



## Controllable synthesis of nanohorn-like architected cobalt oxide for hybrid supercapacitor application



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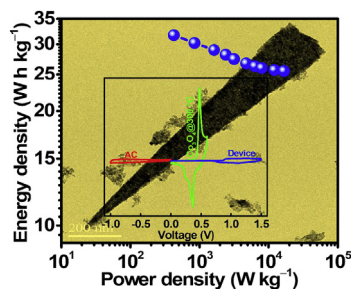
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### HIGHLIGHTS

- Nanohorn-like  $\text{Co}_3\text{O}_4$  architectures are synthesized.
- The high specific capacitance of  $2751 \text{ F g}^{-1}$  is obtained at the optimized temperature.
- Energy density of hybrid supercapacitor is  $\sim 31.70 \text{ Wh kg}^{-1}$ .
- Capacitance retention is 91.37% over 350,000 charge-discharge cycles.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Hybrid device  
Nanoarchitecture  
Cobalt oxide  
Supercapacitor  
High energy  
Electrode materials

### ABSTRACT

We demonstrate a facile and controllable synthesis of horn-like  $\text{Co}_3\text{O}_4$  nanostructures through a solvothermal process followed by calcination at different temperatures. The particle sizes and defects of the as-obtained  $\text{Co}_3\text{O}_4$  nanohorns are controlled with respect to calcining temperatures, while preserving the horn-like morphology. In particular, the  $\text{Co}_3\text{O}_4$  nanohorn electrodes prepared at  $300^\circ\text{C}$  reveal the specific capacitance of  $\sim 2751 \text{ F g}^{-1}$  and the rate capability of 46.8%, which is greater than those of materials obtained at  $350$ ,  $400$ , and  $450^\circ\text{C}$ . In order to enlarge the potential window, a hybrid supercapacitor is configured with the  $\text{Co}_3\text{O}_4$  nanohorn and activated carbon used as positive and negative electrodes, respectively. The as-fabricated hybrid supercapacitor shows high specific capacitance of  $\sim 101 \text{ F g}^{-1}$  and the rate capability of 80.5%. The energy and power densities of hybrid supercapacitor are  $\sim 31.70 \text{ Wh kg}^{-1}$  and  $16.71 \text{ kW kg}^{-1}$ , respectively, along with 91.37% of capacitance retention over 350,000 cycles. These energy and power densities of the hybrid supercapacitors are approximately 8.5 and 3.5 times greater than values of  $\text{Co}_3\text{O}_4$  symmetric supercapacitor.

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<https://doi.org/10.1016/j.jpowsour.2018.09.026>

Received 11 June 2018; Received in revised form 20 August 2018; Accepted 11 September 2018

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## 1. Introduction

Electrochemical energy storage devices have attracted significant attention as essential technology to resolve critical issues in worldwide climate change, scarce fossil fuel-based resources, strong demand in renewable energy storage, and emerging markets of electrical vehicles [1–4]. In particular, electrochemical double layer capacitors (EDLCs), a type of supercapacitors (SCs), have advantages over lithium ion batteries in terms of a high-power density, fast charge-discharge processes, good reversibility and outstanding cycling stability, low maintenance costs, and environmental benignness [4]. However, they still suffer from a low energy density, which limits their practical applications. Thus, highly capacitive active materials have been investigated to improve the specific capacitance (Cs) of electrodes for high energy density.

Among various high capacity materials, cobalt oxide is considered a promising candidate for the replacement of conventional EDLC materials such as activated carbons (ACs) due to its high theoretical capacitance  $\sim 3600 \text{ F g}^{-1}$ , low cost, low environmental footprint, good reversibility, high conductivity, and good cyclic stability [5]. Despite these advantages, actual performances were much lower than expected because the crystallinity, sizes, morphologies, surface areas, and chemical compositions are hard to be controlled. Since SCs store charges at the electrode surface, constructing the nanostructure of electrode materials is beneficial for improving the kinetics of ion diffusion and electron transportation and providing an easy access to active sites and a large surface area [6]. Thus, various nanostructured cobalt oxide materials such as polyhedron, nanorod, nanowire, nanosheet, nanoflake, core-shell, hollow tube, hollow nanonet, and hollow spheres have been investigated for SC applications [5,7–17]. Nonetheless, the potential window of SC based on aqueous electrolyte was limited below 1.23 V because the high capacitance was usually revealed in aqueous electrolytes.

Compared with the previous report of cobalt oxide ( $\text{Co}_3\text{O}_4$ ) [8], the novelties of the present work are as follows: (i) the comprises of the well interconnectivity of particles in the nanohorn can offer the charge ion transport; (ii) the unique nanohorn-like architecture taking benefit of a large interfacial area, several channels for fast and rapid electrolyte ions diffusion and electron transport; (iii) further it provides a facile access to the redox active site from  $\text{Co}_3\text{O}_4$  to enhance the electrochemical behaviour; (iv) the nanohorn-like  $\text{Co}_3\text{O}_4$  is the first time to be explored in supercapacitors application, to the best of our knowledge.

