



## Research Paper

# A simple wet-chemical synthesis, reaction mechanism, and charge storage application of cobalt oxide electrodes of different morphologies



P.S. Gaikar<sup>a</sup>, S.T. Navale<sup>b,c,\*</sup>, V.V. Jadhav<sup>d</sup>, P.V. Shinde<sup>d</sup>, D.P. Dubal<sup>e</sup>, P.R. Arjunwadkar<sup>a</sup>, F.J. Stadler<sup>b,\*</sup>, Mu. Naushad<sup>f</sup>, Ayman A. Ghfar<sup>f</sup>, Rajaram S. Mane<sup>d,f,\*</sup>

<sup>a</sup> Department of Physics, Institute of Science, Nagpur-440008, MS, India

<sup>b</sup> College of Materials Science and Engineering, Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, Nanshan District Key Laboratory for Biopolymers and Safety Evaluation, Shenzhen University, Shenzhen, 518060, PR China

<sup>c</sup> Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, PR China

<sup>d</sup> School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, MS, India

<sup>e</sup> School of Chemical Engineering, The University of Adelaide, SA 5005, Australia

<sup>f</sup> Department of Chemistry, College of Science, Bld#5, King Saud University, Riyadh, Saudi Arabia

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## ABSTRACT

In the present work, cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) electrodes of different morphologies are synthesized onto a stainless-steel (SS) substrate by a simple and cost-effective wet chemical deposition method in presence of different cobalt precursors and then used for energy storage application. Chemical reactions, responsible for different morphologies, are proposed and structural elucidation and morphological evolution studies of Co<sub>3</sub>O<sub>4</sub> electrodes are attempted. Nano-platelets, nano-needles, and nano-grass-type of surface morphologies, corroborated from the scanning electron microscopy and the transmission electron microscopy digital photoimages, for cobalt acetate, cobalt chloride, and cobalt nitrate precursors of Co<sub>3</sub>O<sub>4</sub> electrodes are obtained, respectively. Electrochemical analysis revealed that nano-grass-type Co<sub>3</sub>O<sub>4</sub> electrode exhibits higher specific capacity (SC) (66.40 mAh g<sup>-1</sup> at 1 mA cm<sup>-2</sup> current density), excellent cycle life (~90% after 1000 cycle) and high rate capability (77%) than that of nano-platelets (23.22 mAh g<sup>-1</sup>) and nano-needles (61.22 mAh g<sup>-1</sup>)-type Co<sub>3</sub>O<sub>4</sub> electrodes.

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## 1. Introduction

Energy is the perpetual search for a human being and plays a vital task in the outspread of human civilization and advancement of current technologies. Energy storage is a key technology towards versatile, advanced energy applications and has received significant interest, mutually from industry and academia [1–8]. The increase in apprehension regarding to the environmental pollution and depletion of fossil fuels lead to substantial researches on simplistic, economical, and conservational energy storage systems. One of the main driving forces for investigating energy storage applications in more detail is not only owing to the increasing

demands for electrical devices but also to the predictable diminishing of non-renewable energy sources [1–15]. Over the last decade, a variety of ideal energy storage electrode materials, such as metal oxides, metal nitrides/sulfides, and nanocarbons, have been successfully developed [9]. Amongst several energy storage devices, rechargeable batteries have progressed considerably because of advances in characteristics such as long cycling life, and higher specific capacity (SC). In the context of a variety of ideal energy storage electrode materials, transition metal oxides such as cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) [9], nickel oxide (NiO) [10], manganese oxide (MnO<sub>2</sub>) [13], and titanium dioxide (TiO<sub>2</sub>) [14], iron oxide (Fe<sub>2</sub>O<sub>3</sub>) [15], etc., have attracted interest because of their high redox reactions.

Among various cost-effective and environmentally benign transition metal oxides, Co<sub>3</sub>O<sub>4</sub> has been explored in various applications including lithium-ion batteries [16], electrochemical supercapacitors [17], gas sensors [18], and magnetic devices [19], etc., due to its numerous redox properties [20–22], morphologies,

\* Corresponding author.

