

## Regular Article

# Facile hydrothermal synthesis of carbon-coated cobalt ferrite spherical nanoparticles as a potential negative electrode for flexible supercapattery

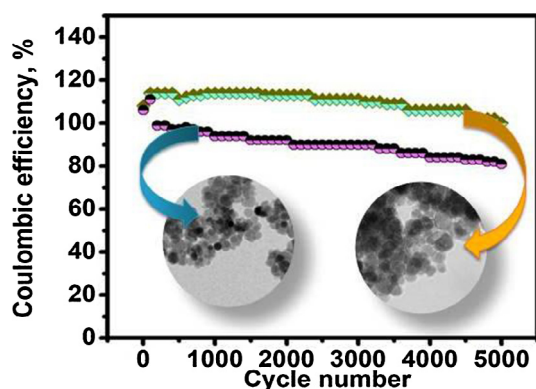


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Battery type electrodes would replace the currently available pseudocapacitive electrodes by the cause of high energy density and long discharge time. In this regard, battery type carbon coated  $\text{CoFe}_2\text{O}_4$  spherical nanoparticles is prepared by the facile hydrothermal method and tested as the possible negative electrode for supercapattery applications. The phase purity, electronic states of elements, and the presence of carbon is inferred through various sophisticated techniques. The calculated surface area of  $\text{CoFe}_2\text{O}_4$  and carbon coated  $\text{CoFe}_2\text{O}_4$  are found to be 9 and  $26 \text{ m}^2 \text{ g}^{-1}$ , respectively. The morphological analysis confirms the formation of uniform  $\text{CoFe}_2\text{O}_4$  nanospheres ( $\sim 25 \text{ nm}$ ) with a thin layer of carbon coating ( $\sim 2 \text{ nm}$ ). The amorphous carbon coating over  $\text{CoFe}_2\text{O}_4$  nanosphere is identified via high-resolution transmission electron microscope. The observed peak and plateau regions in the cyclic voltammogram and galvanostatic charge/discharge curves reveals the battery-type charge storage behaviour of the material. The carbon coated  $\text{CoFe}_2\text{O}_4$  delivers the maximum length capacitance of  $9.9 \text{ F m}^{-1}$  at  $1 \text{ mV s}^{-1}$  with a useful lifespan over 5000 cycles. The electrochemical impedance spectroscopy reveals that the carbon-coated  $\text{CoFe}_2\text{O}_4$  delivers the low charge transfer resistance than  $\text{CoFe}_2\text{O}_4$ . Further, the fabricated supercapattery provides the energy density of  $160 \times 10^{-8} \text{ Wh cm}^{-1}$  at a power density of  $67.2 \mu\text{W cm}^{-1}$ . As well as, the device shows 93% of coulombic efficiency and 75% of the specific capacitance retention over

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11,000 cycles. Overall, it is believed that the carbon-coated  $\text{CoFe}_2\text{O}_4$  can serve as a good candidate for flexible supercapatteries.

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## 1. Introduction

Identification of alternative energy resources from renewable sources is essential to overcome the shortage of available fossil fuels, population growth and thereby increasing energy consumption. However, the energy harvesting from renewable energy sources mainly depends on the climatic and seasonal conditions. Therefore, it is a burning issue to develop efficient energy storage systems for the near future applications. Among the reported energy storage devices, the supercapacitor is considered as an excellent candidate due to its excellent cycle life, fast charge/discharge process, easy device fabrication, rapid energy delivering capacity than batteries and so on. It is mandatory to increase the charge storage capacity of the supercapacitor to meet the demand of high-energy storage device [1–3]. A supercapacitor stores the charge by two different mechanisms, including (i) charge separation at the electrode/electrolyte interface by electrostatic attraction (electric double layer capacitive (EDLC)) and (ii) fast surface redox reaction (Pseudocapacitive). The pseudocapacitive materials exhibit high-energy storage capacity than EDLC due to the surface redox reaction rather than just adsorption on the electrode surface. The most promising materials for pseudocapacitors are  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{RuO}_2$ , etc. These active redox materials store the charge by the electron transfer reaction. The EDL and pseudocapacitive materials belong to the capacitive type. However, it has the broadest scope to improve the energy storage capability of capacitive type materials for the potential applications [1–3].

