher capacitances than the analogous single metal oxides because of their greater electron conductivity and the rapid redox reactions during the electrochemical processes [4]. There are many ternary metal oxides, such as CoMoO_4 , NiCo_2O_4 , ZnCo_2O_4 , MnMoO_4 , etc., are employed as pseudocapacitor electrode materials. Among them, ZnWO_4 is an effective inorganic ternary metal oxide material. Metal tungstate possesses similar properties of ternary metal oxides like a higher oxidation state observed in the tungstate atom and able to crystallize in wolframite structure. As a member of the tungstate family, ZnWO_4 exhibited the greater performance of Li-ion batteries, since Zn and W are excellent electroactive metals that attain greater capacitance for SCs [5].

Inspired from the above works, in this study we report and synthesize a novel $\text{ZnWO}_4@\text{NiO}$ hybrid electroactive material using the simple cost-effective chemical bath deposition method. The as-prepared $\text{ZnWO}_4@\text{NiO}$ electrode shown excellent energy storage performance.

2. Experimental

Initially, nickel (Ni) foams ($1 \times 2 \text{ cm}^2$) were ultrasonically cleaned with 2 M HCl, acetone, ethanol and distilled (DI) water for 15 min. The $\text{ZnWO}_4@\text{NiO}$ composite was synthesized by the chemical bath deposition method. Typically, 0.2 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.2 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 0.2

M Ni(NO₃)₂, 0.4 M CH₄N₂O and 0.4 M NH₄F were dissolved in 70 mL of DI water. The ultrasonically cleaned Ni foams were now immersed in this solution and kept in a hot air oven for 100 °C for 10 h. When the temperature of Ni foams reached to the room temperature, they were cleaned with the DI water and the ethanol. Further, they were dried in the oven at 60 °C for 12 h. The ZnWO₄ and NiO were also prepared by a similar procedure without the addition of Ni sources for ZnWO₄, Zn and W sources for NiO. The average weight of the ZnWO₄, NiO and ZnWO₄@NiO electroactive materials on Ni foam substrates were found to be 4.22, 4.41 and 4.60 mg cm⁻².

2.4 Electrochemical measurements

The electrochemical analysis was carried out using BioLogic –SP150 workstation in 3M KOH aqueous electrolyte employed with the three-electrode cell where Pt wire, Ag/Ag Cl and the prepared samples were used as the counter, reference, and the working electrodes. The CV analysis was performed at various scan rates (10, 20, 50, 75 mV s⁻¹) at the potential range of 0 to 0.6 V. Further, the GCD test was conducted to evaluate the specific capacity (Q_{sc}) obtained from Eq. (1):

$$Q_{sc} = \frac{i \times \Delta t}{m \times 3.6} \quad (1)$$

Here Q_{sc} is the specific capacity in mA h g⁻¹; *i* is the discharge current in Ampere (A); Δ*t* is the discharge time difference in seconds; *m* is the mass of an electroactive material in gram (g).

3. Results and discussions

The composition and phase structure of the products were first analyzed by XRD as shown in Fig. 1. The XRD patterns of the ZnWO₄ sample represented the corresponding peaks as (021), (121), (113) that were well matched with the JCPDS:73-0554, concurrently the peaks of the NiO sample were depicted at (111), (200), (311) and referred to the JCPDS:78-0429. Furthermore, all the dominant peaks were observed at the prepared composite ZnWO₄@NiO clearly shown the crystalline nature and excellent purity of the sample.

Fig. 1 XRD patterns of the $\text{ZnWO}_4@\text{NiO}$ electrode materials on Ni foam

Fig. 2 (a, a1, a2) at different magnifications, depicted the SEM images of ZnWO_4 that exhibited ultrathin nanoflake morphology with a lot of penetrable porous little spaces, parts of the interlinked nanoparticles got together to form many ultra-thin nanoflakes. Fig. 2 (b, b1, b2) of NiO SEM images illustrated the incorporation of many uniform sized nanosheets and manifested the full coherence. Fig. 2 (c, c1, c2) represented the SEM images of $\text{ZnWO}_4@\text{NiO}$ nanoparticles at different magnifications and shown an hierarchical agglomerated cauliflower-like nanoparticles densely deposited on the Ni foam substrate, the unique structure was beneficial to the full contact between electrode materials and electrolyte, and the transportation of electrons during the charge and discharge processes enhanced the electrochemical performance of the as-prepared $\text{ZnWO}_4@\text{NiO}$ electrode.

Fig.2 FE-SEM images (a, a1, a2) ZnWO₄, (b, b1, b2) NiO and (c, c1, c2) ZnWO₄@NiO under different magnifications.