E-mail addresses: [stnavale2@yahoo.com](mailto:stnavale2@yahoo.com) (S.T. Navale), [fjstadler@szu.edu.cn](mailto:fjstadler@szu.edu.cn) (F.J. Stadler), [rajarammane70@srtmun.ac.in](mailto:rajarammane70@srtmun.ac.in), [rsmmane\\_2000@yahoo.com](mailto:rsmmane_2000@yahoo.com) (R.S. Mane).

structural identities, and higher surface area. Until now, successful efforts have been made to synthesize  $\text{Co}_3\text{O}_4$  nanoparticles for energy storage applications by a myriad of techniques, such as electron beam evaporation [23], anodic electro-precipitation [24], one-step shape-controlled synthesis [25], sol-gel [26], and chemical bath deposition which is also known as chemical wet deposition or simply chemical method (CBD) [27]. Among the variety of methods used since few decades, CBD is simple and inexpensive, offers the possibility of preparing good quality large area and uniform thin films by direct deposition based on heterogeneous nucleation and subsequent crystal growth at low temperatures [27]. Generally, CBD is used to deposit metal oxide/chalcogenide films by direct immersion of substrates into aqueous metal-ion complexed baths [28,29]. The synthesis of inorganic nanostructures with desired surface morphologies has been of great importance in mounting functional materials. So far, various nano/microstructures of  $\text{Co}_3\text{O}_4$  such as cubes, discs, flowers, polyhedrons, and sheets, etc., have been attempted by various chemical and physical synthesis routes [30–35]. A few changes in the surface morphology of electro-active materials can significantly influence the electrochemical performance, since the energy storage phenomenon is greatly influenced by surface properties, and different material morphologies can lead to apparent variations in electrochemical performance due to the dissimilarity in ion transfer rate throughout charge storage process and material electrolyte interface properties [22,36–41]. The intention of this article is to construct different  $\text{Co}_3\text{O}_4$  electrodes of different morphologies and turn them into efficient energy storage electrode materials as different morphology demonstrates surface area of its kind, on which diffusion resistance of electrolyte ion, followed charge transfer resistance and electrochemical performance, is greatly dependent.

Herein, a simple and cost-effective CBD method was employed for the synthesis of different morphologies of  $\text{Co}_3\text{O}_4$ . As-synthesized electrodes were characterized for their structural and morphological studies. Electrochemical properties such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) of synthesized  $\text{Co}_3\text{O}_4$  electrodes were systematically carried out to understand the correlation between morphology and electrochemical performance. Significance of electrode morphology in electrochemical studies has been thoroughly investigated and discussed.

## 2. Experimental details

### 2.1. Chemicals

Cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , abbreviated as CC), cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , CN), cobalt acetate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , CA), urea ( $\text{CO}(\text{NH}_2)_2$ ), and ammonium fluoride ( $\text{NH}_4\text{F}$ ) were of analytical grade and used without further purification. All syntheses were carried out in deionized (DI) water.

### 2.2. Syntheses of $\text{Co}_3\text{O}_4$ electrodes

Electrodes of  $\text{Co}_3\text{O}_4$  were synthesized by CBD using the following procedure; firstly 0.1 M of the (i)  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  [CA] (ii)  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [CN], and (iii)  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  [CC] salts taken in different three falcon tubes, then add each falcon tube 0.5 M  $\text{CO}(\text{NH}_2)_2$  and 0.2 M  $\text{NH}_4\text{F}$  they were dissolved in 50 ml of DI water with constant stirring for 30 min, produced a pink coloured solution in each tube (Fig. 1). Ultrasonically cleaned SS substrate-pieces of  $1 \times 3 \text{ cm}^2$  dimensions were vertically immersed inside the tubes and then these tubes were sealed and kept in a water bath at  $90^\circ\text{C}$  for 17 h. After completion of the reactions, pinkish cobalt complex  $[\text{Co}(\text{OH})_2\text{CO}_3 \cdot n\text{H}_2\text{O}]$  were seen on the substrate

surfaces. The obtained films were washed with DI-water and dried in air. In naked eye observation, film electrodes obtained from CA, CN, and CC solutions were dark pink, pink, and faint-pink coloured, respectively (Fig. 1). Finally, the film electrodes were air-annealed at  $400^\circ\text{C}$  in a muffle furnace for 1 h.

