Binder-free synthesis of high-quality nanocrystalline ZnCo_2O_4 thin film electrodes for supercapacitor application

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Abstract. Supercapacitors as energy storage devices have attracted great attention due to their high-specific capacitance, fast rechargeability, high-power density, performance, long cycle life and low-maintenance cost. These unique advantages enable their applications in portable electronic devices, gadgets, hybrid electric vehicles, etc. However, developing flexible, high performance, stable and economic storage devices is the need of time. With this motivation, binder-free ZnCo_2O_4 thin films are synthesized on flexible stainless steel mesh by a hydrothermal method. The structural, morphological and physicochemical properties of ZnCo_2O_4 are investigated using X-ray diffraction, Fourier transform infrared spectroscopy, field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy. FESEM images reveal thin films with flower-shaped microspheres composed of bunched nanowires providing a large surface area ($72 \text{ m}^2 \text{ g}^{-1}$) which is confirmed by Brunauer–Emmett–Teller analysis. The electrochemical performance of the ZnCo_2O_4 thin film electrode exhibited a specific capacitance of 127.8 F g^{-1} at a current density of 1 mA cm^{-2} . It also shows good rate capability and excellent electrochemical cycling stability (80.66% specific capacitance retention after 3000 cycles).

Keywords. Binder-free; flexible; ZnCo_2O_4 ; thin film; supercapacitor.

1. Introduction

Depletion of natural energy resources is posing a great challenge to the scientific society and is also a cause of great concern to the future generation. On the other hand, a multi-fold increase in the consumption of fossil fuels for energy has elevated environmental pollution making the issues more complex. Thus, there is an urgent need to develop alternative renewable, efficient, clean and sustainable energy sources to circumvent the energy crisis. As an economic and sustainable alternative, solar energy, wind energy, geothermal, hydropower, etc., are looked upon with great expectation, although these are non-continuous, inconsistent and depend on several factors. The renewable energy sources require high-capacity energy storage devices for the proper utilization of the produced energy. These issues could be addressed by developing an efficient energy storage device to store the generated energy and use as and when required. On the other hand, the demand for energy in portable devices (mobile phones, laptops, tablet computers, etc.) and hybrid electric vehicles is increasing exponentially throughout the world with the growing population. This led to the development of technology for storage devices with a major focus on supercapacitors and batteries. Batteries, traditional electrostatic capacitors and supercapacitors have been used in the energy storage applications [1–3]. Electrochemical capacitors, also known

as supercapacitors, are superior to batteries and traditional capacitors and are considered as promising candidates for next-generation power storage due to their high-power density, fast recharge capability and long cycle life [4]. Generally, supercapacitors store energy by two important charge storage mechanisms such as charge separation at electrode/electrolyte interfaces i.e. electric double layer capacitors (EDLCs) and charge storage by Faradic redox reactions i.e. pseudocapacitors. In EDLCs, energy storage is comparatively less and is unstable at high-charging–discharging rates [5,6]. Thus, transition metal oxides, composites, conducting polymers and carbonaceous (aerogel, nanofoam, nanotube, etc.) materials have been studied as electrodes for supercapacitors. Among them, some metal oxides, metal ferrites and metal sulphide show very high-specific capacitance, but their acceptance is limited due to high-cost. Hence, the search for alternate transition metal oxides as economic materials with improved performance and abundance is required [7]. Extensive work is performed in this direction to explore and develop inexpensive alternative transition metal oxide-based electrodes with good capacitive character. The transition metal oxide and binary and ternary oxide (MnO_2 , Mn_3O_4 , Fe_3O_4 , Co_3O_4 , CeO_2 , Fe_2O_3 , RuO_2 , WO_3 , NiCo_2O_4 , CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , ZnFe_2O_4 , etc.) [8–20] compositions are being explored as promising electrode materials as supercapacitors, because of their unique properties such as high-specific capacitance,

Figure 1. Schematic representation of the synthesis of ZnCo₂O₄ microspheres.

