



## Rapid hydrothermal synthesis of cobalt oxyhydroxide nanorods for supercapacitor applications



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### ABSTRACT

Cobalt oxyhydroxide (CoOOH) nanorods were synthesized by fast hydrothermal process for supercapacitor electrodes. The structural and morphological studies revealed the formation of CoOOH with hexagonal rhomb-centered crystal structure and excellent rod like morphology of ~5–10 nm diameter. The electrochemical characterization was performed for both half cell and symmetric full cell configuration using cyclic voltammetry, galvanostatic charge/discharge test and impedance spectroscopy in 3 M KOH aqueous electrolyte. The fabricated CoOOH electrodes showed maximum specific capacitance value of 198 F g<sup>-1</sup> for a half cell and 94 F g<sup>-1</sup> for a symmetric capacitor of 10 mg cm<sup>-2</sup> active material per electrode and showed better energy and power densities. Moreover, the CoOOH electrode exhibits good capacitance retention (83%) after 5000 charge/discharge cycles.

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### 1. Introduction

Supercapacitors (SCs) are considered as promising candidates for energy storage and power devices due to their advantages like fast charging/discharging, high power delivery and excellent cyclic life as compared with other energy storage devices [1,2]. SCs have been classified into electrochemical double layer capacitors (EDLCs) that use double-layer capacitance arising from the separation of charge at the interface between the electrode/electrolyte, and the other as pseudocapacitors which utilize fast faradaic redox reactions that occur on electrode surface or inside bulk of material [3]. Recently, the pseudocapacitance materials like metal oxides, sulfides and hydrides received considerable attention in energy storage applications owing to their high power and energy density to meet the demands of modern devices [4–7]. The metal hydroxide like cobalt hydroxide is an excellent material for supercapacitor electrodes since it often shows an extremely high theoretical capacitance value of ~3000 F g<sup>-1</sup> [8]. Moreover, it has lower cost than the commercially used ruthenium based materials, is in natural abundance, is environmental friendly and shows better electrochemical performance in alkaline media [9]. Recently,

different forms of cobalt hydroxide nanomaterials like nanorods (1116 F g<sup>-1</sup>) [9], nanocone (562 F g<sup>-1</sup>) [10], nanowires (993 F g<sup>-1</sup>) [11], nanoflakes (890 F g<sup>-1</sup>) [12] etc. have been reported as potential SC electrode materials. Cobalt oxyhydroxide (CoOOH) is another form of cobalt hydroxide with nonstoichiometric oxyhydroxide and has more oxidation state Co (3+) than in Co(OH)<sub>2</sub> [13,14]. Generally these CoOOH is used as an electrode materials for Ni-Co batteries and as a sensing material in carbon monoxide gas sensor [14–16]. But very few work have been reported CoOOH as a supercapacitor electrode materials and shown comparable specific capacitance values [17,18]. Mostly the asymmetric type of capacitors has been utilized for the above work and afforded specific capacitance values in the range of a few 100–1000 F g<sup>-1</sup> for less than 2 mg cm<sup>-2</sup> mass of active materials. Kong et al. [19] reported a maximum specific capacitance of 72.4 F g<sup>-1</sup> for a comparatively high active material mass of 8 mg cm<sup>-2</sup> in 2 M KOH solution. However, a symmetric supercapacitor of electrode mass 6.21 mg showed a maximum specific capacitance of 44 F g<sup>-1</sup> in 1 M KOH electrolyte [20].

In general, the metal hydroxide nanostructure has been synthesized by hydrothermal reaction due to it being a simple, eco-friendly and inexpensive technique. This technique is a bottom-up process that can conveniently provide control of nucleation, growth and aging of particles in the solution at particular growth

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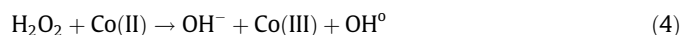
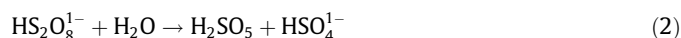
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conditions and can result in bulk quantity of products [21]. Even though the process is simple, the reaction time is quite lengthy (5–48 h) to attain the required nanostructure [10,21]. Generally the synthesis of CoOOH is not a simple process because it involves the transformation of Co (2+) to Co (3+). Since, Co (2+) is much steadier than Co (3+) in most situation, so multi step procedure was involved in the synthesis of CoOOH nanostructures. Initially Co(OH)<sub>2</sub> prepared by chemical technique and the Co(OH)<sub>2</sub> was further oxidized to CoOOH either utilizing chemical precipitation technique or long term hydrothermal process [22–24]. In this present work, we reported a rapid hydrothermal synthesis of CoOOH nanorods in 30 min of reaction time. The supercapacitive properties of CoOOH nanorod was studied by an three electrode (half cell) and symmetric (full cell) configuration with 10 mg cm<sup>-2</sup> of active materials per electrode. Furthermore, the structural, surface and morphology of synthesized nanoparticles were studied and discussed in detail.

