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ChemSci Advances
ISSN: 0000-0000 www.aristonpubs.com/chemsci-advances https://doi.org/XXXX/XXXX

RESEARCH ARTICLE

MOF Derived $CoFe_2O_4$@Carbon Nanofibers for Supercapacitor Application

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ABSTRACT: This research focuses on synthesizing MOF-derived $CoFe_2O_4$ nanoparticles anchored on carbon nanofibers ($CoFe_2O_4$@CNFs) combining hydrothermal and electrospinning methods for supercapacitor electrode applications. The study aims to enhance the supercapacitive performance by combining MOF-derived $CoFe_2O_4$ nanoparticles and carbon nanofibers. Electrochemical assessments revealed that $CoFe_2O_4$@CNFs 600 exhibited a specific capacitance of 527 F/g at a current density of 1 A/g. Furthermore, the electrode demonstrated a power density of 234.93 W/kg and an energy density of 16.58 Wh/kg. This research underscores the potential of combining MOF-derived bimetallic transition metal oxide with carbon nanofibers in improving supercapacitive performance.

Keywords: MOF, Nanofibers, Cobalt ferrite, Carbon Nanofibers, Supercapacitor

Received: 20 January 2024; Revised: 13 February 2024; Accepted: 03 March 2024

1. INTRODUCTION

Supercapacitors has a potential to provide a solution for efficient energy storage [1], offering rapid charge and discharge capabilities for various applications, including portable electronics and hybrid vehicles [2].They fall into two categories: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs rely on physical charge separation through ion adsorption. Pseudocapacitors on the other hand store charges through reversible faradic redox reactions [3], commonly employing transition metal oxides, conductive polymers, and other compounds [4].

Presently, scientists are directing their attention towards the utilization of bimetallic transition metal oxides in electrode applications, where a single molecule hosts two cations. Some of the examples includes $NiCo_2O_4$ [5], $MnFe_2O_4$ [6], $CuFe_2O_4$ [7], and $CoFe_2O_4$ [8]. Among these cobalt ferrite is widely recognized as an inverse spinel structure wherein Co^{2+} ions occupy tetrahedral sites, while Fe^{3+} ions are distributed among both tetrahedral and cubic crystal structure sites. This unique arrangement potentially enhances redox activity, thereby improving charge storage efficiency [9]. MOFs and materials derived from them are gaining prominence in fine chemical synthesis because of their adaptable properties and potent catalytic capabilities. Nonetheless, while pristine MOFs show promise, their low conductivity limits their effectiveness in supercapacitors. Thus, researchers are exploring the use of MOF-derived nanomaterials, created by annealing MOFs as sacrificial templates, as innovative electrode materials. This approach retains the porous structure characteristic of MOFs while significantly enhancing electrical conductivity [10]. Carbon nanofibers (CNFs) possess desirable qualities for supercapacitors such as excellent electrical conductivity, high specific surface area, and significant aspect ratio. Combining CNFs with MOFs can be an interesting approach to enhance the supercapacitive properties. Electrospinning stands out due to its capability to facilitate the incorporation of CNFs with other materials [11-13].

In this study, we synthesized $CoFe_2O_4$ nanoparticles anchored carbon nanofibers ($CoFe_2O_4$@CNFs). For this CoFe MOF was prepared by hydrothermal method. CoFe MOF was then used in electrospinning technique to anchor MOF derived $CoFe_2O_4$ nanoparticles on carbon nanofibers.

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Supercapacitive performance of $CoFe_2O_4$@CNFs has been thoroughly investigated.

2. EXPERIMENTAL DETAILS

2.1. Chemicals

Cobalt nitrate hexahydrate (Co $(NO_3)_2 \cdot 6H_2O$) obtained from SRL Pvt Ltd, along with iron nitrate nonahydrate (Fe $(NO_3)_2 \cdot 9H_2O$), p-phthalic acid (PTA) and polyacrylonitrile (PAN, Mw–150000) from Sigma Aldrich, were used. N, N-dimethylformamide (DMF) from SRL, potassium hydroxide (KOH) from Loba Chemie Pvt Ltd, and double distilled water (DDW) were utilized for solution preparations. For electrode assembly, commercial Ni foam, polyvinylidene fluoride (PVDF), activated carbon, and N-methyl-2-pyrrolidone (NMP) were employed.