longer life stability and environmental benignity. Among the transition metal oxides, metal cobaltite (MCo₂O₄, wherein M refers to divalent metal) with spinel structure-based electrodes is the most studied candidate in supercapacitors due to their excellent redox behaviour. However, the synthesis of the thin film material without using a binder is the preferred choice to retain the electrochemically active surface area which contributes to the performance. In thin film preparation, the material is directly deposited onto the conducting substrates, such as carbon cloth, Ni foam, graphite sheets, Cu foil, Ti foil and stainless steel without using binders, wherein electrodeposition, chemical vapour deposition or vacuum deposition techniques are preferred choices. Furthermore, high-cost and toxicity concerns in substrates such as carbon cloth, Ni foam, Cu foil and Ti foil are the limiting factors. Thus, substrates such as stainless steel mesh or plates are among the most explored substrates due to their low-cost and less toxicity, rough surface and easy availability [21,22]. Thus, developing a simple binder free method for the synthesis of cubic spinel ZnCo₂O₄ microstructures is crucial.

With this motivation, in the present work, we report a facile and scalable hydrothermal approach for the synthesis of ZnCo₂O₄ microspheres on flexible stainless steel mesh (ZnCo₂O₄/FSSM) as an electrode without the aid of a binder. The morphology of the deposited material is studied by field emission scanning electron microscopy (FESEM) and from this it is clearly observed microsphere made up of a bunch of nanowire-like morphology. The electrochemical performance is studied by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) curve and electrochemical impedance spectroscopy (EIS). The electrochemical results show that the ZnCo₂O₄ microspheres exhibit pseudocapacitive properties with good electrochemical performance, rate capability, specific capacitance (127.8 F g^{−1} at a current density of 1 mA cm^{−2}) and excellent cyclic stability (80.66% capacitance retention after 3000 cycles at a current density of 10 mA cm^{−2}).

2. Experimental

2.1 Chemicals

All the chemicals such as zinc acetate dihydrate (Zn(CH₃COO)₂ · 2H₂O, Loba Chemie Pvt. Ltd., 98%), cobalt acetate tetrahydrate (Co(CH₃COO)₂ · 4H₂O, Loba Chemie Pvt. Ltd., 98.5%), urea (CO(NH₂)₂, Merck chemicals, 99%), ammonium fluoride (NH₄F, Merck chemicals, 96%) and potassium hydroxide (KOH) were of analytical grade and used as such without further purification. The thin films were deposited on flexible stainless steel 300 mesh (FSSM-300) procured from micromesh India Pvt. Ltd. Double distilled water was used for preparing solutions and for washing of the precipitate.

2.2 Synthesis of ZnCo₂O₄ microspheres

The typical process used for the synthesis of ZnCo₂O₄ microspheres is shown in figure 1. The substrate (FSSM-300) is cut into 3 × 1 cm and ultrasonically cleaned in a successive step by soaking in a detergent solution, distilled water, acetone and absolute ethanol for 5 min each in order to clean the surface; the precleaned substrate was used for deposition. 5 mM CO(NH₂)₂ and 2 mM NH₄F were dissolved in 40 ml of cationic precursor solution of 0.1 M Zn(CH₃COO)₂ · 2H₂O and 0.2 M Co(CH₃COO)₂ · 4H₂O with magnetic stirring. After stirring for 30 min, a clear pink colour solution was transferred to a 50 ml Teflon-lined stainless steel autoclave in which the stainless steel mesh substrate is fitted vertically and hydrothermal treatments were carried out at 120°C for 12 h in an electric oven. After completion of the reaction, the autoclave was cooled naturally to room temperature, and the thin film deposited on the substrate was washed several times with distilled water and ethyl alcohol. Subsequently, the as-synthesized samples were dried overnight in an electric oven at 60°C. Finally, the dried samples were calcined to form black coloured ZnCo₂O₄.

Figure 2. (a) XRD spectrum, (b) IR spectrum, (c) FESEM and (d) EDS spectrum of ZnCo_2O_4 microspheres.

microspheres at 400°C for 2 h in air at a heating rate of $10^\circ\text{C min}^{-1}$.