In order to achieve high working potential, hybrid SCs (HSCs) is fabricated using two electrodes with different operating potential ranges [18]. Moreover, the device capacitance of EDLC electrodes can be further improved configuring with high capacitance electrodes in an asymmetric manner. These HSCs consist of one battery-type electrode as an energy source and the other SC electrode as a power source, having the synergistic advantages of battery and SC for high energy and power densities [19]. In this work, we demonstrate HSC using nanohorn-like  $\text{Co}_3\text{O}_4$  electrode for improved energy density. The  $\text{Co}_3\text{O}_4$  nanohorn//AC HSC were operated up to 1.5 V, delivering maximum energy density and power density of  $\sim 31.70 \text{ Wh kg}^{-1}$  and  $16.71 \text{ kW kg}^{-1}$  with long term cyclic stability of  $\sim 91.37\%$  over 350,000 charge/discharge cycles.

## 2. Experimental

### 2.1. Synthesis of $\text{Co}_3\text{O}_4$ nanohorn

For the synthesis of  $\text{Co}_3\text{O}_4$  nanohorn, firstly, 2.99 g of cobalt (II) acetate tetrahydrate ( $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ ; 24%; Alfa Aesar) was dissolved in double distilled water of 25 ml under magnetic string to form a clear solution. After stirring for 5 min, 50 ml of N, N-dimethylformamide (DMF; anhydrous 99.8%; Sigma-Aldrich) was added into the mixture and stirred for 10 min. Then, 5 ml of hydrazine monohydrate ( $\text{N}_2\text{H}_4$ ;

64–65%; Sigma-Aldrich) was drop-wise added in the mixed solution. After stirring for 30 min, the mixed reactants were loaded into a 125 mL Teflon-lined stainless-steel autoclave, followed by heating at  $190^\circ\text{C}$  for 12 h. Afterwards, the autoclave was allowed to cool down naturally to room temperature. The precipitate deposited at the bottom of the Teflon container was filtered off, washed by double distilled water and absolute ethanol for several times, and treated by centrifugation at 8000 rpm for 10 min, and dried under vacuum overnight at room temperature. Finally, the as-prepared product was further divided into four parts and treated at different temperature (300, 350, 400, and  $450^\circ\text{C}$ ) for 3 h at  $5^\circ\text{C min}^{-1}$  in an air (ambient) atmosphere. In this synthesis process, DMF was used as a co-solvent, ligand as well as structure-directing agent.

### 2.2. Characterizations

The crystal structure and phase of the synthesized samples were characterized on a Bruker Inc. (Germany) AXS D8 Advance X-ray powder diffractometer (XRD) using  $\text{Cu K}\alpha$  radiation with a wavelength of ( $\lambda$ ) 1.5406 Å. The intensity data were collected over a  $2\theta$  range of  $10\text{--}80^\circ$ . The operating voltage and current were kept at 40 kV and 40 mA, respectively. Fourier transform infrared (FT-IR) spectra of samples were recorded to investigate the presence of different modes of vibrations of the precursor and the metal oxides using a Nicolet 6700, Thermo Scientific FTIR spectrometer under attenuated total reflection (ATR) conditions. The data were obtained in the range of  $500\text{--}4000 \text{ cm}^{-1}$  with the average of thirty-two scans at a resolution of  $4 \text{ cm}^{-1}$ . The surface morphologies, size, and structure of the obtained nanomaterials were studied by EOL, JEM-1400 transmission electron microscopy (TEM) with an acceleration voltage of 200 kV and high-resolution scanning electron microscopy (HR-SEM, FEI, Magellan 400L, accelerating voltage 15 kV) and the corresponding selected area electron diffraction (SAED) patterns. The sample for TEM investigation, the obtained nanomaterials were well dispersed in isopropanol using water bath-sonication. Then, two small drops of well-dispersed solution were dropped on the carbon-coated copper grid and dried at the air in a covered petri dish to evaporate the solvent before sample processing. The preparation of SEM samples was done by few drops of well-dispersed solution on a surface of the silicon wafer and dried at the air in a covered petri dish. The volumetric nitrogen adsorption/desorption isotherms studies were carried out to examine the surface area and pore structure of the synthesized nanomaterials. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area of obtained samples using a BEL Sorp Mini, Microtrac surface area detecting instrument. The pore size distributions were calculated by the Barrette Joynere Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) measurements were performed using a NOVA, Axis Technology.

### 2.3. Electrochemical measurements

All the electrochemical capacitive measurements of the prepared SCs (three and two -electrode configuration) were carried out on an electrochemical station (VMP3, Bio-Logic, France). Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests were used to characterize the electrochemical behaviour of the configured SCs. Electrochemical impedance behaviours of the electrodes were performed over a frequency interval of 100 kHz to 100 mHz by applying a sine wave with an amplitude of 10 mV at an open circuit voltage. All electrochemical measurements were carried out in a 6 M KOH solution as the aqueous electrolyte under ambient temperature and pressure.

The working electrodes were prepared using a slurry coating procedure, which comprised of 80 wt% active material, 10 wt% conducting carbon black (CCB) as the conductive agent, and 10 wt% polyvinylidene fluoride (PVDF) binder with a suitable amount of N-methyl

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