2.2. Synthesis of CoFe MOF

To synthesize CoFe MOF, cobalt nitrate hexahydrate and iron nitrate nonahydrate was dissolved in DMF containing terephthalic acid. The mixture was hydrothermally treated at 150°C for 8 hrs. Resulted CoFe MOF powder was washed with DMF and DDW.

2.3. Synthesis of $CoFe_2O_4$@CNFs

The MOF-derived $CoFe_2O_4$@carbon nanofibers ($CoFe_2O_4$@CNFs) was prepared via electrospinning and subsequent annealing. For this, PAN and CoFe MOF was separately dissolved in DMF solution. The mixture of these solutions was electrospun onto aluminium foil and calcinated at 240 °C in air for 2 hrs. Subsequently, the fibers were annealed in nitrogen at temperatures of 600 °C resulting in $CoFe_2O_4$@CNFs.

2.4. Characterizations

The surface morphology of the $CoFe_2O_4$ nanofibers was studied using a field emission scanning electron microscope (FESEM, Hitachi SU 8010). The microstructure was investigated by transmission electron microscope (TEM, Hitachi/HF-3300, 300 kV).

2.5 Electrochemical measurements

For the fabrication of the electrodes, a mixture of $CoFe_2O_4$@CNFs, activated carbon, and PVDF in a weight ratio of 80:10:10 was used to prepare a slurry in N-methyl-2-pyrrolidone. Then, the slurry was brush coated onto a nickel foam substrate (1 × 3 cm^2) and dried overnight at 50 ◦C. Electrochemical measurements were carried out using a Metrohm Autolab PGSTAT204 workstation in a 1 M KOH solution. For the three-electrode configuration, Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively.

3. RESULTS AND DISCUSSION

FE-SEM analysis was conducted to examine the surface morphology of the $CoFe_2O_4$@CNFs as shown in Fig. 1a and 1b at low and high magnification. FE-SEM images reveal carbon nanofibers of several micrometer lengths with agglomerated $CoFe_2O_4$ nanoparticles anchored on its surface. Following carbonization the structure remained intact, preserving an interconnected conductive network which may be beneficial to enhance electron conductivity. Average diameter of nanofibers is about 154 nm.

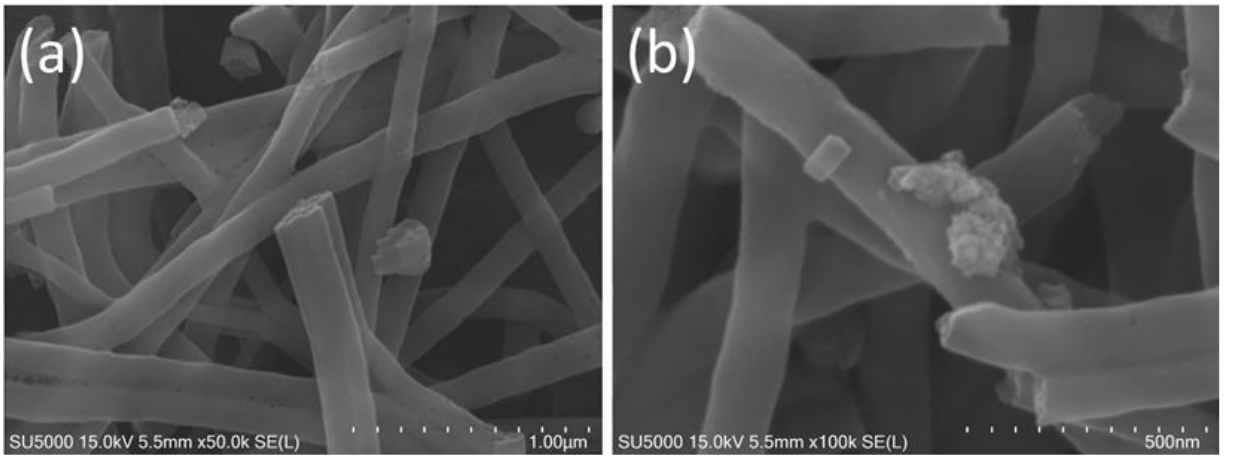

Fig. 1. (a) Low and (b) high magnification FE-SEM images of $CoFe_2O_4$@CNFs.