2.3 Material characterization

X-ray diffraction (XRD) studies were performed (Bruker, D2-Phaser X-ray diffractometer) with $\text{CuK}\alpha_1$ ($1.5406 \text{ \AA}$) radiation in the range of 20 – 80° . The Fourier transform infrared (FTIR) spectra of the powder samples (trace amount in KBr pellets) were recorded from the wavenumber range of 480 to 4000 cm^{-1} by using a Bruker Alfa Spectrometer. The micro-flowers made from the bunch of ZnCo_2O_4 nanowires are obtained by FESEM (Mira3, TESCAN) images at higher magnification ($2,00,000\times$); while elemental composition was studied with an energy dispersive spectroscopy (EDS) (Oxford Instruments) technique. The pore size distributions and specific surface areas of the porous ZnCo_2O_4 nanowires were evaluated by Brunauer–Emmett–Teller (BET) (NOVA 1000e Quantachrome, USA).

2.4 Electrochemical measurements

All the electrochemical experiments were carried out in a 6 M aqueous KOH electrolyte at room temperature using a CHI 608E electrochemical analyser. CV, GCD and EIS were

carried out in a standard three-electrode system with graphite and a saturated Ag/AgCl electrode as the counter and reference electrodes, respectively. The $\text{ZnCo}_2\text{O}_4/\text{FSSM}$ was used as the working electrode. The CV curves were measured under different scan rates of 10 – 100 mV s^{-1} between the potential window 0 and 0.5 V. EIS measurements were carried out in the frequency range of 100 kHz to 1 Hz at an open circuit potential with 5 mV AC perturbation.

3. Results and discussion

The crystalline phase and purity of the as-synthesized sample were determined by powder XRD as shown in figure 2a. The XRD spectra of ZnCo_2O_4 were in good agreement with that reported earlier revealing a cubic spinel structure (JCPDS No: 23-1390). All the characteristic peaks at 18.75 , 30.95 , 36.50 , 38.23 , 44.46 , 55.37 , 59.09 , 65.00 , 73.50 and 77.08° 2θ were assigned to the (111), (220), (311), (222), (400), (422), (511), (440), (620) and (533) planes of cubic spinel ZnCo_2O_4 , respectively. The good crystallinity of the as-prepared ZnCo_2O_4 sample is indicated by sharp and intense peaks. No other XRD peaks were detected supporting the fact that the material is free from contaminants [23].

Table 1. Elemental composition.

Element	Weight %	Atomic %
O K	24.83	55.16
Co K	66.79	40.28
Zn L	8.38	4.56

Figure 2b shows representative IR spectra of ZnCo_2O_4 revealing two sharp peaks at 569 and 665 cm^{-1} which could be attributed to M–O stretching vibrations. The sharp peak at 569 cm^{-1} is a characteristic of the M–O stretching vibration of octahedrally coordinated cobalt ions, and the band at 665 cm^{-1} represents the M–O stretching vibration of tetrahedrally coordinated zinc ions [24].

The morphology of ZnCo_2O_4 is recorded using FESEM (figure 2c) which reveals the formation of a microsphere composed of a bunch of nanowires of ZnCo_2O_4 . The ZnCo_2O_4 nanowires show uniform growth with end to end interconnections which might assist and facilitate charge transfer between the electrode and electrolyte. The elemental composition of the as-synthesized ZnCo_2O_4 microsphere was investigated by EDS (figure 2d). The EDS spectrum shows that the as-prepared sample is composed of Zn, Co and O confirming the successfully formation of ZnCo_2O_4 . The percentage composition of elements in ZnCo_2O_4 is given in table 1. No additional peaks were observed supporting the fact that the material is free from impurities.