Fig. 3 (a) Comparative CV curves of ZnWO₄, NiO and ZnWO₄@NiO electrodes at a scan rate of 20 mV s⁻¹, (b) CV curves of the ZnWO₄ electrode at various scan rates, (c) CV

curves of the NiO electrode at different scan rates. (d) CV curves of the ZnWO₄@NiO electrode at different scan rates,

Fig. 3(a) depicted the comparative CV curves of the as-prepared ZnWO₄, NiO and ZnWO₄@NiO electrodes at a scan rate of 20 mV s⁻¹ in the potential window of 0.0 to 0.6 V. From the CV plots operated at various scan rates exhibited dominant redox peaks and swift kinetic processes exhibited the battery-type behavior of the material. Compared to CV curves of ZnWO₄ and NiO, the oxidation and reduction peaks were shifted to more positive and negative potential regions in the ZnWO₄@NiO electrode. This happened because of uniform deposition of the ZnWO₄@NiO electroactive material on Ni foam surface got enough time to interact with electrolyte ions and active species that resulted in the shift of the redox peaks and increased the current response and the integral area than ZnWO₄ and NiO (Fig. 3(b-d) CV curves at 10, 20, 50, 75 mV s⁻¹ scan rates). Therefore, the ZnWO₄@NiO electrode exhibited a greater energy storage performance among all the three electroactive materials.

Fig. 4 (a) Comparison of GCD plots for ZnWO₄, NiO and ZnWO₄@NiO at 8 A g⁻¹, GCD plots of (b) ZnWO₄, (c) NiO and (d) ZnWO₄@NiO at various current densities. (e) Specific capacity values as a function of current density (f) The cycling performance of the ZnWO₄@NiO electrode at 8 A g⁻¹ and (g) EIS curves of ZnWO₄, NiO and ZnWO₄@NiO electrodes and equivalent circuit inset.

From Fig. 4a, the comparative GCD curves of the ZnWO₄, NiO and ZnWO₄@NiO electrodes at the current density of 8 A g⁻¹ were represented. The specific capacity of ZnWO₄, NiO and ZnWO₄@NiO were calculated from the GCD curves (Fig. 4b, 4c, and 4d), as depicted

in Fig4. The $\text{ZnWO}_4@\text{NiO}$ electrode exhibited the excellent specific capacity values of 225.131, 204.121, 190.082, 179.530, 157.920 mA h g^{-1} , that were predominantly higher than the other prepared electrodes. Fig. 4e shown the specific capacity plot for the three samples. The cycling stability of the $\text{ZnWO}_4@\text{NiO}$ hybrid electrode was elucidated by the capacitance retention at the current density of 8 A g^{-1} (Fig. 4f). Due to the full activation process of $\text{ZnWO}_4@\text{NiO}$, the initial capacity was more and delivered a high rate capability of 83.78% and excellent cycling stability of 94.27% after 4000 cycles.

In Fig. 4g, the $\text{ZnWO}_4@\text{NiO}$ hybrid electrode delivered least series resistance as $\text{ZnWO}_4@\text{NiO}$ ($R_s = 0.18 \text{ ohm}$ and $R_{ct} = 0.42 \text{ ohm}$), NiO ($R_s = 0.27 \text{ ohm}$ and $R_{ct} = 1.18 \text{ ohm}$) ZnWO_4 ($R_s = 0.26 \text{ ohm}$ and $R_{ct} = 0.77 \text{ ohm}$), respectively. This explained the dominant electrical conductivity and less energy loss. Furthermore, compared to the other two electrodes, the $\text{ZnWO}_4@\text{NiO}$ shown a more vertical line at the low-frequency area because of the rigorous ion transportation phenomenon in the electrolyte.

Conclusion:

In this work, we successfully fabricated the $\text{ZnWO}_4@\text{NiO}$ composite using a facile chemical bath deposition method. Further, the as-prepared $\text{ZnWO}_4@\text{NiO}$ has shown an excellent supercapacitive nature and delivered appreciable value of specific capacity as 225.131 mA h g^{-1} . Moreover, the composite exhibited a good rate capability of 83.78% and excellent cycling stability of 94.27% over 4000 cycles. These results explained that $\text{ZnWO}_4@\text{NiO}$ found to be a promising electrode for high-performance energy storage applications.

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Author Contribution Section

Kummara Venkata Guru Raghavendra and Rajangam Vinodh: Data curation, writing-original draft preparation, reviewing and editing.

Chandu V. V. Muralee Gopi and Madhusudana Rao Kummara: Conceptualization and Methodology

Hee-Je Kim: Supervision, Visualization and Investigation.

Conflicts of interest:

The authors declare no conflicts of interest.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

HIGHLIGHTS

- $\text{ZnWO}_4@\text{NiO}$ electrode was prepared by facile CBD method.
- $\text{ZnWO}_4@\text{NiO}$ electrodes exhibit agglomerated cauliflower-like morphology.
- As prepared precursor exhibited the higher energy storage performance than the ZnWO_4 and NiO
- $\text{ZnWO}_4@\text{NiO}$ delivered an excellent higher specific capacity of $225.131 \text{ m Ah g}^{-1}$ at 6 A
- $\text{ZnWO}_4@\text{NiO}$ shown a higher stability than the ZnWO_4 and NiO .