TEM micrographs were recorded to investigate the microstructure of the nanofibers and are shown in Fig. 2a and b. As can be seen, $CoFe_2O_4$ nanoparticles are embedded in the walls of the carbon nanofibers. The selected area electron diffraction (SAED) pattern of $CoFe_2O_4$@CNFs shown in Fig. 2c exhibits characteristic rings. Notably, within the SAED pattern the discernible rings corresponding to crystal planes (311), (220), and (422) of cubic crystal lattice of $CoFe_2O_4$ phase with space group Fd-3m (JCPDS No. 00-002-1045).

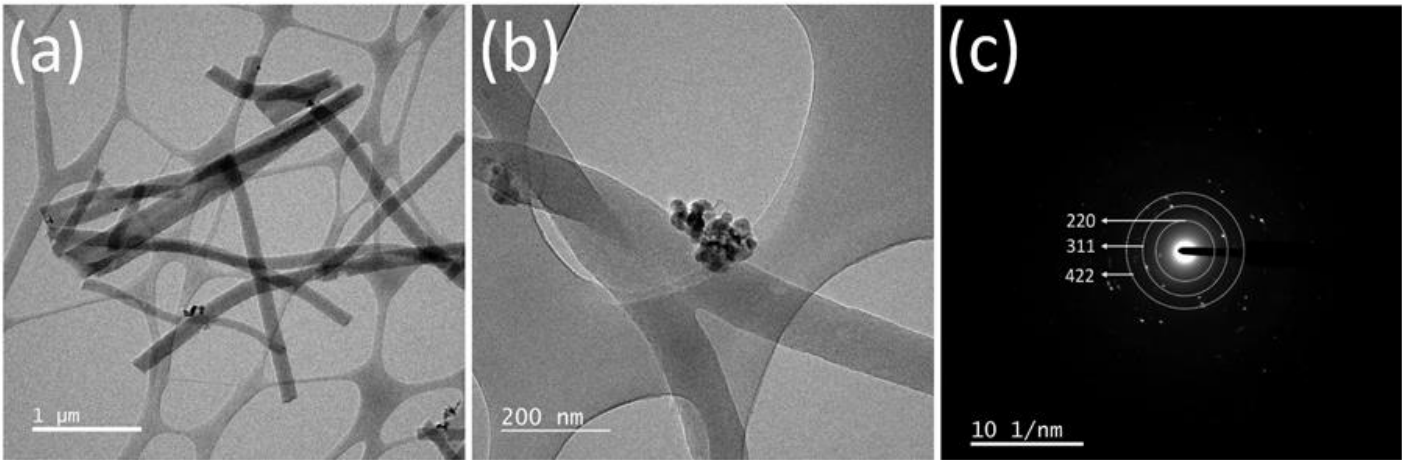

Fig. 2. TEM images at (a) low, and (b) high magnifications and (c) SAED pattern of $CoFe_2O_4$@CNFs.

The electrochemical capacitive properties of $CoFe_2O_4$@CNFs were investigated through cyclic voltammetry (CV) measurements in a 1 M KOH aqueous electrolyte solution. The CV curve measured at a scan rate of 50 mV/s is shown in Fig. 3A. The CV curve has distinct redox peaks. This suggest that the material is pseudocapacitive due to faradic redox reactions [14].

The CV curves measured at different scan rates are presented in Fig. 3B. The CV curves maintained a consistent shape across different scan rates, indicating good reversibility and an effective charge storage mechanism. The rate capability, depicted in Fig. 3B at various scan rates (10-100 mV/s), showed an increase in CV area with higher scan rates. This behavior is attributed to the interplay of ion diffusion, surface adsorption, and charge transfer processes. At high scan rates, any of these processes can become rate-limiting, thus reducing specific capacitance [15].