## 2. Experimental

### 2.1. Synthesis of CoOOH nanorods

Cobalt (II) sulfate heptahydrate (CoSO<sub>4</sub>·7H<sub>2</sub>O) and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) were used as precursors for the hydrothermal process. The process was begun by dissolving equimolar ratio of CoSO<sub>4</sub>·7H<sub>2</sub>O and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 75 mL of deionized water (DI) under vigorous stirring to form a homogeneous pink colored solution (pH ~7). The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 30 min in a hot air oven and then the autoclave was cooled by continuous flow of water. After attain room temperature a brown precipitate was observed in the autoclave with an acidic solution of pH ~2. From these observation the possible reaction mechanism was discussed as per the previous report [25,26]. Potassium persulfate is one of the strongest oxidizing agents known in aqueous solution, under hydrothermal condition the peroxy disulfate first decomposes to peroxy monosulphuric acid and which hydrolysis to hydrogen peroxide. This H<sub>2</sub>O<sub>2</sub> further oxidize Co (II) to Co (III) as represented below [25,26],



Finally, the obtained brown precipitate of CoOOH was washed several times in DI water by repeated centrifugation/ultrasonication, and the product was dried overnight at 80 °C in a hot air oven.

### 2.2. Material characterization

The structure of the synthesized samples was identified by powder X-ray diffractometer (XRD, Rigaku, Ultima IV) using Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) operated at 40 kV and 30 mA in the  $2\theta$  range 10–90°. Morphologies and elemental analysis (EDAX) of CoOOH nanoparticle was observed by scanning electron microscopy (SEM) (JEOL-7500FA field emission SEM (Japan)) and transmission electron microscopy (TEM) (JEOL (Japan) model JEM-2100F). The specific surface area and pore size distribution were analyzed by nitrogen adsorption/desorption measurement using a Quantachrome surface analyzer at 77.35 °C employing the volumetric method. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) technique. The pore size

distribution was estimated from the desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method.

### 2.3. Electrochemical measurements

The supercapacitor electrodes were fabricated by mixing the active materials (70 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone. The obtained paste was coated over a nickel foam substrate of exposed geometric area 1 cm<sup>2</sup> and dried at 75 °C for 12 h in a vacuum oven. The mass of the active material present in each electrode was determined to be 10 mg. Fig. 1 shows the schematic representation of a fabricated symmetric full cell, inset shows the photograph of a single electrode and the fabricated symmetric full cell. For half cell an arrangement includes the working electrode of CoOOH, a platinum counter electrode and a Hg/HgO reference electrode in 3 M KOH aqueous electrolyte. Electrochemical measurements such as cyclic voltammetry, galvanostatic charge/discharge test and impedance spectroscopy were performed at room temperature using ZIVE-SP2 (Korea) electrochemical workstation.

## 3. Results and discussion

The X-ray diffraction pattern of the synthesized CoOOH is shown in Fig. 2. The prominent diffraction peaks of nanorods can be assignable to a CoOOH phase with hexagonal rhomb-centered crystal structure with a space group of *R3m*. The peak positions observed in the XRD pattern is in good agreement with JCPDS card (No. 07-0169). The unit cell parameters were calculated from all diffracted peaks with the help of software program UnitCell (method of TJB Holland and SAT Red ferm, 1995). The calculated unit cell values are  $a = 2.8525 \text{ \AA}$  and  $c = 13.1920 \text{ \AA}$  and the d-spacing at the (003) plane was determined to be  $4.406 \text{ \AA}$ , which is good agreement with those data of JCPDS-07-0169 ( $a = 2.855 \text{ \AA}$  and  $c = 13.156 \text{ \AA}$ ). The broad diffraction peak confirmed the existence of CoOOH nanoparticles and low intensity of diffracted peaks and excess noise in the spectrum is mainly due to the presence of amorphous particles in the synthesized sample. The EDAX analysis of the samples shown in inset of Fig. 2 clearly indicates the presence of cobalt ions in the synthesised sample.

Fig. 3a, shows the SEM images of CoOOH samples and the inset shows the higher magnification image. From these images, the samples show the morphology of agglomerated nanosphere with diameter ranges from 500 to 1000 nm. At a high magnification, it

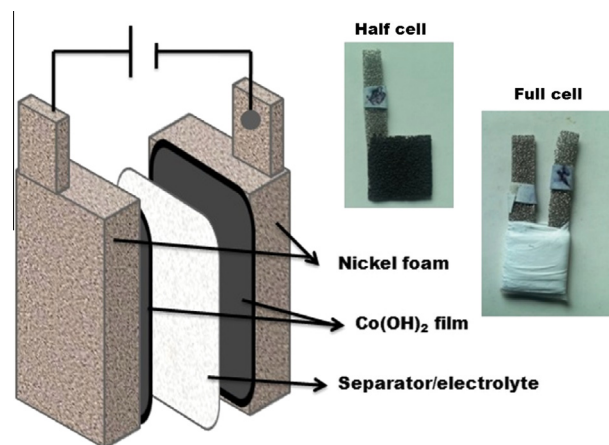


Fig. 1. (a) Schematic representation of the fabricated cell, with inset showing the photograph of a single electrode and the symmetric cell.

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