Hence, an intensive work has been done on the identification of high-energy density battery type charge storing material for replacing capacitive type material. The scientific difference between battery type and pseudocapacitive charge storage mechanism is well-differentiated using band theory [1–3]. According to band theory, the pseudocapacitive material exhibits overlapping of bands which facilitate a continuous redox reaction within the broadband over the potential range. Hence, there is no observation of apparent redox peaks or plateau region in the CV and GCDs. For battery type materials, the valence and conduction bands are separated significantly. Hence, the electron transfer occurs at particular potential, which emerges as a peak or plateau region in the CV or GCDs. When compared to the pseudocapacitive material, the battery type electrode stores an enormous amount of energy [1–3]. Different kind of battery type materials investigated for supercapacitors including nickel, cobalt, bismuth and iron-based (single or mixed) oxides/hydroxides/chalcogenides, layered double hydroxides, and so on [4–6]. The reports illustrated that the morphology, size and surface area are the key points to improve the charge storage capacity. However, the battery type electrodes are severely affected by poor rate capability and lifespan, which can be surmounted by making composite with highly conductive carbon allotropes [7].

Usually, the performance of supercapacitor device depends on the synergistic effect of both positive and negative electrodes. Even though much work has been reported on battery type positive electrodes, an insufficient amount of works is available on negative electrodes [8–10], which stimulated us to find a suitable negative electrode for supercapacitor. In this regard,  $\text{CoFe}_2\text{O}_4$  is chosen for the present study due to its properties of spinel structure, mixed metal oxides with different oxidation states, the high theoretical capacity for Li-ion batteries ( $228 \text{ mAh g}^{-1}$ ), chemical stability and

dynamic electro-catalytic behaviour. The literature depicts that the rate capability and cycling stability of  $\text{CoFe}_2\text{O}_4$  are limited because of its low electronic conductivity [10]. So far, many efforts have been made to improve the performance of  $\text{CoFe}_2\text{O}_4$  using the complicated method of synthesis procedure [10–14]. As well as, the literature depicts that a thin layer of carbon coating on metal oxides has reduced the interface resistance, controlled the volume expansion during charge–discharge cycling, inhibited the side reaction and increased the electrical conductivity [15–19].

In this line, the present work explores the two-step approach of a hydrothermal method for the preparation of  $\text{CoFe}_2\text{O}_4$  nanospheres with a uniform carbon coating. Here, the carbon coating aids to enhance the surface area, sizeable inner electrode charge storage, and improved electrochemical performance of pristine  $\text{CoFe}_2\text{O}_4$  nanospheres [20]. The electrochemical analysis confirmed that carbon coated  $\text{CoFe}_2\text{O}_4$  stores the charge based on battery type mechanism and also it serves as an excellent negative electrode for future flexible supercapattery applications. The fabricated supercapattery stores the charge by both the combination of capacitive (activated carbon as a positive electrode) and battery type (carbon coated  $\text{CoFe}_2\text{O}_4$  as a negative electrode) behaviours.

## 2. Experimental methods and materials

### 2.1. Synthesis of carbon coated $\text{CoFe}_2\text{O}_4$ nanospheres

The stoichiometric amounts of  $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NaOH}$  were used without further purifications. The cationic precursors were dissolved separately in double distilled (DD) water and mixed under stirring. After few minutes, the  $\text{NaOH}$  solution was added dropwise to the above mixture under vigorous stirring. Then, the mixed solution was transferred into 75 ml Teflon lined autoclave and kept at  $180^\circ\text{C}$  for 12 h. After the completion of the reaction, the autoclave was cooled down to room temperature naturally. The resultant product was washed with distilled water and ethanol for several times and dried at  $100^\circ\text{C}$  for 12 h ( $\text{CoFe}_2\text{O}_4$ ). For preparing carbon coated  $\text{CoFe}_2\text{O}_4$ , the  $\text{CoFe}_2\text{O}_4$  nanospheres were dispersed in glucose (50 ml) solution, where the ratio of glucose to  $\text{CoFe}_2\text{O}_4$  was 1:2. The mixed solution was transferred to Teflon lined autoclave and kept at  $150^\circ\text{C}$  for 12 h. After the completion of the reaction, the final product was washed several times with DD water and ethanol and was dried at  $100^\circ\text{C}$  for 12 h. The resultant powder was carbonized at  $450^\circ\text{C}$  for 3 h under an argon atmosphere to obtain the carbon coated  $\text{CoFe}_2\text{O}_4$ .

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4$

The stoichiometric amounts of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NaOH}$  were dissolved separately in DD water and mixed under stirring. The mixed solution was transferred into 75 ml Teflon lined autoclave and kept at  $180^\circ\text{C}$  for 12 h. After the completion of the reaction, the autoclave was allowed to cool down to room temperature. The resultant product was washed with distilled water and ethanol for several times and dried at  $100^\circ\text{C}$  for 12 h.

### 2.3. Characterization techniques

The Bruker D8 Advance with  $\text{Cu K}\alpha$  radiation XRD instrument was used to examine the phase purity and crystallinity of the sam-

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