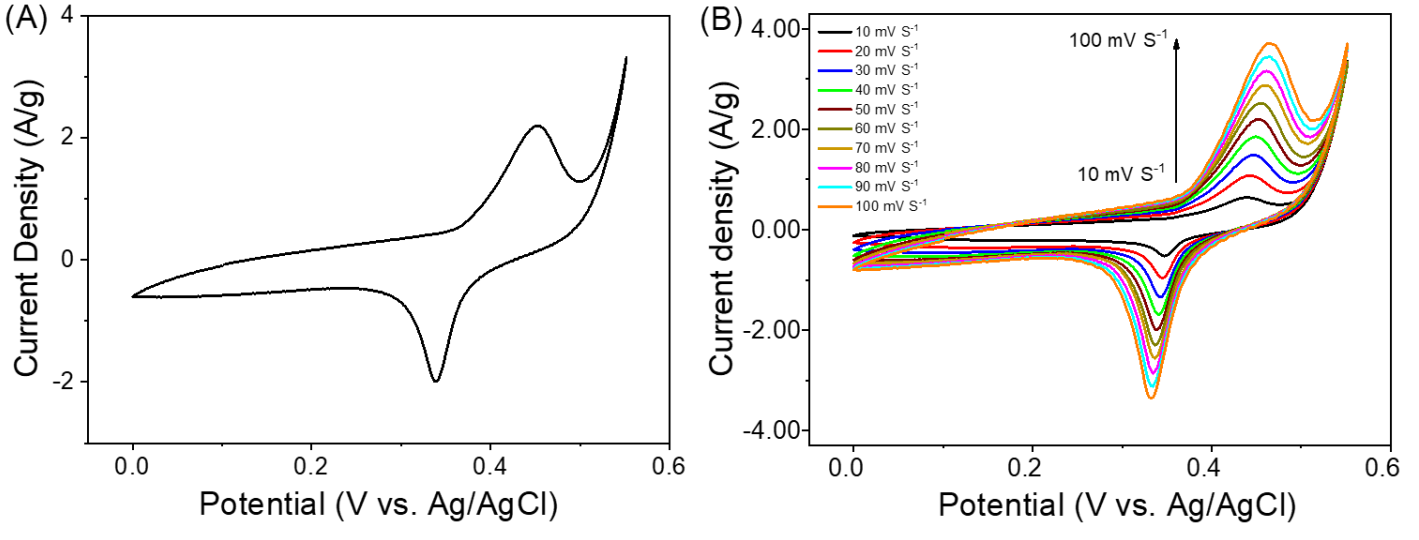

Fig. 3. (A) CV curve at 50 mV/s and (B) the CV curves at various scan rates in 1 M KOH of $CoFe_2O_4$@CNFs.

The galvanometric charge discharge (GCD) curves for $CoFe_2O_4$@CNFs depicted in Fig. 4A exhibit nonlinear characteristics with distinct charge and discharge plateaus, indicating typical faradaic behaviour akin to pseudocapacitors [16]. Specific capacitance was calculated from GCD curves across various current densities within the potential range of 0.0 to 0.47 V. Specific capacitance values obtained from the GCD test are calculated using the equation,

$$\text{Specific Capacitance (CS)} = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where, the I is discharge current, Δt is discharge duration, Δv is voltage window, and the amount of active material is represented by 'm'. The specific capacitance calculated from GCD of $CoFe_2O_4$@CNFs at 1 A/g is 527 F/g. Additionally, the specific capacitance values at various current densities are presented in Table 1. The decline in specific capacitance at higher current densities is attributed to several factors, including insufficient faradaic reaction of active materials within a limited time, increased resistance at high current densities, and potential engagement of only the active surface of the outer electrode for the redox reaction [17]. Energy

density (ED in Wh/kg) and power density (PD in W/kg) are also determined from the GCD curves using the equations (2) and (3). The energy density, and power density at different current densities are presented in Table 1.

$$E.D. = 0.5 \frac{C_{SP}(V_2 - V_1)^2}{3.6} \quad (2)$$

$$P.D. = \frac{ED}{\Delta T} 36000 \quad (3)$$

The electrochemical impedance spectroscopy (EIS) data was collected using an AC voltage of 5 mV across frequencies from 0.01 Hz to 100 kHz. In Fig. 4B, Nyquist plot for $CoFe_2O_4$@CNFs electrode is shown. The Nyquist plot reveal two main regions: a semi-circle and a straight line. At higher frequencies, the semi-circle reflects the charge transfer process, indicating the resistance to redox probe transfer at the electrode interface. The diameter of this semi-circle represents the charge transfer resistance (R_{ct})[18]. The series resistance (R_s) includes ionic resistance of the electrolyte, electrode material resistance, and contact resistance[19]. In the mid-frequency range, Rs and Rct values were measured to be 1.59 Ω/cm^2 and 32.84 Ω/ cm^2, respectively. A linear segment with a 45° slope is evident of the presence of Warburg impedance. This observation suggests that the $CoFe_2O_4$@CNFs electrode material displays pseudocapacitive behaviour [20]. These findings from EIS analysis are consistent with those obtained from CV and GCD experiments.