The pore structure and surface areas of the ZnCo_2O_4 /FSSM-300 mesh sample were further characterized by nitrogen adsorption/desorption measurement and analysed using the Barrett–Joyner–Halenda and BET methods (figure 3). A distinct hysteresis loop observed at a relative pressure of $P/P_0 = 0.8$ –1.0 demonstrated the typical mesoporous characteristics of ZnCo_2O_4 microspheres. The pore size distribution curve (inset in figure 3) shows that the pore size is 2.96 nm

Figure 3. Representative nitrogen adsorption–desorption isotherm of ZnCo_2O_4 microspheres.

which is mainly in the nanoporous range and wide mesoporous range (<50 nm) due to the nanopores present in the microspheres [25,26]. The BET specific surface area and pore volume of ZnCo_2O_4 /FSSM-300 were observed to be 72 $\text{m}^2 \text{g}^{-1}$ and 0.186 $\text{cm}^3 \text{g}^{-1}$, respectively. The large surface area and pore volume are essential for the electrode materials to achieve large specific capacitance as this reduces ion transport limitation in electrodes, ensuring the complete utilization of electrode materials.

The ZnCo_2O_4 /FSSM-300 electrode was further explored for supercapacitor application. The electrochemical performance of the ZnCo_2O_4 microsphere electrode was carried out with a three electrode system using a 6 M KOH electrolyte.

Figure 4a shows the CV curve of the ZnCo_2O_4 electrode within the potential range from 0 to 0.5 V (vs. Ag/AgCl) at different scan rates of 10 to 100 mV s^{-1} . The shape of the CV curves does not appear rectangular as expected and indicates that the electrode represents the pseudocapacitive behaviour (faradic redox reactions). When the scan rate is 10 mV s^{-1} , a distinct pair of redox peaks located at around 0.29 and 0.42 V can be observed, which indicates the energy storage mechanism of the ZnCo_2O_4 microspheres mainly originates from faradaic redox reactions. The shape of the CV curves is not significantly influenced by the increase of scan rates, which indicates improved mass transportation and electron conduction in the host materials. Additionally, with the increasing of the scan rate, the anodic/cathodic peak respectively shifts towards a positive/negative potential, respectively, indicating kinetic irreversibility in the redox process due to polarization and ohmic resistance during the Faradaic process in ZnCo_2O_4 microspheres. The peak current increases almost linearly with the scan rate confirming the pseudocapacitive behaviour [27–29].

Figure 4b shows charge/discharge storage capacity of the as-synthesized electrode which is estimated from GCD curves in the potential range from 0 to 0.4 V at different current densities from 1 to 10 mA cm^{-2} . The charge and discharge curves exhibit typical deviations from a straight and flat line, confirming that the capacitance occurs mainly from the faradic pseudocapacitance. The equation used for the calculation of specific capacitance (C_{sp}) is [30]:

$$C_{\text{sp}} = I \Delta t / m \Delta V, \quad (1)$$

where I (A) is the applied current, Δt (s) is the total discharge time, m (g) is the mass of the electroactive material and ΔV (V) is the potential window. According to this formula, the calculated specific capacitances of the ZnCo_2O_4 microsphere electrode at 1, 2, 3, 5, 8 and 10 mA cm^{-2} were 127.8, 127.1, 124.8, 94 and 81.8 F g^{-1} , respectively. As shown in figure 4c, the maximum specific capacitance is achieved at a current density of 1 mA cm^{-2} . This specific capacitance arises from the direct growth of ZnCo_2O_4 nanowires on the FSSM substrate without using a binder. Further, the values of energy density and power density are plotted in the Ragone plot as

Figure 4. (a) CV curves at different scan rates, (b) GCD curves measured at various current densities, (c) the graph of specific capacitance measured at various current densities and Ragone plot (inset) and (d) Nyquist plot.

shown in the inset of figure 4c. From the Ragone plot, it is observed that the energy density decreases with an increase in power density. The synthesized electrode gives the highest energy density of 7.10 Wh kg^{-1} with a power density of 0.12 kW kg^{-1} . EIS was carried out to investigate the electrical conductivity and ion diffusion. Figure 4d shows the Nyquist plot for the ZnCo_2O_4 microsphere and the inset is an equivalent circuit model. The Nyquist plot is divided into three parts: low, middle and high-frequency ranges. At a low frequency, the slope of the curve demonstrates the Warburg resistance (W), representing the electrolyte diffusion into the electrode. At a high frequency, the intersection point on the real axis shows the solution resistance (R_s) of the electrochemical system and a higher R_s value indicates a lower electrical conductivity of the sample and vice versa. The semicircle displays the charge transfer resistance (R_{ct}) which results from the faradaic reactions and the double-layer capacitance (C_{dl}) on the electrode surface. The ZnCo_2O_4 electrode exhibits a lower R_s ($0.67 \Omega \text{ cm}^{-2}$) and R_{ct} ($1 \Omega \text{ cm}^{-2}$), which is due to the good conductivity of the ZnCo_2O_4 microspheres. The EIS of the electrode before GCD and after 3000 cycles shows that the slopes of the straight line at a low frequency of the