### 2.3. Characterization details

The (CA- $\text{Co}_3\text{O}_4$ )-, (CC- $\text{Co}_3\text{O}_4$ )-, and (CN- $\text{Co}_3\text{O}_4$ )-electrodes were characterized for their structural, compositional and morphological studies. The X-ray diffraction (XRD) patterns were measured out on Rigaku X-ray diffractometer with  $\text{CuK}\alpha$  source ( $\lambda = 0.154 \text{ nm}$ ) in the  $2\theta$  range of  $10^\circ$ – $80^\circ$ . Chemical bonding states present in  $\text{Co}_3\text{O}_4$  were confirmed by using fourier transform infrared (FT-IR, Model: Bruker Tensor 27 Spectrophotometer) and Raman spectroscopy (Model: Hololab series 5000 Raman spectroscopy, Kaiser Optical Systems, Inc.). The specific surface areas of three electrode powders were obtained from Brunauer-Emmett-Teller plots (BET, Model: Belsorp II, BEL Japan Inc.). Surface morphologies were confirmed from plane-view field emission scanning electron microscope digital images (FESEM, Model: JEOL-6300F) operating at 15 kV and selected area electron diffraction (SAED) was performed with a high-resolution transmission electron microscope (HRTEM JEOL-2010). The mass of the thin film electrode was measured on an METTLER TOLEDO XS105 analytical balance with an accuracy of 0.01 mg.

### 2.4. Electrochemical measurements

Electrochemical measurements on the synthesized  $\text{Co}_3\text{O}_4$  electrodes were performed using single channel potentiostat (Model: WPG 100 Won A Tech). A typical three-electrode system, consisting of Ag/AgCl as a reference electrode, platinum plate as a counter electrode, and the deposited sample as working electrode, was used. CV measurements were performed at a scan rate of  $1$ – $10 \text{ mV s}^{-1}$  in the potential window of  $0.18$  –  $0.5 \text{ V}$  for (CA- $\text{Co}_3\text{O}_4$ ) electrodes and  $0.1$  –  $0.5 \text{ V}$  for (CC- $\text{Co}_3\text{O}_4$ ) and (CN- $\text{Co}_3\text{O}_4$ ) electrodes. GCD curves were obtained at current densities of  $1$ – $10 \text{ mA cm}^{-2}$ . All CV and GCD measurements were performed in presence of aqueous  $1 \text{ M NaOH}$  electrolyte. Electrochemical impedance spectroscopy (EIS) was carried out on IVIUMSTAT in the frequency range of  $100 \text{ KHz}$  –  $100 \text{ MHz}$ .

## 3. Results and Discussion

### 3.1. Reaction mechanism

The observed change in color from pink  $[\text{Co}(\text{OH})_2\text{CO}_3 \cdot n\text{H}_2\text{O}]$  to dark black  $[\text{Co}_3\text{O}_4]$  after annealing was due to an oxidation of Co (II) to Co (III) by atmospheric oxygen [1,38]. The following chemical reactions (eq. 1–9) [4,33,40,42–44] could be responsible for the formation of  $\text{Co}_3\text{O}_4$ . Different precursor solutions such as CA, CN, and CC were used for the formation of  $\text{Co}^{2+}$  (Eqs. (1)–(3)). Here,  $\text{CO}(\text{NH}_2)_2$  acted as a reducing agent in the whole reactions which could produce  $\text{CO}_3^{2-}$  (Eqs. (4)–(6)).  $\text{NH}_4\text{F}$ , being as an additive, was helping in promoting the growth to improve the density of the morphology [44]. The fluoride ( $\text{F}^-$ ) ions in the all reactions acted as catalyst (Eq. (7)) since  $\text{F}^-$  is good promoter to different morphology which can be attached to the  $\text{Co}^{2+}$  (Eq. (8)) and after complete the reaction, the ion was liberated (Eq. (9)) to form  $[\text{Co}(\text{OH})_2\text{CO}_3 \cdot n\text{H}_2\text{O}]$ . At the same time, reaction was processed in same container by attaching  $\text{F}^-$  to  $\text{Co}^{2+}$  which might be the plausible reason of obtaining different morphologies from different precursors, i.e. CA, CN, and CC. Finally, formation of  $\text{Co}(\text{OH})_2\text{CO}_3 \cdot n\text{H}_2\text{O}$  was favoured through Eq. (9).

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