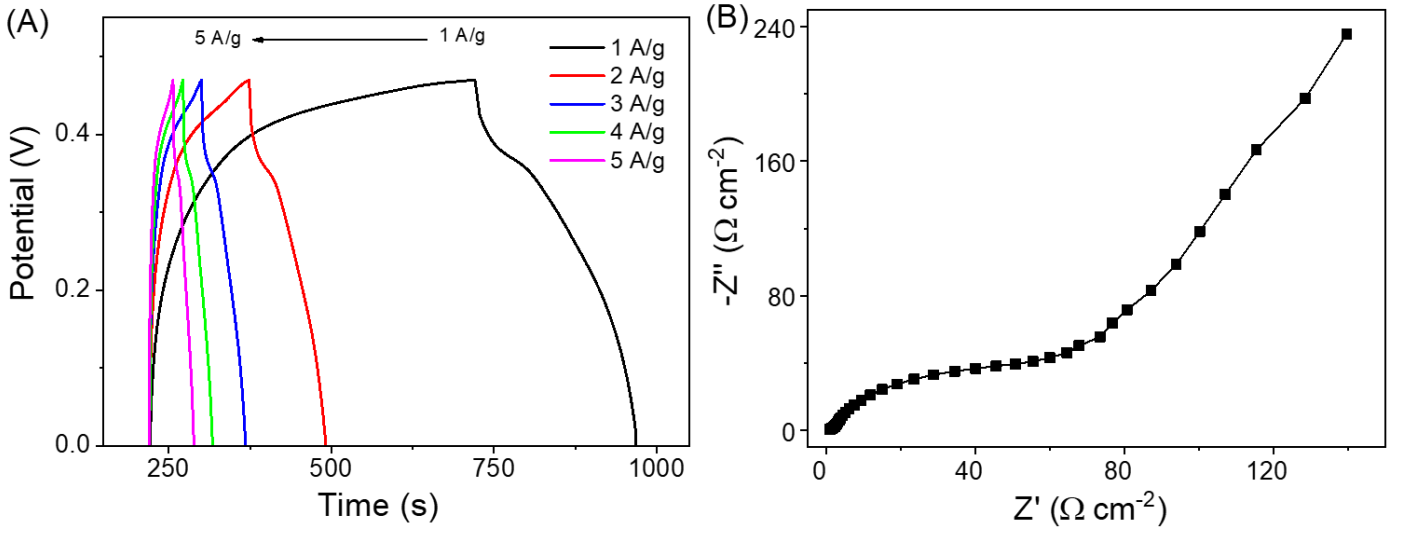

Fig. 4. (A) GCD curves at different current densities and (B) the Nyquist plot of $CoFe_2O_4$@CNFs.

Table 1. Specific capacitance, energy density, and power density of $CoFe_2O_4$@CNFs electrode at different current densities.

Current density (A/g)	Specific capacitance (F/g)	Energy density (Wh/Kg)	Power density (W/Kg)
1	527	16.58	234.9
2	493	15.14	269.8
3	446	13.70	704.5
4	374	11.5	940
5	351	10.76	1173.8

4. CONCLUSIONS

In conclusion, we have developed a facile strategy to anchor MOF derived $CoFe_2O_4$ nanoparticles on carbon nanofibers by electrospinning technique for supercapacitor application. The fibrous structured of carbon combined with MOF derived $CoFe_2O_4$ offers large surface area and abundant exposed active sites as required for superior electrochemical performance. $CoFe_2O_4$@CNFs displayed specific capacitance of 527 F/g at 1 A/g. Furthermore, it has a energy density of 16.58 Wh/kg and a power density of 234.93 W/kg. This work presents the supercapacitive application of metal oxide nanoparticle-modified electrospun carbon nanofibers and puts forward a new path for the preparation of MOF-derived materials.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

ACKNOWLEDGEMENTS

This work is supported by the Science and Engineering Research Board, Department SARTHI for the fellowship. V.D. Chavan and Deok-Kee Kim acknowledge the financial support provided by the National Research Foundation of Korea (NRF), funded by the Ministry of Science and ICT (2016R1D1A1B01009537).

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