two electrodes are almost the same, indicating nearly the equal value of the electrolyte diffusion impedance. In addition, the semicircle of the Nyquist diagram corresponds to the Faradic reactions and it is found that the diameter of the semicircle for the electrode before GCD and after 3000 cycles is almost same, representing the nearly equal value of an interfacial charge-transfer impedance. But from a high frequency, it is clearly seen that the value of R_s has been increased from 0.67 to $0.85 \Omega \text{ cm}^{-2}$. This increase in R_s arises may be due to the dissolution of the electrode material into the electrolyte after 3000 GCD cycles which consequently decreases the specific capacitance [31–33].

For a good electrochemical supercapacitor performance, long time cycling stability is of great importance and cycling stability was evaluated by continuous charging–discharging measurements for 3000 cycles over the potential range of 0 – 0.4 V . Specific capacitance was measured at a constant current density of 10 mA cm^{-2} for 3000 cycles. GCD curves of the first six and the last six cycles are shown in figure 5a and b.

Surface wetting of the ZnCo_2O_4 microsphere electrode by an electrolyte is comparably more in the initial cycles of charge–discharge and exhibits increased specific capacitance

Figure 5. Specific capacitance measured at a constant current density of 10 mA cm^{-2} for 3000 cycles. (a) GCD curves of the first six and (b) the last six cycles.

Figure 6. Specific capacitance at 10 mA cm^{-2} and inset showing retention over 3000 charge–discharge cycles.

(81.1 F g^{-1} at 10 mA cm^{-2}). During the long term cycling test, the specific capacitance is found to decrease consistently which is caused by the distortion in the microstructure of the ZnCo_2O_4 microsphere and may be due to the dissolution of the electrode mass material in the electrolyte (specific capacitance over 3000 cycles is 65.56 F g^{-1} as shown in figure 6). The capacitance retention of the ZnCo_2O_4 microsphere is shown in the inset of figure 6 and it is found to be 80.66% after 3000 cycles. The Columbic efficiency (η) for the cycling test was evaluated from GCD at a constant current density of

10 mA cm^{-2} . The equation used for the calculation of Columbic efficiency is [23]:

$$\eta = t_d/t_c \times 100\%, \quad (2)$$

where t_d is the discharge time and t_c is the charge time. The efficiency was about 100% over the entire cycling measurement, indicating the excellent electrochemical reversibility of the porous ZnCo_2O_4 microspheres. It can be noted that the porous ZnCo_2O_4 microspheres exhibited the capacitance retention of 80.66% after 3000 cycles, which is lower than the Columbic efficiency. The difference between the Columbic efficiency and the capacitance retention may be attributed to the adhesion problem between ZnCo_2O_4 and the FSSM. The adhesion problem probably is decreased by using a binder or by pressing the electrode, but this may cause a decrease in the performance of the electrode.

4. Conclusion

ZnCo_2O_4 microspheres were successfully deposited on the FSSM substrate using a facile binder free hydrothermal method and characterized by XRD, FESEM and FTIR. The XRD and FESEM results show that the material has high crystallinity of the deposited- ZnCo_2O_4 and excellent microsphere formed by a bunch of nanowire-like morphology. The BET analysis shows that the surface area of the synthesized ZnCo_2O_4 nanowires is $72 \text{ m}^2 \text{ g}^{-1}$. The electrochemical performance of the ZnCo_2O_4 microspheres exhibited a good specific capacitance of 127.8 F g^{-1} at 1 mA cm^{-2} , good rate capability and excellent electrochemical cycling stability (80.66% specific capacitance retention after 3000 cycles).

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